

Chapter 6

Solutions

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6.1 Problems for Chapter 1

1.1 [Equivalence of heat and work]

A block of mass $M = 1$ g is at rest in space (vacuum). Another block of the same mass and velocity $V = 1.5$ km/s collides with the first block and the two blocks stick to each other.

(1) Assuming that there is no radiation loss of energy and that there is no rotation of the resultant single block, obtain the temperature of the resultant single block after equilibration. Assume that the specific heat of the material is 2.1 J/g·K.

(2) If rotation of the resultant body is allowed, what can be said about its final temperature? In particular, is it possible not to raise the temperature of the resultant single block? (Only a qualitative discussion will be enough.)

Solution

(1) The total initial macroscopic kinetic energy is $MV^2/2 = 1.125 \times 10^3$ J. The final total kinetic energy of macroscopic motion is (the necessary speed is determined by

the conservation of linear momentum)

$$\frac{1}{2}(2M)(V/2)^2 = \frac{1}{4}MV^2 = 562.5\text{J}. \quad (6.1.1)$$

Therefore, 562.5 J should become the energy of thermal motion. Thus, $562.5/4.2 = 134$ K is the increase in temperature, so the final temperature is 334 K.

(2) Rotational motion can be excited, so the temperature increase is reduced. However, this rotation is due to the non-zero angular momentum around the center of mass of the initial system. Now, the question is whether the rotational kinetic energy can preserve the kinetic energy of relative motion. If the second body has an extremely long thin rod to connect it to the other body to become a single block, then we can reduce the loss of rotational kinetic energy indefinitely (compute the final rotational kinetic energy and compare it with the relative kinetic energy). That is, the temperature increase can be made indefinitely small.

1.2 [Exchange of temperatures]

Suppose there are two water tanks A and B containing the same amount of water. Initially, A is 42°C and B is 25°C . The final state we want is A to be 25°C and B 42°C (that is, the temperatures of A and B are exchanged; e.g., A is the used warm bath water, and B new clean tap water). Assume that the whole system is thermally isolated.

- (1) Is the process reversibly feasible? Explain why.
- (2) Devise a process. No precise statement is needed; only state key ideas.
- (3) If the reader's process in (2) contains mechanical parts (e.g., a heat engine), devise a process without any moving parts. No precise statement is needed; only state key ideas. The reader can use other containers to hold water and can freely move or flow water (ignore dissipation).

Solution

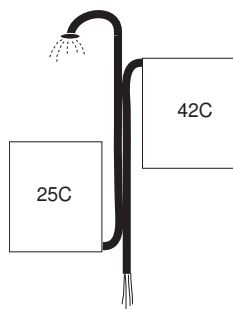
(1) The initial and final states obviously have the same entropy. Thus, if there is a way to connect these two in a quasiequilibrium fashion, it is reversible. Well, is there any quasiequilibrium process connecting them? [Notice that thermodynamics, esp., the second law *postulates* that there is an adiabatic process connecting two equilibrium states of the same system; the process must inevitably reversible in this case. This is usually an assumption; however, depending on the formalism of equilibrium thermodynamics, this can be proved.¹]

(2) Operate a reversible engine between the two tanks until the temperatures become equal. The work produced may be stored by pulling up a weight. Now, use

¹E. H. Lieb and J. Yngvason, "The physics and mathematics of the second law of thermodynamics," *Phys. Rep.*, **310**, 1-96 (1999). This is the state of the art of thermodynamics.

the engine as a heat pump with the aid of the stored energy in the weight.

(3) The answer (2) is fine, but if you wish to commercialize the machinery, you need an engine and a motor, not very economical. In any case moving parts are where troubles start (as is often the case with the hard disk). Thus, we wish to get rid of moving parts. In the actual commercial product, water from the faucet is guided through some clever heat exchange device. Thus, we assume we can freely move water (but slowly). We must reduce the production of entropy, so heat transfer between different temperatures should be maximally avoided. Initially, the temperatures are distinct, so this is impossible. However, we can make this initial mismatch effect indefinitely small by making the amount of water to be equal temperature from both tanks as small as possible. Look at the scheme in the following figure. If the pipe is thin enough, the effect of initial awkward thermal contact is reduced as much as you wish, and the subsequent heat contact can be as isothermal as possible.²



The thermal contact between counter flows can be made indefinitely long by making a tortuous route. Cooled water is drained and warmed water is used for your shower. Such a device is industrially common to save energy,

1.3 [The fourth law of thermodynamics]

(1) For 0.5 moles of a certain substance the equation of state is obtained as:

$$E = \kappa TV^{1/2}, \quad (6.1.2)$$

where E is internal energy, V is volume, T is absolute temperature, and κ is a constant. Write down the equation of state for N moles of this substance.

(2) We can define extensive quantities per molecule $x = X/N$, where $X = E, S, V$ and $x = e, s, v$. Write down the Gibbs relation for one mole (or a molecule) That is, express de in terms of x and other extensive quantities per mole (or molecule).

Solution

(1) Let e and v be internal energy per mole and the volume per mole. The given equation of state can be rewritten as

$$e/2 = \kappa T(v/2)^{1/2} \Rightarrow e = \sqrt{2\kappa T} v^{1/2}, \quad (6.1.3)$$

²There is a way to do gradual temperature change through preparing numerous heat baths with various temperatures, but this is of course only for extremely rich people.

so

$$(E/N) = \sqrt{2\kappa T}(V/N)^{1/2} \Rightarrow E = \sqrt{2\kappa T}N^{1/2}V^{1/2}. \quad (6.1.4)$$

(2) You could use $d(E/N) = dE/N - (E/N)(dN/N)$ and $E = TS - PV + \mu N$ (because E is extensive), but a wiser method is to use

$$e = sT - Pv + \mu \quad (6.1.5)$$

and the Gibbs-Duhem relation, $SdT - VdP + Nd\mu = 0$ or

$$sdT - vdP + d\mu = 0. \quad (6.1.6)$$

Differentiating (6.1.5) and using (6.1.6), we get

$$de = Tds - Pdv. \quad (6.1.7)$$

1.4 [Asymmetric coin and limit theorem]

The law of large numbers applies to an unfair coin as well. Suppose the coin we use has a probability $1/2 + \varepsilon$ to yield a head (H). Otherwise, a tail (T) is yielded. One gets \$1 when H shows up and must pay \$1, otherwise.

(1) Write down the generating function $\omega_N(k)$ for the reader's expected gain per one coin-tossing s_N for the length N coin-tossing sequence.

(2) Compute the mean and the variance of s_N .

(3) Using the **generating function** technique, find the density distribution function f_N for the fluctuation of s_N to demonstrate³ the law of large numbers and the central limit theorem.

Solution

(1) Let X_i be your gain by the i -th tossing. Then, $s_N = (1/N) \sum X_i$.

$$\omega_N(k) \equiv \left\langle \exp \left(ik \frac{1}{N} \sum X_i \right) \right\rangle, \quad (6.1.8)$$

$$= \prod_{i=1}^N \left\langle \exp \left(ik \frac{1}{N} X_i \right) \right\rangle, \text{ due to statistical independence} \quad (6.1.9)$$

$$= \omega(k/N)^N, \quad (6.1.10)$$

where ω is the generating function for the single tossing:

$$\omega(k) = \left(\frac{1}{2} + \varepsilon \right) e^{ik} + \left(\frac{1}{2} - \varepsilon \right) e^{-ik}, \quad (6.1.11)$$

$$= \cos k + 2i\varepsilon \sin k. \quad (6.1.12)$$

³Need not be mathematical; quite a theoretical physicist's way is OK!

(There is no point to streamline this expression.) Therefore,

$$\omega_N(k) = [\cos(k/N) + 2i\varepsilon \sin(k/N)]^N. \quad (6.1.13)$$

(2) [Directly] This is straightforward: the mean is

$$M_N = \langle s_N \rangle = \frac{1}{N} \sum \langle X_i \rangle = (1/2 + \varepsilon) - (1/2 - \varepsilon) = 2\varepsilon. \quad (6.1.14)$$

The variance is:

$$V_N = \langle (s_N - \langle s_N \rangle)^2 \rangle = \left\langle \left(\frac{1}{N} \sum (X_i - 2\varepsilon) \right)^2 \right\rangle, \quad (6.1.15)$$

$$= \frac{1}{N^2} \left\langle \sum_i (X_i - 2\varepsilon)^2 + 2 \sum_{i>j} (X_i - 2\varepsilon)(X_j - 2\varepsilon) \right\rangle. \quad (6.1.16)$$

X_i and X_j are statistically independent, so we can average them separately. Therefore, the cross terms in the above vanish and we obtain

$$V_N = \frac{1}{N} \langle (X_1 - 2\varepsilon)^2 \rangle = \frac{1}{N} (\langle X_1^2 \rangle - 4\varepsilon^2) = \frac{1}{N} (1 - 4\varepsilon^2). \quad (6.1.17)$$

[Using the generating function] We use the generating function: (note that $\omega(0) = 1$)

$$M_N = \left. \frac{d\omega_N(k)}{dik} \right|_{k=0} = -iN[\dots]^{N-1} \left[-\frac{1}{N} \sin \frac{k}{N} + 2i\varepsilon \frac{1}{N} \cos \frac{k}{N} \right]_{k=0} = 2\varepsilon. \quad (6.1.18)$$

The variance is obtained by the logarithmic second derivative (the derivative is evaluated at $k = 0$ at the end; the calculation may be easier if you do it in terms of $e^{\pm ik}$):

$$V_N = -\frac{d^2}{dk^2} \log \omega_N(k) = -N \frac{d^2}{dk^2} \log [\cos(k/N) + 2i\varepsilon \sin(k/N)], \quad (6.1.19)$$

$$= -\frac{d}{dk} \frac{-\sin(k/N) + 2i\varepsilon \cos(k/N)}{\cos(k/N) + 2i\varepsilon \sin(k/N)}, \quad (6.1.20)$$

$$= \frac{1}{N} \left\{ \frac{\cos(k/N) + 2i\varepsilon \sin(k/N)}{\cos(k/N) + 2i\varepsilon \sin(k/N)} + \frac{[-\sin(k/N) + 2i\varepsilon \cos(k/N)]^2}{[\cos(k/N) + 2i\varepsilon \sin(k/N)]^2} \right\}_{k=0}, \quad (6.1.21)$$

$$= \frac{1}{N} (1 - 4\varepsilon^2). \quad (6.1.22)$$

Here, in (6.1.21) the sign in front of the second term is +, because we have an overall – before differentiation.

(3) Assuming N is large, so k/N is small, we Taylor expand $\omega_N(k)$. It is far cleverer to expand $\log \omega$ (partition function!; you should see how partition functions are mathematically natural objects), because we have computed the derivatives.

$$\log \omega_N(k) = ikM_N - \frac{1}{2}k^2V_N + o[k^2]. \quad (6.1.23)$$

Therefore, the inverse-Fourier transformation gives

$$f_N(x) = \frac{1}{2\pi i} \int dk e^{-ikx} \omega_N(k) = \frac{1}{2\pi i} \int dk \exp(-ikx + ikM_N - (k^2/2)V_N), \quad (6.1.24)$$

$$= \frac{1}{2\pi i} \int dk \exp(-(V_N/2)[k^2 - 2ik(x - M_N)/V_N]), \quad (6.1.25)$$

$$= \frac{1}{2\pi i} \int dk \exp(-(V_N/2)[k - i(x - M_N)/V_N]^2 - (1/2V_N)(x - M_N)^2), \quad (6.1.26)$$

$$\propto \exp(-(1/2V_N)(x - M_N)^2). \quad (6.1.27)$$

Needless to say, this is consistent with our calculation above, but this tells us that the distribution is Gaussian with variance $V_N = O[1/N]$; **the central limit theorem is a refinement of the law of large numbers.**

1.5 [How to use Chebyshev's inequality]

(1) We wish to know whether a coin is fair or not. To estimate the probability of H within ± 0.01 , how many throwings do you need? Let us tolerate larger errors once in 100 runs. You may assume that the coin is not grossly unfair.

(2) Theoretically, it is known that if the coin is flipped rapidly, the final surface agrees with the original surface with probability 0.51 (for example, if the original surface is H, then with probability about 0.51 H is obtained). To confirm this bias how many throwings do you think is needed?

Solution

(1) Let p be the true probability for H which is not very different from $1/2$. Let χ_i be the index function of the i -th trial to be up. Then

$$p = E(\chi_1).$$

Chebyshev's inequality tells us

$$P\left(\left|\frac{1}{n} \sum_{i=1}^n \chi_i - p\right| > \varepsilon\right) < \frac{1}{n\varepsilon^2} V(\chi_1).$$

We know $V(\chi_1) = p - p^2 = p(1 - p) \simeq 1/4$. Now, $\varepsilon = 0.01$ and the overall error tolerance is 0.01. Therefore, we may assume

$$\frac{1}{n\varepsilon^2}V(\chi_1) = \frac{10^4}{4n} = 0.01.$$

Therefore, $n = 2.5 \times 10^5$ is needed. That is, if you throw the coin 250,000 times, you can estimate the head probability of the coin within the tolerance about $\pm 2\%$. Or, with confidence level 99% you can find p within 2%.

(2) The answer depends on the level of your precision demand. Since the unfairness is of 1% order, you must be able to estimate p at least to this order. The answer to (1) gives a practical answer, if you reduce the confidence level to, say, 95%. If you wish to stick to the 99% confidence level, then 250,000 trials are not enough; ε should be halved at least, and you need 10^6 trials. See Diaconis et al., “Dynamical Bias in the Coin Toss,” *SIAM Review* **49**, 211 (2007). The lesson is, “If we have this much trouble analyzing a common coin toss, the reader can imagine the difficulty we have with interpreting typical stochastic assumptions in an econometric analysis.”

1.6 [A Monte Carlo method to determine π]

There is a unit square (1×1 square) and in it is inscribed a disk of radius $1/2$ sharing the centers of mass. Randomly dropping points uniformly on the square, and counting the number of points landing on the disk, we can measure π (or rather $\pi/4$ directly). How many points do we need to obtain 3 digits below the decimal point of $\pi/4$ with probability more than 99%?

Solution

Let us introduce an iid variable X such that $X = 1$ if the point lands on the disk and 0, otherwise, and uniformly distributed on the unit square. Then, we expect

$$\langle X \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N X_i = \pi/4. \quad (6.1.28)$$

The variance of X is $\pi(1 - \pi/4)/4 < 3/16$. Therefore, Chebyshev tells us that

$$Prob. \left(\left| \frac{1}{N} \sum X_i - \frac{\pi}{4} \right| > 10^{-3} \right) \leq \frac{3/16}{10^{-6}N}. \quad (6.1.29)$$

This upperbound should be less than 10^{-2} , so $N \simeq 2 \times 10^7$ is needed.

1.7 [Law of large numbers does not hold, if the distribution is too broad (if fluctuations are too wild)]

The Cauchy distribution that is defined by the following density distribution function

$$p(x) = \frac{1}{\pi} \frac{a}{x^2 + a^2}. \quad (6.1.30)$$

does not satisfy $E(|X|) < +\infty$ (needless to say, the variance is infinite). Actually, the density distribution of

$$E_n = \frac{X_1 + \cdots + X_n}{n} \quad (6.1.31)$$

has exactly the same distribution function as X_1 , if $\{X_j\}$ all obey the same Cauchy distribution and are statistically independent. Let us demonstrate this.

(1) What is the **characteristic function** of the Cauchy distribution? You can look up the result, but even in that case you must explain why the result is correct.

(2) Show what we wish to demonstrate.

Solution

(1)

We have only to compute

$$\omega(k) = \int_{-\infty}^{\infty} dx e^{ikx} p(x) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dx \left(\frac{1}{x - ia} - \frac{1}{x + ia} \right) e^{ikx} = e^{-a|k|}. \quad (6.1.32)$$

It may be a good occasion to review contour integration, Cauchy's theorem, etc.

(2) The characteristic function for E_n is given by $\omega(k/n)^n$. This is in our case exactly $\omega(k)$ itself. QED!

1.8 [St. Petersburg Paradox by Daniel Bernoulli]

Let $\{X_i\}$ be iid with

$$P(X_1 = 2^n) = 2^{-n} \quad (6.1.33)$$

for all positive integers n .

(1) Show that $E(X_1) = \infty$.

Thus, it seems that if X_1 is the gambler's gain, the reader can participate in this gambling game with any entry price and still can expect a positive gain. However, any sensible person would pay \$1000 as a fair price for playing. Why? This is the 'paradox.'

(2) Needless to say, the law of large numbers does not hold for E_n . This implies that empirically obtainable expectation and theoretical one should have some discrepancy. Indeed, it can be proved (the reader need not show this; not very easy) that for any positive ε

$$P(|E_n / \log_2 n - 1| > \varepsilon) \rightarrow 0 \quad (6.1.34)$$

in the $n \rightarrow \infty$ limit. Recall that E_n is the expected payoff. Explain why the reader does not wish to pay \$1000. (Or for this to be a fair price how many times does the

reader have to play?)

Solution

(1) This is obvious:

$$E(X_1) = \sum_m 2^m 2^{-m}. \quad (6.1.35)$$

(2) The above estimate implies with high probability (asymptotically) $E_n \sim \log_2 n$. That is, you must wait until $\log_2 n = 1000$ to have break-even. That is $n = 2^{1000} \simeq 10^{300}$.

1.9. Explain ‘Bertrand’s paradox’ in about 10 lines (without using outrageous fonts). What lesson can you learn? [You can easily find a detailed account in the web.]

Solution

Wikipedia: [http://en.wikipedia.org/wiki/Bertrand's_paradox_\(probability\)](http://en.wikipedia.org/wiki/Bertrand's_paradox_(probability)) gives a good account of this topic. In short, being random or uniform sampling is a rather tricky idea. We need a detailed empirical analysis of what we mean by ‘uniform’ or ‘random’. This is the lesson.

However, this article may have given you an idea that there is a general principle to ‘rescue’ the ambiguity inherent in the concept of ‘lack of knowledge’ following Jaynes (‘maximum ignorance principle’ or, in essence, to use fully the symmetry in the problem). This implies that we must perform a detailed analysis of what is NOT known. If symmetry principles are used inadvertently, we can easily get nonsensical result. A classic example is *von Mises’ wine/water paradox*. You can look this up in the web, and perhaps will see proposals to resolve the paradox. The resolutions require more detailed analysis of what is not known.

1.10 [System with dissipation]

There is a classical particle system described by the canonical coordinates $\{q, p\}$ (q and p are collective notations for position and momentum coordinates of all the particles in the system). In terms of the Poisson bracket and the system Hamiltonian the equation of motion may be written as

$$\frac{dq}{dt} = [q, H], \quad \frac{dp}{dt} = [p, H] - \alpha p,$$

where α is a small positive constant. That is, the system is not perfectly classical mechanical, but contains a certain effect of dissipation.⁴

- (1) Demonstrate that the [Liouville’s theorem](#) is violated for this system.
- (2) Demonstrate that the system energy decreases. (Assume that $H = K + U$ as

⁴This model may look artificial, but similar models are used to study nonequilibrium systems.

usual and K is quadratic in p .)

(3) However, show that if H is time dependent, then the system energy may be maintained.

Solution

(1) Let us check the incompressibility of the flow defined by this differential equation:

$$\frac{\partial}{\partial q} \frac{dq}{dt} + \frac{\partial}{\partial p} \frac{dp}{dt} = -\alpha \frac{\partial p}{\partial p} = -3N\alpha, \quad (6.1.36)$$

where N is the number of the point particles and 3 is the spatial dimensionality ($3N$ is the number of p coordinates).

(2) Let us compute

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + [H, H] + \frac{\partial H}{\partial p} \cdot (-\alpha p) = -2\alpha K, \quad (6.1.37)$$

where K is the kinetic energy and is positive definite. Therefore, H decreases. Here K being a quadratic form (a homogeneous function of order 2) is used.

(3) As you can see from (6.1.37), if H is explicitly time dependent, you can do whatever you want. (For example, although it is not physically interesting, $H(t) = U + e^{2\alpha t} K$ would do.)

1.11 The following can be read in a textbook. Point out the error in the argument.

“In general, there is no logical “room” for adding extra assumptions, such as equal a priori probability. The evolution of an actual system is determined by the laws of mechanics (or quantum mechanics). If the results of using any extra assumptions always agree with the logical consequence of the laws of mechanics, and it should be possible to show that fact. If they do not agree with the laws of mechanics, then the extra assumptions are wrong.”

Solution

Dynamical laws are differential laws, so they must not be discussed without auxiliary conditions such as initial conditions. Such conditions are given independent of the dynamical laws. That is, there is a room to introduce extra assumptions. For example, when we sample from the phase volume, it seems that we can only sample according to the probability measure absolutely continuous with respect to the Riemann volume, but this has nothing to do with the dynamical laws. However, when we study chaotic dynamical systems, observability condition of chaos is a condition on the initial condition.

As can be seen from this example, it is simple minded or too haste to conclude that some universal properties applicable to systems obeying dynamical laws is only

due to dynamical laws. Another example is the unavoidable external disturbances. Therefore, small stochastic perturbations are always there. That this is the reason for the statistical nature of the system is logically perfectly legitimate assertion. If the disturbance is universal, then the results would also be universal.

To be more precise, there is no verification of dynamical laws for many body systems. Therefore, at least purely logically no one can conclude that “If they do not agree with the laws of mechanics, then the extra assumptions are wrong.”

1.12 Classically, the microcanonical distribution may be written as

$$\hat{W}(E) = \frac{1}{N!h^{3N}} \int \delta(H(q, p) - E) dq dp. \quad (6.1.38)$$

Show that this can be expressed as follows:

$$\hat{W}(E) = \frac{1}{N!h^{3N} |\text{grad } H|} d\sigma, \quad (6.1.39)$$

where σ is the area element of the constant energy surface and $\text{grad } H$ is the $3N$ -dimensional gradient vector of the system Hamiltonian H with respect to the canonical variables (q_i, p_i) .

Solution

Notice that $dpdq = d\sigma dE$. If the $6N - 1$ dimensional canonical coordinates in the surface is collectively written as σ , then H can be written in terms of E and σ . Notice that the following formula for the d -function holds:

$$\delta(f(E) - E_0) = \frac{1}{|f'(E_0)|} \delta(E - E_0). \quad (6.1.40)$$

If as $f(E) = H(E, \sigma)$ is adopted, then we must use the partial derivative of H with respect to E as f' , but it is the directional derivative H perpendicular to the isoenergetic surface, so its absolute value must be identical to the absolute value of the gradient. Thus we have demonstrated (6.1.39).

1.13 [Equipartition of energy with the aid of microcanonical ensemble]

Within the microcanonical ensemble formalism⁵ for a classical fluid consisting of N interacting but identical particles,

(1) Show that the temperature T can be expressed in terms of the average of the reciprocal kinetic energy as ($N \gg 1$ may be assumed)

$$k_B T = \frac{2}{3N \langle K^{-1} \rangle}, \quad (6.1.41)$$

⁵Use $W(E)$, the phase volume of the states with the total energy not exceeding E .

where K is the total kinetic energy of the system.

Comment: We are NOT discussing ideal systems. The system can have any interaction among particles. T is defined thermodynamically as $1/T = \partial S/\partial E$.

(2) In the thermodynamic limit show that this is equivalent to

$$k_B T = \frac{2}{3} \langle \kappa \rangle, \quad (6.1.42)$$

where κ is the average kinetic energy per particle. This is essentially the equipartition of kinetic energy. [Hint. the reader may use intuitively the weak law of large numbers.]

Solution

(1) Although I asked the case with $N \gg 1$ to use $W(E)$ instead of the energy shell volume (i.e., $W(E + \delta E) - W(E)$), if you carefully do a similar calculation below, you get the result true for small N as well.

The phase volume $W(E)$ of the states $H = \sum p_i^2/2m + V(q) \leq E$ is computed as

$$W(E) = \int_{V(q) \leq E} dq \int_{\sum p_i^2/2m \leq E - V(q)} dp = \int_{V(q) \leq E} dq C_N [m(E - V(q))]^{3N/2}, \quad (6.1.43)$$

where C_N is a geometrical factor we need not calculate. Temperature is defined by

$$\frac{1}{T} = k_B \frac{d}{dE} \log W(E) = \frac{3N}{2} \frac{\int dq (E - V(q))^{3N/2-1}}{\int dq (E - V(q))^{3N/2}}. \quad (6.1.44)$$

You may have expected the derivative to consist of two terms, but the derivative with respect to the integration range for $\{q\}$ vanishes, because the integrand vanishes there: $V(q) = E$. The above formula is the average of $(E - V(q))^{-1}$ over the configuration space. It is not yet the desired result that is an average over the phase space. Now, we use (again) the **fact** that for high-dimensions the total volume is almost on the skin. Therefore,

$$\int_{K \leq \mathcal{E}} dp K^{-1} = \frac{1}{\mathcal{E}} \int_{K \leq \mathcal{E}} dp. \quad (6.1.45)$$

That is, the configuration space average and the phase space average agree:⁶

$$\beta = \frac{3}{2} N \langle K^{-1} \rangle. \quad (6.1.46)$$

⁶If you use the energy shell, perhaps the first step in the above calculation may be slightly more complicated, but this last step is trivial.

(2) Let k_i be the kinetic energy of the i -th particle. $K = \sum k_i$. Notice that the law of large numbers implies

$$N\langle K^{-1} \rangle = N \left\langle \frac{1}{\sum k_i} \right\rangle = \left\langle \frac{1}{\sum_i k_i/N} \right\rangle \rightarrow \frac{1}{\langle k_i \rangle} = \frac{1}{\langle K \rangle/N} = N/\langle K \rangle. \quad (6.1.47)$$

Here, we intuitively assumed that k_i are iid random variables.

1.14 [Generalized homogeneous function]

As we will learn **much later**, various thermodynamic quantities diverge near the second-order phase transition point (critical point). The free energy density f as a function of temperature $\tau \propto T - T_c$ and pressure p behaves as⁷

$$f(\lambda^{y_1}\tau, \lambda^{y_2}p) = \lambda^d f(\tau, p), \quad (6.1.48)$$

where $\lambda (> 0)$ is a scaling factor, d is the spatial dimensionality, and y_1 and y_2 are real constants (related to the so-called critical exponents). That is, f is a generalized homogeneous function.⁸

Formulate the counterpart of **Euler's theorem** and demonstrate it. You may freely use the method of characteristics.

Solution

(1) Differentiating the given formula wrt λ and subsequently setting $\lambda = 1$ gives the quasilinear PDE:

$$y_1\tau \frac{\partial f}{\partial \tau} + y_2p \frac{\partial f}{\partial p} = d f. \quad (6.1.49)$$

This must be a necessary and sufficient condition for a differentiable function f to satisfy the (generalized) homogeneity relation. To prove sufficiency, we must solve (6.1.49) with the aid of the method of characteristics.⁹ The characteristic equation reads

$$\frac{d\tau}{y_1\tau} = \frac{dp}{y_2p} = \frac{df}{d f}. \quad (6.1.50)$$

You may combine these three fractions in any way, but here let us choose the least sophisticated combinations:

$$\frac{d\tau}{y_1\tau} = \frac{dp}{y_2p}, \quad \frac{d\tau}{y_1\tau} = \frac{df}{d f}. \quad (6.1.51)$$

⁷Precisely speaking, this is the singular part of the free energy as we will learn later. Peculiar phenomena near the critical point are governed by this part of the free energy.

⁸B. Widom realized from the empirical data that if f is a generalized homogeneous function, then critical peculiar phenomena can be explained in a unified fashion.

⁹See Supplements

The general solution to these ODEs are

$$\tau^{1/y_1}/p^{1/y_2} = C_1, \quad \tau^{d/y_1}/f = C_2, \quad (6.1.52)$$

where C_1 and C_2 are integration constants. Hence, the general solution to (6.1.50) is given by

$$f(\tau, h) = \tau^{d/y_1} g(\tau^{1/y_1}/p^{1/y_2}), \quad (6.1.53)$$

where g is a well-behaved function (differentiable, bounded, etc.). Indeed,

$$f(\lambda^{y_1}\tau, \lambda^{y_2}p) = (\lambda^{y_1}\tau)^{d/y_1} g((\lambda^{y_1}\tau)^{1/y_1}/(\lambda^{y_2}p)^{1/y_2}) = \lambda^d \tau^{d/y_1} g(\lambda\tau^{1/y_1}/\lambda p^{1/y_2}) = \lambda^d f(\tau, p). \quad (6.1.54)$$

Another (much smarter) way to solve the characteristic equation (6.1.50) is to introduce the so-called ‘dilation parameter’ λ as follows:

$$\frac{d\tau}{y_1\tau} = \frac{dp}{y_2p} = \frac{df}{df} = \frac{d\lambda}{\lambda}. \quad (6.1.55)$$

This is solved as the following three ODEs:

$$\frac{d\tau}{y_1\tau} = \frac{d\lambda}{\lambda}, \quad \frac{dp}{y_2p} = \frac{d\lambda}{\lambda}, \quad \frac{df}{df} = \frac{d\lambda}{\lambda}. \quad (6.1.56)$$

The general solutions are

$$\tau/\lambda^{y_1} = C_1, \quad p/\lambda^{y_2} = C_2, \quad f/\lambda^d = C_3, \quad (6.1.57)$$

where C_i are integration constants. Thus, the general solution to (6.1.49) reads

$$F(\tau/\lambda^{y_1}, p/\lambda^{y_2}, f/\lambda^d) = 0, \quad (6.1.58)$$

where F is a well-behaved function. In other words, for any $\lambda (> 0)$

$$f = \lambda^d G(\tau/\lambda^{y_1}, p/\lambda^{y_2}). \quad (6.1.59)$$

Here, G is an appropriate differentiable function.

1.15. [Mixing entropy and Gibbs’ paradox]

We have two ideal gases with the same volume V , pressure P , and temperature T . These two gases consist of different chemical species. Assume the whole system is thermally isolated during the following processes.

(1) Two boxes containing the above gases are connected. That is, now the total volume of the mixture is $2V$. Find the entropy change due to this procedure of joining

two boxes.

(2) Find the entropy change if two gases are mixed into a single volume of V .

(3) How can you actually measure the entropy change in (1) experimentally?

Solution

(1) See the illustration at the end.

Before answering the question, let us consider the indistinguishable case. The entropy formula for the gas in box V is

$$S_1 = Nk_B \left(\log \frac{V}{N} + \frac{3}{2} \log \frac{E}{N} + c \right). \quad (6.1.60)$$

If two boxes are joined, then

$$S_{1+2} = 2Nk_B \left(\log \frac{2V}{2N} + \frac{3}{2} \log \frac{2E}{2N} + c \right) = 2S_1 \quad (6.1.61)$$

as expected.

Now, the distinguishable case.

$$S_{1+2} = (2N)k_B \left(\log \frac{2V}{N} + \frac{3}{2} \log \frac{E}{N} + c \right) = 2S_1 + 2Nk_B \log 2 \quad (6.1.62)$$

This can be considered as the superposition of each gas expanded to $2V$:

$$S'_1 = Nk_B \left(\log \frac{2V}{N} + \frac{3}{2} \log \frac{E}{N} + c \right) = S_1 + Nk_B \log 2. \quad (6.1.63)$$

Superposing these two, we have

$$S_{1+2} = 2S_1 + 2Nk_B \log 2. \quad (6.1.64)$$

(2) Indistinguishable case:

Obviously

$$S_{1+2} = 2Nk_B \left(\log \frac{V}{2N} + \frac{3}{2} \log \frac{2E}{2N} + c \right) = 2S_1 - 2Nk_B \log 2. \quad (6.1.65)$$

This is the entropy decrease due to compression = halving the volume.

The distinguishable case: This is a simple superposition, so

$$S'_{1+2} = 2S_1 \quad (6.1.66)$$

mechanically, and T is related to the average kinetic energy K of the system.

Using the Boltzmann formula, we can write

$$dS = k_B \frac{1}{w} \frac{\partial w}{\partial E} dE + k_B \frac{1}{w} \frac{\partial w}{\partial V} dV. \quad (6.1.68)$$

Therefore, if we can compute partial derivatives in the above and identify their meanings, we should accomplish what we desire. This is actually what Boltzmann did in 1864. The demonstration is not very trivial, so here we wish to use the following relation

$$k_B \frac{1}{w} \frac{\partial w(E, V)}{\partial V} \rightarrow \frac{P}{T} \quad (6.1.69)$$

(in the thermodynamic limit) and consider only the energy derivative. We can write

$$w(E, V) = \int_{[E]} d\mathbf{q} d\mathbf{p} - \int_{[E-\delta E]} d\mathbf{q} d\mathbf{p} = \delta E \frac{\partial}{\partial E} \int_{[E]} d\mathbf{q} d\mathbf{p}, \quad (6.1.70)$$

where $[E]$ denotes the phase volume with energy not larger than E . We assume that the gas is confined in the volume V . Let $E = K(\mathbf{p}) + U(\mathbf{q})$, where K is the total kinetic energy and U the total intermolecular potential energy. The phase integration may be written as

$$\int_{[E]} d\mathbf{q} d\mathbf{p} = \int d\mathbf{q} \int_{K(\mathbf{p}) \leq E - U(\mathbf{q})} d\mathbf{p}. \quad (6.1.71)$$

Thus, the integration with respect to \mathbf{p} is the calculation of the volume of the $3N$ -sphere of radius $\sqrt{2m(E - U(\mathbf{q}))}$.

(1) Show that

$$\frac{\partial}{\partial E} \int_{[E]} d\mathbf{q} d\mathbf{p} = \int d\mathbf{q} \frac{S_{3N}}{3N} 2m \frac{3N}{2} [2m(E - U(\mathbf{q}))]^{3N/2-1}, \quad (6.1.72)$$

where S_{3N} is the surface area of the $3N - 1$ -dimensional unit sphere.

(2) Using this formula, we can differentiate the integrand with E . Obtain

$$\frac{1}{w(E, V)} \frac{\partial w(E, V)}{\partial E} = k_B \left(\frac{3N}{2} - 1 \right) \left\langle \frac{1}{K(\mathbf{p})} \right\rangle. \quad (6.1.73)$$

(3) We know from the kinetic theory that the average kinetic energy of a point particle is proportional to T (precisely speaking, the average of $\mathbf{p}^2/2m = 3k_B T/2$). Assuming that all the kinetic energies of the particles are statistically independent,¹⁰

¹⁰This is not really a trivial statement; we need that the system is ‘normal.’ That is, the intermolecular interaction range must be very short, and the interactions are sufficiently repulsive in the very short range.

demonstrate that the formula in (2) is indeed equal to $1/T$.

Solution

(1) The integration with respect to \mathbf{p} in (6.1.71) is the calculation of the volume of the $3N$ -sphere of radius $\sqrt{2m(E - U(q))}$.

$$\int_{[E]} d\mathbf{q}d\mathbf{p} = \int d\mathbf{q} S_{3N} \int_0^{\sqrt{2m(E-U(q))}} p^{3N-1} dp = \int d\mathbf{q} \frac{S_{3N}}{3N} [2m(E - U(q))]^{3N/2}, \quad (6.1.74)$$

where S_{3N} is the area of the unit $3N - 1$ -sphere. From this,

$$\frac{\partial}{\partial E} \int_{[E]} d\mathbf{q}d\mathbf{p} = \int d\mathbf{q} \frac{S_{3N}}{3N} 2m \frac{3N}{2} [2m(E - U(q))]^{3N/2-1} \quad (6.1.75)$$

(2) The result of (1) gives us w , so we must differentiate this once more.

$$\frac{\partial^2}{\partial E^2} \int_{[E]} d\mathbf{q}d\mathbf{p} = \int d\mathbf{q} \frac{S_{3N}}{3N} (2m)^2 \frac{3N}{2} \left(\frac{3N}{2} - 1 \right) [2m(E - U(q))]^{3N/2-2}, \quad (6.1.76)$$

$$= \int d\mathbf{q} \frac{S_{3N}}{3N} (2m) \frac{3N}{2} \left(\frac{3N}{2} - 1 \right) [2m(E - U(q))]^{3N/2-1} \frac{1}{K(p)}, \quad (6.1.77)$$

$$= \frac{\partial}{\partial E} \int d\mathbf{q} \frac{S_{3N}}{3N} \left(\frac{3N}{2} - 1 \right) [2m(E - U(q))]^{3N/2} \frac{1}{K(p)}, \quad (6.1.78)$$

$$= \left(\frac{3N}{2} - 1 \right) w(E, V) \left\langle \frac{1}{K(p)} \right\rangle. \quad (6.1.79)$$

That is,

$$\frac{1}{w(E, V)} \frac{\partial w(E, V)}{\partial E} = \left(\frac{3N}{2} - 1 \right) \left\langle \frac{1}{K(p)} \right\rangle. \quad (6.1.80)$$

(3) We wish to demonstrate in the $N \rightarrow \infty$ limit

$$\left(\frac{3N}{2} - 1 \right) \left\langle \frac{1}{K(p)} \right\rangle = \frac{1}{k_B T}. \quad (6.1.81)$$

Obviously,

$$\left(\frac{3N}{2} - 1 \right) \left\langle \frac{1}{K(p)} \right\rangle = \left\langle \frac{1}{(3K(p)/2)/N} \right\rangle. \quad (6.1.82)$$

The law of large numbers tells us (cf. 1.13) that

$$3K(p)/2)/N = \frac{3}{2} \frac{1}{N} \sum \frac{p^2}{2m} \rightarrow \frac{3}{2} \left\langle \frac{p^2}{2m} \right\rangle = k_B T. \quad (6.1.83)$$

1.17 [Superrelativistic ideal gas]

Consider a super-relativistic gas consisting of particles whose energy $\varepsilon = c|\mathbf{p}|$, where c is the speed of light, and \mathbf{p} is the particle translational momentum.

(1) We have learned that the equation of state and the constant volume specific heat C_V of an ideal gas may be obtained almost dimensionally, if we accept the basic postulate of statistical mechanics. Following this logic, find the pressure and C_V .

(2) Calculate the entropy to determine the constant corresponding to ‘ c ’ (the constant in the entropy formula).

Solution

(1) Classically, we have only to consider the phase volume $\tilde{W}(V, E)$ whose dimension is $[q]^{3N}[p]^{3N}$. Therefore,

$$\tilde{W}(V, E) \sim V^N E^{3N}. \quad (6.1.84)$$

(Quantum mechanically, $[W] = 1 = [q]^{3N}/[h/p]^{3N} \sim [V]^N[E]^{3N}$.) This implies that

$$S = k_B \log \tilde{W}(V, E) = Nk_B(\log V + 3 \log E + c_N) = Nk_B \left[\log \frac{V}{N} + 3 \log \frac{E}{N} + c \right]. \quad (6.1.85)$$

Therefore,

$$\frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_E = \frac{Nk_B}{V} \Rightarrow PV = Nk_B T, \quad (6.1.86)$$

and

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V = \frac{3Nk_B}{E} \Rightarrow E = 3Nk_B T. \quad (6.1.87)$$

Therefore, $C_V = 3Nk_B$.

(2) Let us do this honestly. $|\mathbf{p}| = h|\mathbf{n}|/2L$, where L is the edge length of the box: $L^3 = V$, and \mathbf{n} is a 3-dim positive integer vector. Therefore,

$$\tilde{w}(E, V) = \frac{1}{N!} \sum_{\{\mathbf{n}_i\}: \sum |\mathbf{n}_i| \simeq 2LE/ch} 1. \quad (6.1.88)$$

Here, \simeq implies the value between $E - \delta E$ and E (thin shell); in this calculation this is easier). This is not easy to evaluate directly, but a standard trick is to use the

Laplace transformation (or to use the generating function):¹¹

$$\omega(t) = \int_0^\infty dE \tilde{w}(E, V) e^{-tE}. \quad (6.1.89)$$

Using (6.1.88), we can compute this as

$$\omega(t) = \frac{1}{N!} \int_0^\infty dE \sum_{\{\mathbf{n}_i\}: \sum |\mathbf{n}_i| \simeq 2LE/ch} e^{-\sum |\mathbf{n}_i|cht/2L} = \frac{1}{N!} \left(\sum_{\mathbf{n}} e^{-|\mathbf{n}_i|cht/2L} \right)^N. \quad (6.1.90)$$

The sum may be calculated as an integral over the first octant in the 3D space:

$$\sum_{\mathbf{n}} e^{-|\mathbf{n}_i|cht/2L} = \frac{1}{8} \int_0^\infty dn 4\pi n^2 e^{-|\mathbf{n}_i|cht/2L} = (8\pi) \left(\frac{L}{cht} \right)^3 \quad (6.1.91)$$

Therefore,

$$\omega(t) = \frac{1}{N!} (8\pi)^N \left(\frac{L}{cht} \right)^{3N}. \quad (6.1.92)$$

This implies (inverse Laplace transform; see an appropriate table. We ignore the difference between nN and $nN - 1$)

$$\tilde{w}(E, V) = \left(\frac{8\pi}{c^3 h^3} \right)^N \frac{V^N E^{3N}}{N! (3N)!}. \quad (6.1.93)$$

With the aid of Stirling's formula this reads

$$\tilde{w}(E, V) = \left(\frac{eV}{N} \right)^N \left(\frac{eE}{3N} \right)^{3N} \left(\frac{8\pi}{c^3 h^3} \right)^N. \quad (6.1.94)$$

Therefore, entropy reads

$$S = Nk_B \left(\log \frac{V}{N} + 3 \log \frac{E}{N} + \log \frac{8e^4 \pi}{9c^3 h^3} \right). \quad (6.1.95)$$

¹¹Laplace transformation is not so popular among physicists, but it is only a variant of Fourier transformation. However, it is extremely useful in solving linear constant coef ODEs. See Applicable Analysis

http://web.me.com/oono/ApplicableMath/ApplicableMath_files/AMII-33.pdf.

1.18 [Application of the Sackur-Tetrode equation¹²]

The following data are all under 1 atm.

The melting point of mercury is 234.2 K and the heat of fusion is 2.33 kJ/mol. The absolute entropy of solid mercury just at the melting temperature is 59.9 J/K·mol. The entropy increase of liquid between the melting point and the boiling point is 26.2 J/K·mol. The boiling point is 630K and the evaporation heat is 59.3 kJ/mol.

- (1) Calculate the absolute entropy of mercury gas just above the boiling point.
- (2) Assuming that mercury vapor is a monatomic ideal gas, obtain Planck's constant. The reader may use the value of k_B .

Solution

(1) We obtain the absolute entropy of mercury gas at 1 atm just above the boiling point simply by adding required entropy increases:

$$S = 59.9 + \frac{2330}{234.2} + 26.2 + \frac{59300}{630} = 190.1 \text{ J/mol}\cdot\text{K}.$$

(2) The translational entropy of an ideal gas is

$$S = Nk_B \left\{ \log \frac{V}{N} + \frac{3}{2} \log T + \frac{5}{2} + \frac{3}{2} \log \frac{2\pi mk_B}{h^2} \right\}.$$

With the aid of the ideal gas law $PV = Nk_B T$ this can be rewritten as

$$\log P = \frac{5}{2} \log T + \frac{5}{2} + \log \left\{ k_B^{5/2} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right\} - \frac{S}{Nk_B}.$$

Here S is the entropy in the vapor phase for which the classical ideal gas law holds. Therefore, if this S is estimated correctly, then the above equation should be very accurate.

$$\log \left\{ k_B^{5/2} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right\} = \frac{S}{Nk_B} + \log p - \frac{5}{2} \log T - \frac{5}{2} = 22.84 + 11.52 - 18.61 = 15.74$$

If we use the known parameter values, we get 15.82, an excellent agreement. $m = 0.20059/N_A$ and this gives $h = 6.81 \times 10^{-34}$ Js (6.623×10^{-34} Js is the accepted value).

1.19 [Negative temperature]

Let us consider the two state spin system containing 1 mole of spins as discussed

¹²The best elementary exposition is found in F. Mandl, *Statistical Physics* (Wiley, 1971) Section 7.6.

in the [text](#). Assume that under the magnetic field B , the energy gap between the up and down spin states is 600 K per spin. Suppose the initial temperature of the magnet is -500K .

- (1) What is the temperature of this system measured with an ideal gas thermometer containing 10^{-6} moles of monatomic gas particles?
- (2) If, instead, the original negative temperature system is thermally equilibrated with a 1 mole of ideal monatomic gas that is initially 200K, what is the equilibrium temperature?

Solution

- (1) The relation between the magnetization and the temperature can be solved as

$$m = N_A \tanh \frac{300}{T}. \quad (6.1.96)$$

We have already computed the problem

$$300N_A k_B \tanh \frac{300}{500} = -300k_B N_A \tanh \frac{300}{T} + \frac{3}{2}n k_B T \quad (6.1.97)$$

In this case we may expect that the temperature is extremely high, so

$$300N_A \tanh \frac{300}{500} = 161N_A \simeq \frac{3}{2}nT \Rightarrow T = 1.07 \times 10^8 \text{K}. \quad (6.1.98)$$

Since the temperature is outrageously high, we must pay attention to relativity. That is, the gas must be superrelativistic. Then, is the temperature higher or lower? (You can of course get the answer quantitatively easily.)

- (2)

$$161N_A k_B + \frac{3}{2}200N_A k_B = -300N_A k_B \tanh \frac{300}{T} + \frac{3}{2}N_A k_B T \quad (6.1.99)$$

That is, we must solve

$$361 = -300 \tanh \frac{300}{T} + \frac{3}{2}T \quad (6.1.100)$$

That is, $T = 374\text{K}$.

6.2 Problems for Chapter 2

2.1 [On derivation of canonical distribution]

A textbook of statistical mechanics has the following derivation of the canonical distribution:

“The distribution function must not depend on the properties of particular systems, but must be universal. That is, the probability $P(E_I)$ (resp., $P(E_{II})$) for the system I (resp., II) to have energy E_I (resp., E_{II}) and the probability $P(E)$ for the compound system of I and II to have energy $E = E_I + E_{II}$ must have the same functional form. This must be so, as long as we expect statistical mechanics holds universally. Therefore,

$$P(E_I)P(E_{II}) = P(E_I + E_{II}). \quad (6.2.1)$$

For this equation to be valid, we can prove that $P(E)$ must have the following functional form:

$$P(E) = Ce^{-\beta E}, \quad (6.2.2)$$

where C is a constant.”

Is this argument correct?

Solution

Here, we must interpret C as the normalization constant. Therefore, C must be a functional of E (or rather, the system Hamiltonian). This implies that $P(E)$ is not a simple function of E but a functional of the system Hamiltonian, so, although (6.2.2) is a solution, we cannot conclude from (6.2.1), even if we assume smoothness (recall **Cauchy**), that this is the only solution; we may conclude that $\log P$ is a linear functional of H , but no further restriction is possible.

Everyone knows that (6.2.1) is incorrect, generally speaking, since $\sum_{E_I} P(E_I)P(E_{II}) = P(E)$. Precisely speaking, we must say that (6.2.1) holds for the most probable partition of energy. As can be seen from the correct answer $P = e^{-\beta(E-A)}$,

$$P_I(E_I)P_{II}(E_{II}) = P_{I+II}(E_I + E_{II}) \quad (6.2.3)$$

holds for the most probable partition of energy.

2.2 [Elementary problem about spin system]

Due to the ligand field the degeneracy of the d -orbitals of the chromium ion Cr^{3+} is lifted, and the spin Hamiltonian has the following form

$$H = D(S_z^2 - S(S+1)/2), \quad (6.2.4)$$

where $D > 0$ is a constant with $S = 3/2$ (the cation is in the term ${}^4F_{3/2}$).

(0) Why can you apply statistical mechanics to this ‘single’ ion?

(1) Compute the occupation probability of each energy level at temperature T (you may use the standard notation $\beta = 1/k_B T$).

(2) Calculate the entropy.

(3) At high temperatures approximately we have $C = k_B(T_0/T)^2$ with $T_0 = 0.18$ K. Determine D in K.

Solution

(0) Statistical mechanics exploits the fact that any macroscopic system may be considered as a set of numerous statistically independent collection of subsystems. That is, if there is statistical independence and additivity, we may apply the statistical mechanics framework to the collection.

(1) There are 4 states but there are only two energy levels with $E = 3D/8$ and $-13D/8$. Therefore, $S_z = \pm 3/2$ is with $p = 1/2(1 + e^{2\beta D})$ and $S_z = \pm 1/2$ is with $p = 1/2(1 + e^{-2\beta D})$.

(2) The easiest method is to use the [Shannon formula](#):¹³

$$S = -2k_B \left[\frac{1}{2(1+x)} \log \frac{1}{2(1+x)} + \frac{x}{2(1+x)} \log \frac{x}{2(1+x)} \right] = k_B \left\{ \log[2(1+x)] - \frac{x}{1+x} \log x \right\}, \quad (6.2.5)$$

where $x = e^{2\beta D}$.

(3) Setting x as above, we have

$$C = T \frac{dS}{dT} = -(2D\beta) \frac{dS}{d2D\beta} = -2D\beta \frac{dx}{d2D\beta} \frac{dS}{dx} = -2D\beta x \frac{dS}{dx} = k_B(2D\beta)^2 \frac{x}{(1+x)^2}. \quad (6.2.6)$$

Therefore,

$$C = k_B(D/k_B)^2/T^2. \quad (6.2.7)$$

This implies $D/k_B = T_0$. That is, D is 0.18K.

2.3. [Vapor pressure of silicon]

The chemical potential μ_s of the atom in a solid is essentially given by the binding energy Δ of atom in the solid: $\mu_s = -\Delta$. Obtain the formula for the equilibrium vapor pressure of solid, and estimate the vapor pressure at room temperature of

¹³There are several ways to compute entropy. If you know probability explicitly, the Shannon formula may be useful. In this case, you must not forget that the sum is over the *elementary events*. The microcanonical way is probably the least useful in practice. When you compute S from the canonical ensemble, use $S = (E - A)/T$ with E being calculated by the Gibbs-Helmholtz relation $\partial(A/T)/\partial(1/T) = -\partial \log Z/\partial\beta = E$.

silicon for which $\Delta = 3\text{eV}$.

Solution

This is a typical Physics 100 level question. We may assume that the gas is ideal, so its chemical potential is given by $\mu = k_B T \log(n/n_Q)$. The chemical potential of the atom in the solid is $-\Delta$. Therefore the equilibrium condition (the identity of chemical potentials in two phases) gives

$$n = n_Q e^{-\beta\Delta} \Rightarrow p = k_B T n \quad (6.2.8)$$

We know $\hat{m} = 28$, so

$$n_Q = 28^{3/2} \times 10^{30} \simeq 1.5 \times 10^{32}. \quad (6.2.9)$$

Therefore,

$$P = k_B T n_Q e^{-\beta\Delta} = 1.38 \times 10^{-23} \times 300 \times 1.5 \times 10^{32} e^{-3/0.026}, \quad (6.2.10)$$

$$= 4.8 \times 10^{-39} \text{ (Pa)}. \quad (6.2.11)$$

2.4 [Specific heat]

Suppose that a (3D) classical mechanical system has the following Hamiltonian

$$H = \sum_{i=1}^N a_k |\mathbf{p}_k + \mathbf{c}_k|^s \quad (6.2.12)$$

where a_k ($k = 1, \dots, N$), s are positive constants, and \mathbf{c}_k are constant 3-vectors. Without any explicit calculation compute the specific heat.

Solution

The partition function Z reads

$$Z = \frac{V^N}{N! h^{3N}} \prod_k \int d^3 p e^{-\beta a_k |\mathbf{p} + \mathbf{c}_k|^s}. \quad (6.2.13)$$

First of all, \mathbf{c}_k may be ignored by shifting the integration ranges. You could use the scaled variable λ defined by $\beta a_k p^s = \lambda^s$ for each integral. However, the author recommends you to use Dimensional Analysis.

A recommended solution begins here. $\beta a_k p^s$ is dimensionless, so

$$[p] = [\beta a_k]^{-1/s}. \quad (6.2.14)$$

On the other hand,

$$[Z h^{3N} / V^N] = [p]^{3N} \propto [\beta^{-3N/s}] = (k_B T)^{3N/s}. \quad (6.2.15)$$

Therefore, even the internal energy (the *Gibbs-Helmholtz relation*):

$$E = \frac{\partial \beta A}{\partial \beta} = -\frac{\partial \log \beta^{-3N/s}}{\partial \beta} \quad (6.2.16)$$

is independent of a_k , so is C .

From the fact that a_k is factored out, without any calculation you may conclude that C is independent of a_k .

Eq.(6.2.16) is correct, so you can proceed with this result, but let us proceed in a more conventional way (although this is not a recommended approach). (6.2.13) reads

$$Z = \frac{V^N}{N!h^{3N}} \prod_k (\beta a_k)^{-3/s} \int 4\pi \lambda^2 e^{-\lambda^s} d\lambda \propto \prod_k (\beta a_k)^{-3/s}. \quad (6.2.17)$$

The Gibbs-Helmholtz relation immediately tells us that E is not dependent on a_k . $E = 3Nk_B T/s$ and $C = 3Nk_B/s$.

The potential energy of a permanent electric dipole \mathbf{p} is $U = -\mathbf{p} \cdot \mathbf{E}$ in the electric field \mathbf{E} . Obtain the electric susceptibility of the system.

Solution

We must obtain the expectation value of the polarization \mathbf{P} per unit volume of the gas. In this case we ignore the interaction among gas particles, so the partition function becomes a product of one particle partition functions. Furthermore, since the translational motion of the particles has nothing to do with the polarization, we have only to compute the canonical partition function for a single dipole:

$$z(\mathbf{E}) = \int d\mathbf{e} e^{\beta p \mathbf{e} \cdot \mathbf{E}} = \int d\mathbf{e} e^{\beta p E \cos \theta}, \quad (6.2.18)$$

where \mathbf{e} is the directional unit vector of the dipole moment with respect to the electric field direction, $E = |\mathbf{E}|$, and the angle between \mathbf{E} and \mathbf{p} (or \mathbf{e}) is θ . The integration is on the unit sphere and can be computed as

$$z(\mathbf{E}) = 2\pi \int d\theta \sin \theta e^{\beta p E \cos \theta} = 2\pi \int_{-1}^1 dx e^{\beta p E x} = \frac{4\pi}{\beta p E} \sinh \beta p E. \quad (6.2.19)$$

From the structure of z we can immediately see

$$\langle \mathbf{p} \rangle = k_B T \frac{\partial}{\partial \mathbf{E}} \log z(\mathbf{E}) = p L(\beta p E) \frac{\mathbf{E}}{E} \quad (6.2.20)$$

where $L(x)$ is the Langevin function

$$L(x) = \coth x - \frac{1}{x}. \quad (6.2.21)$$

$\langle \mathbf{p} \rangle$ times the number of particle per volume n (= the number density) is the polarization $\mathbf{P} = n\langle \mathbf{p} \rangle$.

The correspondence to thermodynamics is as follows. $-k_B T N \log z(\mathbf{E})$ is, as \mathbf{E} is written explicitly, not the Helmholtz free energy $A(\mathbf{P})$, but its Legendre transformation $\Phi(\mathbf{E}) = A(\mathbf{P}) - \mathbf{P} \cdot \mathbf{E}$. That is,

$$dA = -SdT + \mathbf{E} \cdot d\mathbf{P}, \quad d\Phi = -SdT - \mathbf{P} \cdot d\mathbf{E}. \quad (6.2.22)$$

Therefore,

$$\mathbf{P} = -\frac{\partial}{\partial \mathbf{E}} \Phi(\mathbf{E}) = k_B T N \frac{\partial}{\partial \mathbf{E}} \log z(\mathbf{E}), \quad (6.2.23)$$

which is equivalent to (including the correct sign) (6.2.20).

To obtain the susceptibility (dielectric constant), we must differentiate \mathbf{P} with respect to \mathbf{E} . It is a diagonal matrix proportional to the unit 3×3 matrix I as

$$\varepsilon = \beta p^2 N L'(\beta p N) I. \quad (6.2.24)$$

2.6 [Internal degree of freedom]

There is a classical ideal gas of volume V consisting of N molecules whose internal degrees of freedom are expressed by a single (quantum-mechanical) harmonic oscillator with a frequency ν . The frequency depends on the volume of the system as

$$\frac{d \log \nu}{d \log V} = \gamma. \quad (6.2.25)$$

- (1) Obtain the pressure of the system.
- (2) Obtain the constant pressure specific heat C_P .

Solution

- (1) The partition function is given by

$$Z = Z_0 Z_I, \quad (6.2.26)$$

where Z_0 is the canonical partition function for the classical ideal gas, and Z_I is the partition function for the internal harmonic degree of freedom. You may use the already computed [results](#):

$$Z_0 = \frac{V^N}{N!} \left(\frac{2mk_B T}{h^2} \right)^{3N/2} \quad (6.2.27)$$

and

$$Z_I = \left(\frac{1}{2 \sinh \beta h \nu / 2} \right)^N. \quad (6.2.28)$$

Therefore

$$P = - \left. \frac{\partial A}{\partial V} \right|_T = \frac{Nk_B T}{V} + P_I, \quad (6.2.29)$$

where

$$P_I = \left. \frac{\partial k_B T \log Z_I}{\partial V} \right|_T = -Nk_B T \frac{\cosh \beta h\nu/2}{\sinh \beta h\nu/2} \frac{\beta h}{2} \frac{\partial \nu}{\partial V} = -\frac{Nh\nu}{2V} \gamma \coth \frac{\beta h\nu}{2}. \quad (6.2.30)$$

Notice that if we write the total energy of the internal degrees of freedom

$$U = \frac{Nh\nu}{2} \coth \frac{\beta h\nu}{2} = \frac{h\nu}{2} + \frac{h\nu}{e^{\beta h\nu} - 1}, \quad (6.2.31)$$

then

$$P_I = -\gamma \frac{U}{V}. \quad (6.2.32)$$

That is,

$$P = \frac{Nk_B T}{V} - \gamma \frac{U}{V}. \quad (6.2.33)$$

(2) The best way is to use enthalpy $H = E + PV$:

$$C_P = \left. \frac{\partial H}{\partial T} \right|_P. \quad (6.2.34)$$

Again, you may use the results you know (you may assume there is only translational and oscillatory degrees of freedom): the internal energy is

$$E = \frac{3}{2}Nk_B T + \frac{Nh\nu}{2} \coth \frac{\beta h\nu}{2}. \quad (6.2.35)$$

Therefore,

$$H = \frac{5}{2}Nk_B T + (1 - \gamma)U. \quad (6.2.36)$$

Use (6.2.31).

$$C_P = \frac{5}{2}Nk_B + (1 - \gamma)Nk_B \left(\frac{\beta h\nu}{e^{\beta h\nu} - 1} \right)^2 e^{\beta h\nu}. \quad (6.2.37)$$

2.7 [Application of equipartition of energy]¹⁴

¹⁴original credit: B. Widom

The internal motion of some ring puckering molecules (e.g., cyclobutanone) can be described by the following Hamiltonian:

$$H = \frac{p^2}{2m} + ax^4, \quad (6.2.38)$$

where m is the effective mass of the oscillator and a is a positive constant. Obtain the constant volume specific heat of this gas around the room temperature. Do not forget the contribution of translational degrees of freedom, etc.

Solution

We use the equipartition of energy:

$$2 \left\langle \frac{p^2}{2m} \right\rangle = k_B T. \quad (6.2.39)$$

and

$$4 \langle ax^4 \rangle = k_B T. \quad (6.2.40)$$

Therefore,

$$\langle H \rangle = \frac{3}{4} k_B T. \quad (6.2.41)$$

We must pay attention to the translational and rotational degrees of freedom. This gives $3k_B T$. Therefore,

$$C_V = \frac{15}{4} k_B \quad (6.2.42)$$

per molecule.

2.8. [Equipartition of energy for relativistic gas]

For a classical relativistic ideal gas show that the counterpart of the law of equipartition of kinetic energy reads

$$\left\langle \frac{1}{2} \frac{mv_x^2}{\sqrt{1 - v^2/c^2}} \right\rangle = \frac{1}{2} k_B T. \quad (6.2.43)$$

Solution

The total energy of the particle ε is obtained from the Lorentz invariance $\mathbf{p}^2 - \varepsilon^2/c^2 = -m^2c^2$ as

$$\varepsilon = c\sqrt{\mathbf{p}^2 + m^2c^2}. \quad (6.2.44)$$

We know the general relation to demonstrate the equipartition:

$$\left\langle p_x \frac{\partial \varepsilon}{\partial p_x} \right\rangle = \langle p_x v_x \rangle = k_B T. \quad (6.2.45)$$

Note that

$$p_i = \frac{mv_i}{\sqrt{1 - (v/c)^2}}, \quad (6.2.46)$$

This concludes the demonstration.

2.9 [An equality about canonical ensemble]

Let Φ be the total potential energy of classical system. Show

$$\langle \Delta \Phi \rangle = \beta \langle (\nabla \Phi)^2 \rangle. \quad (6.2.47)$$

Here, the Laplacian and the nabla are understood as operators in the $3N$ -space.

Solution

Let $H = K + \Phi$, where K is the total kinetic energy.

$$\begin{aligned} \langle \Delta \Phi \rangle &= \frac{1}{Z} \int d\Gamma (\text{div grad} \Phi) e^{-\beta(K+\Phi)}, \\ &= \frac{1}{Z} \int d\Gamma \text{div} (e^{-\beta H} \nabla \Phi) - \frac{1}{Z} \int d\Gamma \nabla \Phi \cdot \nabla e^{-\beta H}, \\ &= -\frac{1}{Z} \int d\Gamma \nabla \Phi \cdot \nabla e^{-\beta H} = \beta \langle (\nabla \Phi)^2 \rangle. \end{aligned}$$

The contribution from the boundary may be ignored thanks to the Boltzmann factor.

2.10 [Density operator for free particles: perhaps an elementary QM review]

The canonical density operator is given by

$$\rho = \frac{1}{Z} e^{-\beta H}, \quad (6.2.48)$$

where H is the system Hamiltonian and Z is the canonical partition function. Let us consider a single particle confined in a 3D cube of edge length L . We wish to compute the position representation of the density operator $\langle x | \rho | x' \rangle$ (x and x' are 3D position vectors, and bras and kets are normalized).

Let $U(\beta) = e^{-\beta H}$ and $H = p^2/2m$. There are two ways to compute $\langle x | U(\beta) | x' \rangle$:
A.

(1) Show that

$$\frac{\partial}{\partial \beta} \langle x | U(\beta) | x' \rangle = \frac{\hbar^2}{2m} \Delta_x \langle x | U(\beta) | x' \rangle, \quad (6.2.49)$$

where Δ_x is the Laplacian with respect to the coordinates x .

(2) What is the initial condition (i.e., $\langle x | U(0) | x \rangle$)?

(3) Solve the equation in (1) with the correct initial condition. You may use a simple boundary condition assuming the volume is very large (and temperature is not too low).

(4) Compute Z , using the result in (3). You may use (3) to study the finite volume system as long as the temperature is not too low.

B.

We can directly compute $\langle x|U(\beta)|x' \rangle$ with the aid of the momentum representation of $U(\beta)$:

$$\langle p|U(\beta)|p' \rangle = e^{-\beta p^2/2m} \delta(p - p').$$

(5) We use

$$\langle x|U(\beta)|x' \rangle = \int d^3p d^3p' \langle x|p \rangle \langle p|U(\beta)|p' \rangle \langle p'|x' \rangle.$$

What is $\langle x|p \rangle$? You may assume the infinite volume normalization (i.e., the δ -function normalization: $\langle p|p' \rangle = \delta(p - p')$).

(6) Perform the integral in (5).

Solution

A(1) We immediately obtain

$$-\frac{d}{d\beta}U = HU, \tag{6.2.50}$$

so its position representation is obtained as given. Notice that

$$\langle x|H|x' \rangle = -\frac{\hbar^2}{2m} \Delta_x \delta(x - x'). \tag{6.2.51}$$

(2) $U(0) = 1$, so $\langle x|U(0)|x \rangle = \delta(x - x')$ (if you use the continuum approximation) or $= \delta_{x,x'}$ (if you honestly treat the finiteness of the system).

(3) This is a diffusion equation, so the solution may be obtained by looking up any standard textbook; it is the Green's function with the vanishing boundary condition at infinity

$$\langle x|U(\beta)|x' \rangle = \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} e^{-mk_B T(x-x')^2/2\hbar^2}.$$

This clearly exhibits that quantum effect becomes important at low temperatures (as can easily be guessed from the thermal wave length proportional to $1/\sqrt{T}$).

(4) $Z = \text{Tr}U(\beta)$, so

$$Z = \int d^3x \langle x|U(\beta)|x \rangle = \int d^3x \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} = V \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2}.$$

This is consistent with (2.2.3).

(5) $|p\rangle$ is an eigenket of H belonging to the eigenvalue $p^2/2m$: $H|p\rangle = (p^2/2m)|p\rangle$. Therefore,

$$-\frac{\hbar^2}{2m}\Delta_x\langle x|p\rangle = \frac{p^2}{2m}\langle x|p\rangle.$$

The boundary condition is a periodic boundary condition. The equation is essentially the harmonic oscillator equation, so the solution must be proportional to $e^{ipx/\hbar}$. We need a normalization condition:

$$\int d^3x e^{i(p-p')x/\hbar} = h^3\delta(p-p'),$$

so

$$\langle x|p\rangle = \frac{1}{h^{3/2}}e^{ipx/\hbar}.$$

(6)

$$\langle x|U(\beta)|x'\rangle = \int d^3p \langle x|p\rangle e^{-\beta p^2/2m} \langle p|x'\rangle = \int d^3p e^{-\beta p^2/2m + i(x-x')p/\hbar}.$$

This is a simple Gaussian integral, so indeed the answer agrees with (3) above.

2.11 [Density operator for a spin system]

Let ρ be the density operator of a single 1/2 quantum spin system whose Hamiltonian¹⁵ is given by $H = -\gamma\boldsymbol{\sigma} \cdot \mathbf{B}$, where $\boldsymbol{\sigma}$ is $(\sigma_x, \sigma_y, \sigma_z)$ in terms of the Pauli spin operators.

- (1) Obtain the matrix representation of ρ that diagonalizes σ_z .
- (2) Find the average of σ_y .
- (3) Obtain the matrix representation of ρ that diagonalizes σ_x .

Solution

- (1) We take the direction of \mathbf{B} to be the z axis.

$$\rho = \frac{1}{C} \begin{pmatrix} e^{\beta\gamma B} & 0 \\ 0 & e^{-\beta\gamma B} \end{pmatrix}, \quad (6.2.52)$$

where C is the normalization constant: the trace of the matrix in the above formula, so $C = 2 \cosh \beta\gamma H$.

If you wish to do the original problem we need the following calculation. Notice that $(\mathbf{n} \cdot \boldsymbol{\sigma})^2 = I$, where \mathbf{n} is a unit vector.

$$e^{\gamma\mathbf{B} \cdot \boldsymbol{\sigma}} = \sum_{n=0}^{\infty} \frac{1}{(2n)!} (\gamma B)^{2n} + \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} (\gamma B)^{2n+1} \frac{\mathbf{B}}{B} \cdot \boldsymbol{\sigma} = \cosh \gamma B + \frac{\mathbf{B}}{B} \cdot \boldsymbol{\sigma} \sinh \gamma B. \quad (6.2.53)$$

¹⁵Precisely speaking, this is the interaction Hamiltonian of the system with the magnetic field.

(2)

$$\langle \sigma_y \rangle = \text{Tr} \sigma_y \rho = \text{Tr} \begin{pmatrix} 0 & ie^{\beta\gamma B} \\ -ie^{-\beta\gamma B} & 0 \end{pmatrix} = 0. \quad (6.2.54)$$

This should be obvious without any calculation.

(3) With the basis that diagonalizes σ_z we have

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (6.2.55)$$

Therefore

$$\sigma_x \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}. \quad (6.2.56)$$

That is, the following orthogonal (actually, unitary as well) matrix:

$$U = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \quad (6.2.57)$$

diagonalizes σ_x as $U^* \sigma_x U$. Therefore,

$$U^* \begin{pmatrix} 0 & ie^{\beta\gamma B} \\ -ie^{-\beta\gamma B} & 0 \end{pmatrix} U = \frac{1}{2} \begin{pmatrix} 1 & -\tanh \beta\gamma B \\ -\tanh \beta\gamma B & 1 \end{pmatrix}. \quad (6.2.58)$$

2.12 [Legendre vs Laplace]

Consider an ideal gas consisting of N atoms under constant pressure P and temperature T .

(1) What is the most convenient partition function and the thermodynamic potential? Compute the partition function. You may use the ideal gas canonical partition function.

(2) Obtain the enthalpy of the system.

Solution

(1) We should use the pressure ensemble:

$$Q = \int dV Z(T, V) e^{-\beta PV}. \quad (6.2.59)$$

This is related naturally to the Gibbs free energy: $A + PV = G = -k_B T \log Q$. (Since $N \gg 1$, you need not worry about ± 1 in N .)

$$Q = \int_0^\infty dV \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} V^N e^{-\beta P V} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} (\beta P)^{-N}. \quad (6.2.60)$$

This gives

$$G = -N k_B T \log \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} + N k_B T \log \frac{P}{k_B T}, \quad (6.2.61)$$

which is

$$G = A - k_B T \log N! + N k_B T \log \frac{PV}{k_B T} = A + N k_B T = A + PV. \quad (6.2.62)$$

Consistent!

(2) We can use an analogue of the Gibbs-Helmholtz relation

$$H = \frac{\partial G/T}{\partial 1/T} = -\frac{\partial \log Q}{\partial \beta} = \frac{5}{2} N k_B T. \quad (6.2.63)$$

Thermodynamically, $H = E + PV = E + N k_B T$. Consistent. This is of course consistent with the constant pressure specific heat.

2.13 [Constant magnetic field ensemble]

The following situation is the same as **1.18**: N lattice sites have spins of $S = 1$ (in the term 3P), and the spin Hamiltonian has the following form:

$$H = D S_z^2. \quad (6.2.64)$$

(1) Consider this as the constant magnetic field (B) ensemble (also constant T is assumed), and construct the corresponding generalized canonical partition function. The magnetization is given by $M = \mu \sum S_{zi}$.

(2) Compute the magnetization as a function of the magnetic field and temperature.

Solution

(1) Since

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{B}{T} dM + \dots, \quad (6.2.65)$$

the generalized partition function reads

$$Z_H = (1 + e^{-\beta D + \beta \mu B} + e^{-\beta D - \beta \mu B})^N. \quad (6.2.66)$$

(2) The resulting generalized Massieu function

$$\psi = k_B \log Z_H \quad (6.2.67)$$

satisfies

$$d\psi = -Ed \left(\frac{1}{T} \right) + Md \left(\frac{B}{T} \right) + \dots \quad (6.2.68)$$

Therefore,

$$M = \frac{\partial \psi}{\partial (B/T)} = N \frac{\mu(e^{-\beta D + \beta \mu B} - e^{-\beta D - \beta \mu B})}{1 + e^{-\beta D + \beta \mu B} + e^{-\beta D - \beta \mu B}} = N \frac{\sinh \beta \mu B}{e^{-\beta D}/2 + \cosh \beta \mu B}. \quad (6.2.69)$$

2.14 [Absorption of mixed ideal gas, or convenient partition function]

There is a gas mixture consisting of two distinct atomic species A and B . The mixture is an ideal gas and the partial pressures of X is p_X ($X = A$ or B). The gas is in equilibrium with an adsorbing metal surface on which there are adsorption sites. Atom X adsorbed at the site is with energy $-E_X$ on the average relative to the one in the gas phase, where $X = A$ or B . Each surface site can accommodate at most one atom. Assume that [Hint: I assume that you know how to calculate the chemical potentials of the atoms, knowing the molecular weights.]

- (1) Write down the ‘partition function’ (use the most convenient one) for the single site.
- (2) Obtain the average surface concentration n_X ($X = A$ or B) of atoms A and B .
- (3) Under a given (partial) pressures of A and B $n_E : n_A : n_B = 1 : 1 : 18$ (here E means empty). Find the maximum concentration n_A obtainable with changing only the partial pressure of B . (UIUC Qual F95).

Solution

(1) Each adsorption site has three states, empty, occupied by A and occupied by B . Therefore, for a single site the grand partition function reads

$$\Xi = 1 + e^{\beta(E_A + \mu_A)} + e^{\beta(E_B + \mu_B)}, \quad (6.2.70)$$

where μ_X is the chemical potential of X that can be written as

$$\mu_X = k_B T \log(\beta p_X / n_{QX}) = k_B T \log(p_X / p_{QX}) \quad (6.2.71)$$

Here, n_{QX} is the ‘quantum density’ depending on T and the mass (see **1.4.5**), and $p_{QX} = n_{QX} k_B T$ may be called the ‘quantum pressure.’ Therefore,

$$\Xi = 1 + p_A e^{\beta E_A} / p_{QA} + p_B e^{\beta E_B} / p_{QB}. \quad (6.2.72)$$

You need not compute n_Q that is a matter of simple calculation as in **1.4.5**.

(2) As seen in **6-2** we may write

$$d(k_B T \log \Xi) = SdT + pdV + N_A d\mu_A + N_B d\mu_B + \dots, \quad (6.2.73)$$

so if we apply this to each site N_X may be interpreted as n_X :

$$n_A = \frac{\partial(k_B T \log \Xi)}{\partial \mu_A} = \frac{p_A e^{\beta E_A} / p_{QA}}{1 + p_A e^{\beta E_A} / p_{QA} + p_B e^{\beta E_B} / p_{QB}}, \quad (6.2.74)$$

$$n_B = \frac{p_B e^{\beta E_B} / p_{QB}}{1 + p_A e^{\beta E_A} / p_{QA} + p_B e^{\beta E_B} / p_{QB}}, \quad (6.2.75)$$

$$n_E = \frac{1}{1 + p_A e^{\beta E_A} / p_{QA} + p_B e^{\beta E_B} / p_{QB}}, \quad (6.2.76)$$

(3) It should be intuitively obvious that A absorption is facilitated if there is no competition. Hence, the maximum concentration should be accomplished by $p_B = 0$. Now, $n_A = n_E$ for a given p_B , so we must conclude that $p_A e^{\beta E_A} / p_{QA} = 1$. Therefore, the max conc must be 0.5.

2.15 [Absorption on catalytic surface]

There are N absorption centers on the catalyst surface exposed to a gas (ideal gas) of a certain chemical. Each absorption center can accommodate at most two particles. The partition function for the single particle absorption state is a_1 and the two particle absorption state is a_2 .

(1) Write down the single site (grand) partition function.

(2) Let $a_1 = 0$ (i.e., absorption is possible only when a pair is formed). The average number of particles absorbed on the catalytic surface is n_0 . Find the chemical potential of the particles.

(3) Now, the pressure of the chemical is doubled (with the temperature kept constant) and the average number of particles absorbed on the catalytic surface is n_1 . Find n_1 in terms of N and n_0 . a_1 is still assumed to be zero.

(4) If $a_1 > 0$, does the number of absorbed molecules increase from n_0 in (2) (i.e., the $a_1 = 0$ case)? Demonstrate your answer and give a brief physical explanation.

Solution

(1)

$$\Xi_{single} = 1 + a_1 e^{\beta \mu} + a_2 e^{2\beta \mu}. \quad (6.2.77)$$

(2) The average particle numbers in the system (= the catalytic surface; notice that the gas phase is treated as a chemical reservoir) is obtained by $\partial \log \Xi / \partial (\beta \mu)$

($\Xi = \Xi_{single}^N$):

$$n_0 = N \frac{2a_2x^2}{1 + a_2x^2}, \quad (6.2.78)$$

where $x = e^{\beta\mu}$ (called *fugacity*). Therefore, we have two possibilities, but x cannot be negative, since $\beta\mu \in \mathbf{R}$:

$$x = \sqrt{\frac{n_0/N}{(2 - n_0/N)a_2}}. \quad (6.2.79)$$

Therefore,

$$\mu = k_B T \log \sqrt{\frac{n_0/N}{(2 - n_0/N)a_2}}. \quad (6.2.80)$$

(3) If the pressure is doubled, the fugacity doubles. Therefore, (6.2.79) tells us that

$$2 \sqrt{\frac{n_0/N}{(2 - n_0/N)a_2}} = \sqrt{\frac{n_1/N}{(2 - n_1/N)a_2}}. \quad (6.2.81)$$

Solving this for n_1 , we get

$$n_1 = \frac{8n_0}{2 + 3n_0/N}. \quad (6.2.82)$$

(4) Equation (6.2.78) now reads

$$n = N \frac{a_1x + 2a_2x^2}{1 + a_1x + a_2x^2}. \quad (6.2.83)$$

This may be written as

$$n = N \left(1 + \frac{a_2x^2 - 1}{1 + a_1x + a_2x^2} \right). \quad (6.2.84)$$

$a_1x > 0$ implies that if $a_2x^2 > 1$ (i.e., $n/N > 1$), then increasing a_1 (that is, favoring monomers) decreases the number of the absorbed molecules; otherwise, opposite.

Physically (or intuitively), this should be natural, because if monomers are favored when dimers are also sufficiently favored, they compete the sites. Thus, the double occupancy fraction decreases, so does the total number of absorbed molecules.

2.16 [Gas under a weight]

Suppose there is a vertical cylindrical container of cross section s whose top wall is a movable piston of cross section s with mass M . The piston is assumed to move only in the vertical direction (z -direction) and feels gravity. The container contains

$N (\gg 1)$ classical noninteracting particles with mass m .

(1) Write down the Hamiltonian of the gas + piston system (write the piston vertical momentum as p_M).

(2) Obtain the pressure P of the gas, and write the Hamiltonian in terms of P and the volume of the gas $V = sz$, where z is the position of the piston from the bottom of the container.

(3) Now, the mechanical variables are the phase variables of the gas system and the piston momentum p_M and $z = V/s$. Compute the canonical partition function of the whole system.

(4) You should have realized that the calculation in (3), apart from the unimportant contribution in the thermodynamic limit of the piston momentum, is the calculation of the pressure ensemble. [That is, the heavy piston acts as a constant pressure device.] Obtain the equation of state of the gas in the cylinder (a trivial question).

Solution

(1)

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{p_M^2}{2M} + Mgz. \quad (6.2.85)$$

(2) From the force balance, we have

$$Ps = Mg \Rightarrow PV = Mgz. \quad (6.2.86)$$

Therefore, (6.2.85) can be rewritten as

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{p_M^2}{2M} + PV. \quad (6.2.87)$$

(3)

$$Z = \frac{1}{N!h^{3N+1}} \int d^N \mathbf{p} d^N \mathbf{q} dp_M dz e^{-\beta H}, \quad (6.2.88)$$

$$= \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \left(\frac{2\pi M k_B T}{h^2} \right)^{1/2} \int V^N e^{-\beta PV} \frac{dV}{s} \quad (6.2.89)$$

$$= \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \left(\frac{2\pi M k_B T}{h^2} \right)^{1/2} (\beta P)^{-N}. \quad (6.2.90)$$

Notice that this is almost the pressure ensemble for the ideal gas.

(4) We know (see **2.12**) the above Z is proportional to the pressure ensemble partition function Q :

$$Z = Q \left(\frac{2\pi M k_B T}{h^2} \right)^{1/2}, \quad (6.2.91)$$

where

$$Q = \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} (\beta P)^{-N}. \quad (6.2.92)$$

We know from the Laplace-Legendre correspondence that $G = -k_B T \log Q$:

$$G = -N k_B T \log \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} + N k_B T \log \frac{P}{k_B T}, \quad (6.2.93)$$

$dG = -SdT + VdP$, so

$$V = \left. \frac{\partial G}{\partial P} \right|_T = \frac{N k_B T}{P}. \quad (6.2.94)$$

This is the equation of state as expected. The enthalpy of the gas can be obtained by the Gibbs-Helmholtz relation

$$H = \left. \frac{\partial(G/T)}{\partial(1/T)} \right|_P = \frac{5}{2} N k_B T. \quad (6.2.95)$$

2.17 [Ideal gas with the aid of grand canonical ensemble]

Let us study the classical ideal gas with the aid of the grand canonical ensemble. Let μ be the chemical potential.

- (1) Compute the grand canonical partition function for a monatomic ideal gas. Assume that the mass of the atom is m .
- (2) Find the internal energy and the pressure as a function of chemical potential μ .
- (3) Suppose the expectation value of the number of particles is N . How is the chemical potential determined?
- (4) Are the results obtained above (especially the results of (2)) consistent with what you already know?

Solution

- (1) By definition

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} V^N e^{b\mu N} = \exp \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V e^{b\mu} \right] \quad (6.2.96)$$

(2) From this we get

$$P = \frac{k_B T}{V} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V e^{\beta\mu}. \quad (6.2.97)$$

Since

$$d(PV/T) = -Ed(1/T) + (P/T)dV + Nd(\mu/T), \quad (6.2.98)$$

$$E = T^2 \left. \frac{\partial k_B \log \Xi}{\partial T} \right|_{\mu/T, V} = \frac{3}{2} k_B T \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V e^{\beta\mu}. \quad (6.2.99)$$

Noice that this is equal to $3PV/2$.

(3) Since

$$N = \frac{1}{k_B} \frac{\partial}{\partial \beta\mu} \frac{PV}{T} = \frac{\partial}{\partial \beta\mu} \log \Xi = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V e^{\beta\mu}, \quad (6.2.100)$$

we obtain

$$\mu = k_B T \log \frac{N}{V} \left(\frac{2\pi m k_B T}{h^2} \right)^{-3/2}. \quad (6.2.101)$$

The result agrees with the result obtained in the text. If $n \ll n_Q$ (i.e., the classical case without overlapping of de Broglie wave packets), μ deviates verymuch to the negative side ($\mu \ll 0$).

(4) Thus, as has already been stated at various places, the results of the grand canonical ensemble completely reproduces the properties of the classic ideal gas.

2.18 [To obtain the microcanonical partition function with the aid of Laplace inverse transformation]

Starting from

$$Z = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}, \quad (6.2.102)$$

obtain the microcanonical partition fuction $w(E, V)$ (with the aid of Laplace inverse transformation).

Solution

$$w(E, V) = \frac{1}{2\pi i} \int_{\beta^* - 9\infty}^{\beta^* + i\infty} Z(\beta) e^{\beta E} d\beta. \quad (6.2.103)$$

If you can demonstrate the following formula, you may use it:

$$\frac{1}{2\pi i} \int_{s' - i\infty}^{s' + i\infty} \frac{e^{sx}}{x^{k+1}} ds = \frac{x^k}{\Gamma(k+1)}. \quad (6.2.104)$$

If k is an integer, this is almost self-evident with the aid of Goursat's theorem, but in our case k need not be an integer.

2.19 [Equivalence of canonical and grand canonical ensembles]

Let us check the equivalence of grand canonical and canonical ensembles. That is, if we compute thermodynamic quantities in the thermodynamic limit, both give the same answers. Even experimentalists should look at this proof at least once in their lives.

The grand partition function $\Xi(T, \mu)$ and canonical partition function $Z(T, N)$ (the ground state energy is taken to be the origin of energy) are related as

$$\Xi(T, \mu) = \sum_{N=0}^{\infty} Z(T, N) e^{\beta \mu N}.$$

Let us assume that the system consists of N (which is variable) particles in a box of volume V and the total interaction potential Φ among particles is bounded from below by a number proportional to the number of particles N in the system: $\Phi \geq -NB$, where B is a (positive) constant. (The system Hamiltonian generally has the form of $H = K + \Phi$, where K is the kinetic energy.)

Through answering the following almost trivial questions, we can demonstrate the ensemble equivalence (rigorously).

(1) Show that there is a constant a such that

$$Z(T, N) \leq \left(\frac{aV}{N} \right)^N. \quad (6.2.105)$$

Actually, show (classically)

$$Z(T, N) \leq Z_0(T, N) e^{\beta NB},$$

where Z_0 is the canonical partition function for the ideal gas (e.g., (1.7.3)). This is just eq.(6.2.105) above

(2) Show that the infinite sum defining the grand partition function actually converges. The reader may use eq.(6.2.105) and $N! \sim (N/e)^N$ freely.

(3) Choose N_0 so that

$$\sum_{N=N_0}^{\infty} Z(T, N) e^{\beta \mu N} < 1.$$

Show that this N_0 may be chosen to be proportional to V (that is, N_0 is at most extensive).

(4) Show the following almost trivial bounds:

$$\max_N Z(T, N) e^{\beta \mu N} \leq \Xi(T, \mu) \leq (N_0 + 1) \max_N Z(T, N) e^{\beta \mu N}.$$

(5) We are almost done, but to be explicit, show that $PV/Nk_B T$ obtained thermodynamically from the canonical partition function and that directly obtained from the grand partition function agree.

Solution

(1) The canonical partition function reads

$$Z(T, N) = \frac{1}{N!} \int d\Gamma e^{-\beta(K+\Phi)} \leq \frac{1}{N!} \int d\Gamma e^{-\beta K} e^{\beta B N} = Z_0(T, N) e^{\beta N B}, \quad (6.2.106)$$

where Z_0 is the canonical partition function of the ideal gas. We know the kinetic part may be factorized into the individual particle contributions, and $N! \sim (N/e)^N$, so there must be a satisfying the inequality.

Remark. The estimate is also correct quantum mechanically, so our proof being checked here is quite general.

(2) The grand partition function is a positive term series, and each term is bounded by the estimate in (1), so

$$\Xi(T, \mu) = \sum_{N=0}^{\infty} Z(T, N) e^{\beta \mu N} \leq \sum_{N=0}^{\infty} \left(\frac{aV}{N} \right)^N e^{\beta \mu N} = \sum_{N=0}^{\infty} \left(\frac{aV e^{\beta \mu}}{N} \right)^N.$$

That is, with the aid of Stirling's formula,

$$\Xi(T, \mu) \leq \sum_{N=0}^{\infty} \frac{1}{N!} (aV e^{\beta \mu - 1})^N = \exp(aV e^{\beta \mu - 1}).$$

The grand canonical partition function is a sum of positive terms, and bounded from above, so it must converge to a positive number.

For many realistic systems the interaction potentials have sufficiently hard repulsive cores, so the convergence is much quicker.

(3) This is the tail estimation to majorize it. Any crude choice will do, so we first 'overestimate' the sum beyond N_0 as

$$\sum_{N=N_0}^{\infty} Z(T, N) e^{\beta \mu N} \leq \sum_{N=N_0}^{\infty} \frac{1}{N!} (aV e^{\beta \mu - 1})^N \simeq \sum_{N=N_0}^{\infty} \left(\frac{aV e^{\beta \mu}}{N} \right)^N \quad (6.2.107)$$

Here, Stirling's formula has been used. For example, if we assume

$$\frac{aV e^{\beta \mu}}{N_0} < 0.1, \quad (6.2.108)$$

then

$$\sum_{N=N_0}^{\infty} Z(T, N)e^{\beta\mu N} < \sum_{N=N_0}^{\infty} 0.1^N. \quad (6.2.109)$$

The sum on the RHS is obviously bounded by 0.2 (by 1/9, at worst $N_0 = 1$). Thus, the choice (6.2.108) is enough. Such N_0 can clearly be chosen proportional to V .

(4) The grand partition function is a sum of positive terms, so it must be larger than any one term, especially larger than the largest term, in it:

$$\max_N Z(T, N)e^{\beta\mu N} \leq \Xi(T, \mu). \quad (6.2.110)$$

Notice that the largest term cannot be less than 1, because the $N = 0$ term is never smaller than 1.¹⁶ To obtain the upper bound Ξ is divided into the sum up to $N_0 - 1$ and that beyond $N_0 - 1$:

$$\Xi(T, \mu) = \sum_{N=0}^{N_0-1} Z(T, N)e^{\beta\mu N} + \sum_{N=N_0}^{\infty} Z(T, N)e^{\beta\mu N}. \quad (6.2.111)$$

The second term on the right hand side is bounded by 1, which is not larger than the maximum term in the sum, so it is bounded by $\max_N Z(T, N)e^{\beta\mu N}$. Therefore,

$$\Xi(T, \mu) \leq \sum_{N=0}^{N_0-1} Z(T, N)e^{\beta\mu N} + \max_N Z(T, N)e^{\beta\mu N}. \quad (6.2.112)$$

The sum in the above inequality must be less than the number of terms \times the largest term:

$$\sum_{N=0}^{N_0-1} Z(T, N)e^{\beta\mu N} \leq N_0 \max_N Z(T, N)e^{\beta\mu N}. \quad (6.2.113)$$

Therefore, we have

$$\Xi(T, \mu) \leq (N_0 + 1) \max_N Z(T, N)e^{\beta\mu N}. \quad (6.2.114)$$

Combining this with (6.2.110) we get the desired result.

¹⁶Notice that $Z(T, 0) \geq 1$: recall

$$Z(T, N) = \sum w(E, N)E^{-\beta E},$$

and $N = 0$ term is of course included, which is 1. This means $\max_N Z(T, N)e^{\beta\mu N} \geq 1$.

(5) The grand canonical ensemble asserts

$$\frac{PV}{Nk_B T} = \frac{1}{N} \log \Xi(T, \mu).$$

From the above inequality

$$\frac{1}{N} \log \left(\max_N Z(T, N) e^{\beta \mu N} \right) \leq \frac{PV}{Nk_B T} \leq \frac{1}{N} \log \left(\max_N Z(T, N) e^{\beta \mu N} \right) + \frac{1}{N} \log(N_0 + 1).$$

Notice that

$$\frac{1}{N} \log \max_N Z(T, N) e^{\beta \mu N} = \frac{1}{N} \max_N \{-\beta A + \beta \mu N\}$$

is a Legendre transformation of A (recall $dA = -SdT - PdV + \mu dN$ or $A = -PV + \mu N$). Therefore, $\min_N \{A - \mu N\} = -PV$. This is the PV obtained thermodynamically with the aid of the canonical ensemble results. That is,

$$\left(\frac{PV}{Nk_B T} \right)_{th} \leq \frac{PV}{Nk_B T} \leq \left(\frac{PV}{Nk_B T} \right)_{th} + \frac{1}{N} \log(N_0 + 1).$$

$\log(N_0 + 1)$ is bounded by a number proportional to $\log V$ as demonstrated in (3), so in the $N \rightarrow \infty$ limit the rightmost term behaves at worst as $(\log N)/N$, and may be ignored. Therefore, the pressure obtained thermodynamically from the Helmholtz free energy (obtained by the canonical ensemble) and the pressure directly obtained statistical mechanically with the aid of the grand canonical ensemble agree:

$$\left(\frac{PV}{Nk_B T} \right)_{th} = \frac{PV}{Nk_B T}.$$

2.20 [Legendre transformation in [convex analysis](#)]

(1) We know that $-S$ is a convex function of internal energy E . Using the general property of the Legendre transformation, show that Helmholtz free energy A is convex upward as a function of T . You may assume any derivative you wish to compute exists.

(2) When a phase transition occurs, the curve of $S(E)$ has a linear part as a function of E (that is, E can change under constant $T = T_e$). Then, A as a function has a cusp at $T = T_e$ (that is, all the states corresponding to the flat part is collapsed to a point, the one-to-one nature of the Legendre transformation can be lost, if there is a phase transition). To illustrate this point, let us consider the following toy function

$$f(x) = \begin{cases} 2 \tanh(x+1) - 2 & \text{for } x < -1, \\ 2x & \text{for } -1 \leq x \leq 1, \\ (x-1)^2 + 2x & \text{for } x > 1. \end{cases}$$

Sketch its Legendre transform $f^*(\alpha) = \sup_x[\alpha x - f(x)]$. [Do not try to compute the explicit formula.]

Solution

(1) $-S$ is a convex function of E , so that it is also a convex function of $-E$. We know

$$-\frac{A}{T} = \sup_T[-E/T - (-S)]. \quad (6.2.115)$$

Therefore, $-A/T$ is a convex function of $1/T$. A dirty way to proceed is to perform differentiation twice.

$$\frac{d(-A/T)}{d(1/T)} = -A - \frac{1}{T} \frac{dA}{d(1/T)} = -A + T \frac{dA}{dT}. \quad (6.2.116)$$

Therefore,

$$\frac{d^2(-A/T)}{d(1/T)^2} = -T^2 \frac{d}{dT} \left(-A + T \frac{dA}{dT} \right) = -T^3 \frac{d^2 A}{dT^2} > 0 \quad (6.2.117)$$

Therefore, A is a concave function of T .

(2) We consider the Legendre transformation

$$f^*(\alpha) = \sup_x[\alpha x - f(x)] \quad (6.2.118)$$

For $\alpha > 2$ this is easy, and we obtain $f^*(\alpha) = \alpha^2/2 - 1$. Between -2 and 2 of x the slope of f does not change and is 2 , so $\alpha = 2$, which means $f^*(2) = 0$ is a cusp. For $\alpha < 2$, analytic calculation is not wise. We know α cannot be negative, and in the $\alpha \rightarrow 0$ limit, $f^* \rightarrow 4$, because $\lim_{x \rightarrow -\infty} f(x) = -4$. Since f^* is convex, we can easily sketch its overall shape as below:

Remember that convex functions are continuous.

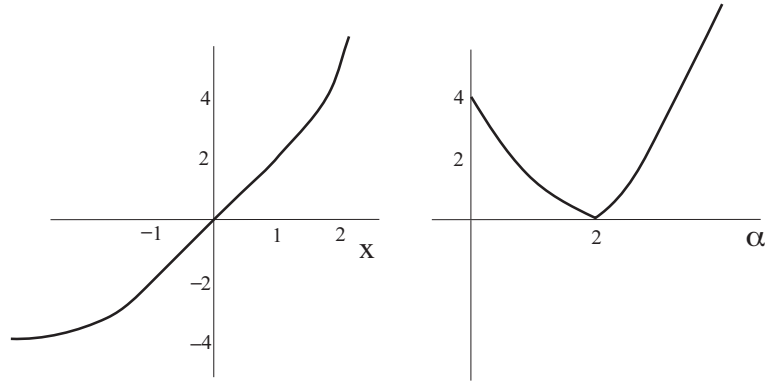
2.21 [Information]

Suppose there are two fair dice. We assume that one dice is red and the other is green (that is, distinguishable). Let us record the numbers that are up in this order as (n, m) ($n, m \in \{1, 2, \dots, 6\}$).

(1) To know a particular pair of numbers (a, b) unambiguously what information (in bits) do you need?

(2) You are told that the sum $a + b$ is not less than 5. What is the information you gain from this message?

(3) Next, you are told, one of the dice shows the face less than 3. What is the



Left: f , Right: f^* .

information you gain? (You must know the info obtained from (2) already.)

(4) Now, you are told that actually, the one of the dice in (3) is the red one. What is the information carried by this message?

(5) Finally, you are told that face pair is actually (2, 5). What is the information in this final statement?

Solution

(1) There are 36 distinguishable states and they are all equally probable. Therefore, the total uncertainty is $\log_2 36 = 5.16$ bits, or the surprisal you have when you are told, say, (1, 1) actually happens is 5.16 bits. That is, you need 5.16 bits of information to pinpoint a particular elementary event.

(2) There is no simpler way than actually to list all elementary states up: (1,1), (1,2), (1,3), (2,1), (2,2), (3, 1). These 6 states are excluded. Remaining are 30 states, all equally probably, so $\log_s 30 = 4.91$ bits is the uncertainty. That is, $5.16 - 4.91 = 0.25$ bits is the information in the message.

(3) Red = 1: Green = 4, 5 or 6

Red = 2: Green = 3, 4, 5 or 6.

Therefore, there are $7 \times 2 = 14$ states remaining. This uncertainty is $\log_2 14 = 3.81$. We had 4.91 bits of uncertainty, so this message must have conveyed 1.1 bits.

(4) Obviously, 1 bit.

(5) There is no uncertainty remaining, so 2.81 bits (this is, needless to say, the surprisal of an event of probability 1/7)

2.22 [Variational principle for free energy (classical case)¹⁷]

Let $H = H_0 + V$ be a system Hamiltonian.

(1) Show that_q

$$A \leq A_0 + \langle V \rangle_0,$$

¹⁷This holds quantum mechanically as well, but the proof is not this simple.

where A is the free energy of the system with H and A_0 that with H_0 . $\langle \rangle_0$ is the average over the canonical distribution of the system with the Hamiltonian H_0 . The inequality is (sometimes) called the Gibbs-Bogoliubov inequality.

(2) We can use the inequality to estimate A . If we can compute A_0 and $\langle V \rangle_0$ (that is the free energy for the system with H_0 and the average with respect to this system), then we can estimate the upper bound of A . Its minimum may be a good approximation to A . This is the idea of the variational approximation. Let us study an unharmonic oscillator with the Hamiltonian

$$H = \frac{1}{2m}p^2 + \frac{1}{2}kx^2 + \frac{1}{4}\alpha x^4,$$

where m , k and α are positive constants. Let us define

$$H_0 = \frac{1}{2m}p^2 + \frac{1}{2}Kx^2.$$

Choose K to obtain the best estimate of A (you need not compute the estimate of A ; it is easy but messy). You may use all the available results in the text.

Solution

(1)

$$\langle e^{-\beta V} \rangle_0 = \frac{1}{Z_0} \int d\Gamma e^{-\beta V} e^{-\beta H_0} = \frac{Z}{Z_0} = e^{-\beta(A-A_0)}.$$

Therefore, with the aid of **Jensen's inequality**

$$e^{-\beta \langle V \rangle_0} \leq e^{-\beta(A-A_0)}.$$

That is, we are done.

(2) We know

$$A_0 = k_B T \log \left[\frac{\hbar \sqrt{K/m}}{k_B T} \right]$$

and (with the aid of $\langle x^4 \rangle_0 = 3\langle x^2 \rangle_0^2$ and equipartition of energy)

$$\left\langle \frac{1}{4}\alpha x^4 \right\rangle_0 = \frac{3\alpha}{4K^2} (k_B T)^2.$$

That is,

$$A \leq k_B T \log \left[\frac{\hbar \sqrt{K/m}}{k_B T} \right] + \frac{1}{2}(k/K - 1)k_B T + \frac{3\alpha}{4K^2} (k_B T)^2.$$

Minimizing the right hand side wrt K , we obtain

$$\frac{1}{2K} - \frac{k}{2K^2} - \frac{3\alpha}{8K^3} k_B T = 0.$$

If $\alpha = 0$ clearly we get the right answer $K = k$. Solving this, we obtain

$$K = \frac{1}{2} \left(k + \sqrt{k^2 + 3\alpha k_B T} \right).$$

2.23 [Gibbs-Bogoliubov's inequality (quantum case)]¹⁸
Gibbs-Bogoliubov's inequality

$$A \leq A_0 + \langle H - H_0 \rangle_0 \quad (6.2.119)$$

holds in quantum statistical mechanics as well.

(1) Demonstrate Peierls' inequality:

$$\text{Tr} e^{-\beta H} \geq \sum_i e^{-\langle i|H|i \rangle}, \quad (6.2.120)$$

where $\{|i\rangle\}$ is an arbitrary orthonormal basis.

(2) Let $\{|i\rangle\}$ be the orthonormal basis consisting of the eigenstates for H_0 . Then,

$$e^{-\beta A} \geq \sum_i e^{-\beta \langle i|H|i \rangle} = e^{-\beta A_0} \sum_i e^{\beta(A_0 - \langle i|H_0|i \rangle)} e^{-\beta \langle i|(H-H_0)|i \rangle}. \quad (6.2.121)$$

Show Gibbs-Bogoliubov's inequality with the aid of Jensen's inequality.

Soln.

(1) We need Klein's inequality: Let f be convex C^1 . Then,

$$\text{Tr}[f(\rho) - f(\sigma) - (\rho - \sigma)f'(\rho)] \geq 0. \quad (6.2.122)$$

Let $\rho|x\rangle = c|x\rangle$ and $\sigma|y\rangle = y|y\rangle$.

$$\text{Tr}[f(\rho) - f(\sigma) - (\rho - \sigma)f'(\rho)] = \sum_x \langle x|[f(\rho) - f(\sigma) - (\rho - \sigma)f'(\rho)]|x\rangle \quad (6.2.123)$$

$$= \sum_x \langle x| \left[f(x) - \sum_y |y\rangle f(y) \langle y| - (x - \sum_y |y\rangle y \langle y|) f'(x) \right] |x\rangle \quad (6.2.124)$$

¹⁸M D Girardeau and R M Mazo, "Variational methods in statistical mechanics,"

Notice that $\sum_{x,y} \langle x|y\rangle \langle y|x\rangle = 1$, so

$$\text{Tr}[f(\rho) - f(\sigma) - (\rho - \sigma)f'(\rho)] = \sum_x |\langle x|y\rangle|^2 [f(x) - f(y) - (x - y)f'(x)] \quad (6.2.125)$$

2.24 (1) For any density operator P

$$A \leq \text{Tr}P(H + k_B T \log P), \quad (6.2.126)$$

where A is the free energy for the system whose hamiltonian is H .

(2) Suppose P is the canonical density operator $P = e^{\beta(A_0 - H_0)}$ for a system with the Hamiltonian H_0 . Show that the above inequality is just Gibbs-Bogoliubov's inequality.

2.25 [Convexity of free energy] (Ruelle)

$$A[\sum \lambda_i H_i] \geq \sum A[\lambda_i H_i]. \quad (6.2.127)$$

Soluton

Hölder + Peierls proves this.

2.26 [Thermodynamic perturbation theory]

Suppose the system Hamiltonian is given as $H = H_0 + \epsilon H_1$, where ϵ is a (small) constant. Demonstrate the following expansion formula:

$$A = A_0 + \epsilon \langle H_1 \rangle_0 - \frac{1}{2} \beta \epsilon^2 \langle (H_1 - \langle H_1 \rangle_0)^2 \rangle_0 + \dots, \quad (6.2.128)$$

where A is the free energy of the system, A_0 is the free energy in case $H_1 = 0$, and $\langle \rangle_0$ is the expectation with respect to the canonical distribution with the Hamiltonian H_0 .

2.27 [Jarzynski's equality].¹⁹

A single stranded DNA with a certain binding protein is stretched slowly until the protein dissociates from the DNA. Then, the length of the DNA is returned slowly to the rather relaxed state where the binding of the molecule does not affect the DNA tension. The work W dissipated during the cycle is measured at 300K and the experimental results were as follows:

¹⁹Inspired by Rustem Khafizov and Yan Chemla's experiment on SSB. The numbers are only fictitious. although the magnitudes are realistic.

W in pNnm	number of times	βW	$e^{-\beta W}$
78-82	4	19.3	4.04×10^{-9}
83-87	15	20.5	1.21×10^{-9}
88-92	7	21.74	3.62×10^{-10}
93-97	4	22.94	1.082×10^{-10}
98-102	1	24.15	3.23×10^{-11}

What is the best estimate of the (Gibbs) free energy change due to binding of the protein in the relaxed state of the single stranded DNA? How is your estimate different from the simple average $\langle W \rangle$?

Solution

Notice that $k_B T = 4.14 \text{ pNnm}$. $e^{-\beta W}$ is written in the above table. Thus,

$$\sum e^{-\beta W} = 373.1 \times 10^{-10} \Rightarrow \langle e^{-\beta W} \rangle = 1.2 \times 10^{-9} \quad (6.2.129)$$

That is, our estimate of ΔA is 85.0 pNnm. If we directly average the result, we obtain 87.4 pNnm. Of course, we have ‘confirmed’ the second law $\langle W \rangle \geq \Delta A$.

Although we wrote A in the above, its definition is complicated.

2.28 [Fluctuation and spring constant]²⁰

Inside the F_1 ATPase is a rotor γ to which a long actin filament (it is a straight stiff bar of length 30 nm) is perpendicularly attached. Thus, the filament swings back and forth when the ATPase is waiting for an ATP molecule.

(1) The root mean square angle fluctuation of the stiff filament was 30 degrees at 290K. If the temperature is raised by 10%, by what percentage will the angular fluctuation change? Assume that the molecular structure is not affected by this temperature change.

(2) What is the torsional spring constant of this rotor captured by the surrounding ring?

(3) Now, adding an appropriate polymers to the ambient solution, the effective viscosity of the solution is doubled. What is the mean square angle fluctuation of the filament? You may assume that the polymers do not affect the ATPase itself.

Solution

(1) Suppose θ is the angular deviation around the equilibrium direction. Then, the torsional spring constant k reads

$$\tau = k\theta, \quad (6.2.130)$$

²⁰If you wish to see the structure of the ATPase or to learn about how you can be alive, see K. Kinosita, K. Adachi, and H. Itoh, “Rotation of F_1 ATPase: how an ATP-driven molecular machine may work,” *Ann. Rev. Biophys. Biomol. Struct.*, **33**, 245 (2005).

where τ is the torsion. Since, k^{-1} is the ‘susceptibility’ of θ against τ , the fluctuation-response relation tells us

$$k^{-1} = \left. \frac{\partial \theta}{\partial \tau} \right|_T = \beta \langle (\delta \theta)^2 \rangle. \quad (6.2.131)$$

That is,

$$\langle (\delta \theta)^2 \rangle = k_B T / k. \quad (6.2.132)$$

Since we may assume k does not depend on T , the fluctuation should change by about 5%.

(2) You must measure the angle in radians.

$$k = 1.382 \times 10^{-23} \times 290 / (\pi/6)^2 = 1.46 \times 10^{-20} \quad (6.2.133)$$

The unit is J/rad. Is it reasonable? It is about 15 pNnm/rad, a reasonable value.

(3) No change. The formula does not depend on the viscosity, so the amplitude of the fluctuation never changes. This is true however gooey the solution is. It is true that the oscillation becomes slow, but then small fluctuations can be accumulated to a size as large as when the viscosity is very low.

2.29 [Thermodynamic fluctuations]

(1) Suppose X and y are nonconjugate pair with respect to energy, X extensive and y intensive. Prove that $\langle \delta X \delta y \rangle = 0$.

(2) Let X and x be a conjugate pair (wrt energy). Show $\langle \delta X \delta x \rangle = k_B T$.

(3) Express $\langle \delta \mu^2 \rangle$ in terms of a single thermodynamic derivative. The system is assumed to be described in terms of S, V, N (or their conjugate variables).

(4) Show with the aid of grand partition function that

$$k_B T^2 \left. \frac{\partial E}{\partial T} \right|_{\mu, V} = \langle \delta E^2 \rangle - \mu \langle \delta E \delta N \rangle.$$

(5) Let X be an extensive quantity. What can you conclude about $\langle \delta S \delta X \rangle$? The result is pedagogically suggestive, because entropy fluctuation means spatially local heat transport: that is, local temperature change.

Solution

(1) Recall that you can choose any combination of variables as independent variables as long as one variable is chosen from each conjugate pair $\{X, x\}$. We know $\langle \delta X_i \delta X_j \rangle$, so in this case, we should use the all extensive independent variable set.

$$\langle \delta X \delta y \rangle = \left\langle \delta X \sum_Y \frac{\partial y}{\partial \Sigma_Y} Y \delta Y \right\rangle = k_B T \sum_Y \frac{\partial Y}{\partial x} \frac{\partial y}{\partial Y} = k_B T \frac{\partial y}{\partial x} = 0.$$

In more detail for those who are skeptic:

$$dx = \sum_j \frac{\partial x}{\partial X_j} \Big|_{X_1 \dots \check{X}_j \dots X_n} dX_j, \quad (6.2.134)$$

where \check{X}_j implies to remove the variable under the check mark. Therefore,

$$\frac{\partial x_i}{\partial x_k} \Big|_{x_1 \dots \check{x}_k \dots x_n} = \sum_j \frac{\partial x_i}{\partial X_j} \Big|_{X_1 \dots \check{X}_j \dots X_n} \frac{\partial X_j}{\partial x_k} \Big|_{x_1 \dots \check{x}_k \dots x_n}. \quad (6.2.135)$$

We put (6.2.134) into $\langle \delta X \delta y \rangle$ (regarding X is a representative of $\{X_j\}$ and y that of $\{x_k\}$ (the derivatives are mere constants, so you can take them out of the average symbol). Now, (6.2.135) tells you what you want.

(2)

$$\langle \delta X \delta x \rangle = \left\langle \delta X \frac{\partial x}{\partial Y} \delta Y \right\rangle = k_B T \sum_Y \frac{\partial Y}{\partial x} \frac{\partial x}{\partial Y} = k_B T.$$

(3) Taking into account of (1) above, we should choose μ, S, V as independent variables.

$$\delta^2 S = -\frac{1}{2T} (\delta N \delta \mu + \dots) = -\frac{1}{2T} \frac{\partial N}{\partial \mu} \Big|_{S,V} \delta \mu^2 + \dots$$

Therefore,

$$P(\delta \mu \dots) \propto \exp \left\{ -\frac{1}{2k_B T} \left(\frac{\partial N}{\partial \mu} \Big|_{S,V} \delta \mu^2 + \dots \right) \right\}.$$

That is,

$$\langle \delta \mu^2 \rangle = k_B T \frac{\partial \mu}{\partial N} \Big|_{S,V}.$$

(4) Since

$$\Xi = \sum_{N=0}^{\infty} Z_N(T) e^{\beta \mu N} = \sum_{N=0}^{\infty} \int dE w_{E,N} e^{-\beta E + \beta \mu N},$$

$$\langle E \rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} \int dE w_{E,N} E e^{-\beta E + \beta \mu N}.$$

Therefore,

$$\begin{aligned} \frac{d\langle E \rangle}{d\beta} &= \frac{1}{\Xi} \sum_{N=0}^{\infty} \int dE W_{E,N} E (\mu N - E) e^{-\beta E + \beta \mu N} \\ &\quad - \frac{1}{\Xi^2} \sum_{N=0}^{\infty} \int dE w_{E,N} E e^{-\beta E + \beta \mu N} \sum_{N=0}^{\infty} \int dE w_{E,N} (\mu N - E) e^{-\beta E + \beta \mu N}, \\ &= \langle \delta E (\mu \delta N - \delta E) \rangle \end{aligned}$$

(5)

$$\langle \delta S \delta X \rangle = k_B T \left. \frac{\partial X}{\partial T} \right|_x.$$

That is, the temperature derivative is the cross correlation with entropy fluctuation. This is, although trivial, worth remembering.

2.30 [Equilibrium fluctuation]

- (1) Obtain $\langle \delta S \delta V \rangle$.
- (2) Obtain $\langle \delta P \delta T \rangle$.

Solution

(1) Perhaps, the cleverest way is to use the [fluctuation-response relation](#). We immediately obtain

$$\langle \delta S \delta V \rangle = k_B T \left. \frac{\partial V}{\partial T} \right|_P. \quad (6.2.136)$$

There is no simple trick, if you wish to use thermodynamic fluctuation theory. Choose S and V as independent variables.

$$\frac{1}{2k_B T} [\delta S \delta T - \delta P \delta V] = \frac{1}{2k_B T} \left[\left. \frac{\partial T}{\partial S} \right|_V + 2 \left. \frac{\partial T}{\partial V} \right|_S \delta V \delta S - \left. \frac{\partial P}{\partial V} \right|_S \delta V^2 \right]. \quad (6.2.137)$$

Therefore, (with the aid of the [formulas](#) for 2 variate Gaussian distribution)

$$\langle \delta S \delta V \rangle = k_B T \left. \frac{\partial T}{\partial V} \right|_S = -k_B T \left. \frac{\partial S}{\partial P} \right|_T = k_B T \left. \frac{\partial V}{\partial T} \right|_P. \quad (6.2.138)$$

(2) There is no simple trick. Choose T and P as independent variables.

$$\frac{1}{2k_B T} [\delta S \delta T - \delta P \delta V] = \frac{1}{2k_B T} \left[\left. \frac{\partial S}{\partial T} \right|_P \delta T^2 + 2 \left. \frac{\partial S}{\partial P} \right|_T \delta T \delta P - \left. \frac{\partial V}{\partial P} \right|_T \delta P^2 \right]. \quad (6.2.139)$$

Therefore, (with the aid of the formulas for 2 variate Gaussian distribution)

$$\langle \delta T \delta P \rangle = k_B T \frac{1}{\frac{\partial V}{\partial P} \Big|_T \frac{\partial S}{\partial T} \Big|_P + \frac{\partial S}{\partial P} \Big|_T^2} \frac{\partial S}{\partial P} \Big|_T. \quad (6.2.140)$$

This is OK as an answer, but we can go further, if we realize

$$\langle \delta T \delta P \rangle = k_B T \frac{1}{\frac{\partial(V,S)}{\partial(P,T)}} \frac{\partial S}{\partial P} \Big|_T = k_B T \frac{\frac{\partial(S,T)}{\partial(P,T)}}{\frac{\partial(V,S)}{\partial(P,T)}} = k_B T \frac{\partial(S,T)}{\partial(V,S)} = -k_B T \frac{\partial T}{\partial V} \Big|_S. \quad (6.2.141)$$

2.31 [Fluctuation and Le Chatelier-Braun's principle]

(1) Show that

$$\langle \delta x \delta X \rangle^2 \leq \langle \delta x^2 \rangle \langle \delta X^2 \rangle$$

where x and X are conjugate pair of thermodynamic variables (wrt energy).

(2) What is the relation between this inequality and the [Le Chatelier-Braun principle](#)?

Solution

(1) The easiest way is to use the following obvious inequality valid for any real t :

$$0 \leq \langle (\delta X + t \delta x)^2 \rangle = \langle \delta X^2 \rangle + 2t \langle \delta x \delta X \rangle + t^2 \langle \delta x^2 \rangle \quad (6.2.142)$$

Since $\langle \delta x^2 \rangle \geq 0$, we have its discriminant to be negative:

$$\langle \delta x \delta X \rangle^2 - \langle \delta X^2 \rangle \langle \delta x^2 \rangle \leq 0. \quad (6.2.143)$$

(2) We know $\langle \delta x \delta X \rangle = k_B T$, and (use clever way of calculating fluctuations)

$$\langle \delta X^2 \rangle = k_B T \frac{\partial x}{\partial X} \Big|_y^{-1}, \quad \langle \delta x^2 \rangle = k_B T \frac{\partial X}{\partial x} \Big|_Y^{-1}. \quad (6.2.144)$$

Therefore,

$$\frac{\partial x}{\partial X} \Big|_y \leq \frac{\partial x}{\partial X} \Big|_Y. \quad (6.2.145)$$

Thus we have learned that Le Chatelier-Braun principle is a realization of $|\cos \theta| \leq 1$ (or Cauchy-Schwarz inequality) just as Hesenberg's uncertainty relation.

2.32 [Fluctuation of internal energy]

For a classical monatomic ideal gas consisting of N atoms, compute the fluctuation of its internal energy (under constant T and P). Or show

$$\langle (E - \langle E \rangle)^2 \rangle / \langle E \rangle^2 = 2/3N. \quad (6.2.146)$$

Solution

The Gibbs relation $dE = TdS - PdV$ implies

$$\langle \delta E^2 \rangle = T^2 \langle \delta S^2 \rangle - 2TP \langle \delta S \delta V \rangle + P^2 \langle \delta V^2 \rangle. \quad (6.2.147)$$

The volume fluctuation can be found as

$$\langle \delta V^2 \rangle = -k_B T \left. \frac{\partial V}{\partial P} \right|_T = k_B \frac{V}{P}. \quad (6.2.148)$$

The entropy fluctuation can be calculated with the aid of S and P as independent variables, we conclude

$$\delta T = \left. \frac{\partial T}{\partial S} \right|_P \delta S + \dots, \quad (6.2.149)$$

so

$$\langle \delta S^2 \rangle = T \left. \frac{\partial S}{\partial T} \right|_P = k_B C_P = \frac{5}{2} k_B^2 N. \quad (6.2.150)$$

Therefore, we need a result we have already **obtained**:

$$\langle \delta S \delta V \rangle = k_B T \left. \frac{\partial V}{\partial T} \right|_P = k_B V. \quad (6.2.151)$$

Combining all the results, we obtain

$$\langle \delta E^2 \rangle = k_B T^2 C_P - 2P k_B T^2 \left. \frac{\partial V}{\partial T} \right|_P - P^2 k_B T \left. \frac{\partial V}{\partial P} \right|_T, \quad (6.2.152)$$

$$= k_B^2 T^2 \left(\frac{5}{2} N - 2N + N \right) = \frac{3}{2} (k_B T)^2 N. \quad (6.2.153)$$

We know $\langle E \rangle = 3k_B T N / 2$, so we arrive at the desired result.

2.33 [Stability and related topics, e.g., Le Chatelier-Braun]

(1) Suppose a phase transition from phase I to phase II occurs upon increasing the magnetic field in the z -direction. What can you say about the **relation** between the magnetisms of the phases?

(2) Suppose phase I is a low temperature phase and II a high temperature phase.

The phase transition I \rightarrow II is first order. What can you say about the sign of the latent heat ΔH of this phase transition?

(3) Which specific heat is larger, C_B or C_M (under constant magnetic field, and under constant magnetization, respectively)?

(4) Suppose there is a dielectric material between a parallel plate capacitor. The two plates of the capacitor may be short-circuited by a switch. What can you say about the relation between the heat capacity of the dielectric material under the open- and short-circuited conditions? Let ε be its dielectric constant, that may or may not depend on temperature.

(5) Suppose there is a liquid that crystallizes upon heating. Discuss the latent heat for this transition.²¹

Solution

(1) The internal energy must be convex, so the susceptibility must be nonnegative, if M is differentiable with respect to B . At the phase transition this is not usually the case, but still the convexity must hold, so M must increase in the second phase.

(2) The argument is the same as above (we did this problem before!). Increasing T must increase S , so S is larger for II. Therefore, $\Delta H = T\Delta S > 0$ if we go from I to II. That is latent heat must be absorbed by the system.

(3) This can be answered with the aid of **Braun's principle**:

$$\left. \frac{\partial x}{\partial X} \right|_y < \left. \frac{\partial x}{\partial X} \right|_Y. \quad (6.2.154)$$

Thus,

$$\left. \frac{\partial T}{\partial S} \right|_B = \frac{T}{C_B} < \left. \frac{\partial T}{\partial S} \right|_M = \frac{T}{C_M}. \quad (6.2.155)$$

That is, $C_B > C_M$: under constant B M is reorganized to absorb more heat. This is a hint to the next problem.

(4) When short-circuited, the electric field across the dielectric material is maintained to be constant (actually, zero). When, the circuit is open, then the surface charge (if any) on the dielectric material is kept constant; electric flux D is maintained. Therefore, thermodynamically we expect $C_E \geq C_D$. Now, ε is given, so we know the relation between D and E : $D = \varepsilon EV$ (D is extensive but E is not! $D = \varepsilon E$ is a relation for a unit volume! Here, we assume V does not change). We should proceed

²¹ Johari, et al., "Endothermic freezing on heating and exothermic melting on cooling," J. Chem. Phys., **123**, 051104 (2005): α -cyclodextrin + water + 4-methylpyridine (molar ratio of 1:6:100). For this system a liquid's endothermic freezing on heating and the resulting crystal's exothermic melting on cooling occur. C_p decreases on freezing and increases on melting. Melting on cooling takes longer than freezing on heating.

a step further. (E in this problem is, of course, not the internal energy).

$$\left. \frac{\partial S}{\partial T} \right|_E = \left. \frac{\partial S}{\partial T} \right|_D + \left. \frac{\partial S}{\partial D} \right|_T \left. \frac{\partial D}{\partial T} \right|_E. \quad (6.2.156)$$

With the aid of a Maxwell's relation we obtain

$$\left. \frac{\partial S}{\partial D} \right|_T = - \left. \frac{\partial E}{\partial T} \right|_D = \frac{D}{\varepsilon^2 V} \frac{d\varepsilon}{dT}. \quad (6.2.157)$$

Also

$$\left. \frac{\partial D}{\partial T} \right|_E = \frac{D}{\varepsilon} \frac{d\varepsilon}{dT}. \quad (6.2.158)$$

Therefore,

$$C_E = C_D + T \frac{ED}{\varepsilon^2} \left(\frac{d\varepsilon}{dT} \right)^2. \quad (6.2.159)$$

This tells us that if ε does not depend on T , then there is no difference between the two specific heat. This should be intuitively obvious, because no 'reorganization' of the material is expected upon heating.

(5) The original paper contains the answer.

2.34 [Chemical equilibrium constant²²]

The reaction



may be described as follows, if A and B are sufficiently dilute:

$$\frac{d[A]}{dt} = k_- [B] - k_+ [A] = - \frac{d[B]}{dt}. \quad (6.2.161)$$

For all $t > 0$ show that

$$\frac{[B]_F(t)}{[A]_B(t)} = K, \quad (6.2.162)$$

holds. Here, F denotes the forward reaction starting with pure A , and R denotes the reverse reaction starting with the same moles of B as A . That is, if these two reactions are started simultaneously, then the concentration ratio at time t as (6.2.162) is time-independent and equal to the chemical equilibrium constant. [However, this cannot

²²A. B. Adib, "Symmetry Relations in Chemical Kinetics Arising from Microscopic Reversibility," Phys. Rev. Lett., **96**, 028307 (2006).

be a general relation, but holds only under ideal solution and reaction conditions.]

Solution

Since $[A] + [B] = C$ (constant), $[B]_F(t)$ obeys

$$\frac{d[B]_F(t)}{dt} = -(k_+ + k_-)[B]_F(t) + k_+C$$

with the initial condition $[B]_F(0) = 0$. Similarly,

$$\frac{d[A]_B(t)}{dt} = -(k_+ + k_-)[A]_B(t) + k_-C$$

with the initial condition $[A]_B(0) = 0$. Therefore,

$$[B]_F(t) = \frac{k_+}{k_- + k_+}C (1 - e^{-(k_- + k_+)t}),$$

$$[A]_B(t) = \frac{k_-}{k_- + k_+}C (1 - e^{-(k_- + k_+)t}).$$

These formulas tell us what we wish to have, because $K = k_+/k_- = [B]_{eq}/[A]_{eq}$.

6.3 Problems for Chapter 3

3.1 [Fermions and bosons; the ultimate elementary problem]

There is a system with only three states with energies 0, ε and ε ($\varepsilon > 0$, i.e., excited states are degenerate). There are three identical particles without spin.

(1F) If the particles are fermions, write down the canonical partition function.

(2F) Find the probability of finding N particles in the ground state.

(3F) Compute the average occupation number N_0 of the ground state.

(1-3B) Repeat the same problems assuming that the particles are bosons.

(4) Consider the high temperature limit. (UIUC Qual Spring00)

Solution

(1F) Since all the one-particle states must be occupied, and there is only one microstate for the system:

$$Z = e^{-2\beta\varepsilon}. \quad (6.3.1)$$

(2F) Since the one-particle ground state is always occupied by a particle, $P(N) = \delta_{N,1}$.

(3F) 1; there is no fluctuation at all.

(1-3B) The microstates of the system may be classified according to the number of particles occupying the one-particle ground state: $n = 3, 2, 1$, or 0. They respectively correspond to the microstates with the total energy 0, ε , 2ε or 3ε . The degeneracy of the macrostate designated by n is $\binom{3-n+1}{1} = 4-n$. Therefore, the canonical partition function is given by

$$Z = 1 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + 4e^{-3\beta\varepsilon}. \quad (6.3.2)$$

The probability that the one-particle ground state is occupied by n particles is given by

$$P(n) = \frac{1}{Z}(4-n)e^{-(3-n)\beta\varepsilon}. \quad (6.3.3)$$

The expectation value $\langle n \rangle$ is

$$\langle n \rangle = \frac{3 + 4e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + 4e^{-3\beta\varepsilon}}. \quad (6.3.4)$$

(4) For the fermion case nothing changes even at high temperatures. For bosons in the $\beta \rightarrow 0$ limit, all 10 microstates are equally probable:

$$P(n) = (4-n)/10, \quad \langle n \rangle = 1. \quad (6.3.5)$$

3.2 [Elementary problem for boson systems]

There are 100 identical spinless bosons whose s -th one-particle state has an energy $E_s = s\varepsilon$ ($s \in \mathbf{N}$) and is described by a wave function $\phi_n(r)$ (normalized). These particles do not interact.

(1) How many microstates with the energy 4ε does the system have?

(2) When the system is in equilibrium with the particle reservoir (chemostat) of temperature T and chemical potential μ , on the average 99 particles occupy the one-particle ground state ($s = 0$), and one particle occupies the one-particle first excited state ($s = 1$). The other one-particle states are negligibly occupied, Find μ and $\beta = 1/k_B T$ in terms of ε .

Solution

(1) This is a problem of partitioning an integer. The microstates with the total energy 4ε are

$$4 = 1 + 1 + 1 + 1, \quad (6.3.6)$$

$$= 1 + 1 + 2, \quad (6.3.7)$$

$$= 2 + 2, \quad (6.3.8)$$

$$= 1 + 3, \quad (6.3.9)$$

$$= 4. \quad (6.3.10)$$

That is, there are 5 distinct microstates.

(2) Since

$$\langle n_0 \rangle = \frac{1}{e^{-\beta\mu} - 1} = 99, \quad (6.3.11)$$

$$\langle n_1 \rangle = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} = 1, \quad (6.3.12)$$

we have

$$-\beta\mu = \log(100/99) = 1.005 \times 10^{-2}, \quad (6.3.13)$$

$$\beta(\varepsilon - \mu) = \log 2 = 0.693. \quad (6.3.14)$$

Hence, $\beta = 0.692/\varepsilon$ and $\mu = -0.01445\varepsilon$. Clearly recognize that μ is **negative** (does not exceed the ground state energy)!

3.3 [Basic problem for quantum ideal gas: isothermal compression]

In a cylinder with a piston are N identical particles. The temperature is maintained constant.

The fermion case:

(1) Suppose the system is maintained at $T = 0$, and the volume has been reversibly halved. What is the relation between the initial energy e_i per particle and the final energy e_f per particle?

(2) In the process described in (1) what is the ratio P_f/P_i , where P_i is the initial pressure and P_f the final pressure.

(3) Now, suppose the system is maintained at a positive temperature T . As in (1) we halve the volume of the system reversibly. How does the ratio e_f/e_i change as a function of T ? You may assume T is sufficiently close to $T = 0$.

The boson case:

(4) Suppose the density of the condensate is positive at the initial temperature. After the volume is halved reversibly does the density of the condensate remain positive?

(5) Suppose $T = 0$ when the volume is reversibly halved. Find the ratio P_f/P_i , where P_i is the initial pressure and P_f the final pressure.

Solution

(1) Let us write $gD_t(\varepsilon) = aV\varepsilon^{1/2}$ with a numerical constant a . We know the following relation:

$$N = \frac{2}{3}gD_t(\mu(0))\mu(0) = \frac{2}{3}aV\mu(0)^{3/2}, \quad (6.3.15)$$

$$E = \frac{2}{5}gD_t(\mu(0))\mu(0)^2 = \frac{2}{5}aV\mu(0)^{5/2}. \quad (6.3.16)$$

From these formulas we get the relation

$$E/N = \frac{3}{5}\mu(0) \quad (6.3.17)$$

we already **know**. Since N is constant, $\mu(0) \propto V^{-2/3}$, so

$$e_f/e_i = (V/2)^{-2/3}/V^{-2/3} = 2^{2/3}. \quad (6.3.18)$$

(2) We use the universal relation $P \propto E/V$ for any ideal gas

$$P_f/P_i = 2(e_f/e_i) = 2^{5/3}, \quad (6.3.19)$$

where the factor 2 comes from the volume ratio V_f/V_i .

(3) In contrast to the $T = 0$ case, the particles need not be pushed up with the energy levels. Consequently, the increase ratio of the energy is expected to decrease with T .

(4) If the volume is decreased, the energy level spacings widen. Therefore, more particles fall to the ground state. That is, N_0 should increase. Quantitatively, we have only to **look** at $N_1 = AVT^{3/2}$. Since T is kept constant, N_1 halves.

(5) Since $E \propto VT^{5/2}$, $P = (2/3)(E/V)$ does not depend on the system volume. Hence, there is no pressure change: the ratio is unity. We can regard the ground state as a pressure buffer.

3.4 [Basic problem for quantum ideal gas: adiabatic free expansion]

In a thermally isolated cylinder with a piston is an ideal gas, whose initial temperature is T_i . The piston is pulled suddenly to increase the volume by 10%.

The fermion case: Suppose the ideal gas is fermionic.

(1F) Find the final pressure P_f in terms of P_i , the initial pressure.

(2F) Which is correct, $T_i < T_f$, $T_i = T_f$ or $T_i > T_f$?

(3F) Suppose the initial temperature is $T = 0$. Express the final temperature T_f approximately in terms of the Fermi temperature T_F before the expansion.

The boson case: Suppose the ideal gas is bosonic.

(1B) Find the final pressure P_f in terms of P_i , the initial pressure.

(2B) Suppose the initial temperature is sufficiently low and the condensate does not disappear by expansion. What is the final temperature T_f ?

(3B) Suppose the initial temperature is less than T_c . After expansion, the final temperature becomes exactly T_c (for the expanded system). Find the initial temperature T_i in terms of the T_c before expansion.

Solution

(1F) The internal energy E does not change, because the system is adiabatic and free expansion does not do work. Therefore,

$$PV = \frac{2}{3}E \quad (6.3.20)$$

implies

$$P_i V = P_f (1.1V). \quad (6.3.21)$$

Hence, $P_f = 0.91P_i$.

(2F) Expansion makes packing energy level denser, so to keep the total energy the only way is to occupy more excited states. Therefore, $T_i < T_f$.

This relation cannot be obtained purely thermodynamically. We have

$$\left. \frac{\partial T}{\partial V} \right|_E = \frac{\partial(T, E)}{\partial(V, T)} \frac{\partial(V, T)}{\partial(V, E)} = -\frac{1}{C_V} \left. \frac{\partial E}{\partial V} \right|_T, \quad (6.3.22)$$

(this is thermodynamics) and

$$\left. \frac{\partial E}{\partial V} \right|_T = \frac{3}{2} \left[\left. \frac{\partial P}{\partial V} \right|_T V + P \right] \quad (6.3.23)$$

(this is no more a thermodynamic relation, since we have used (??)). To proceed further, we need the equation of state. Let us first consider the classical case $PV = Nk_B T$:

$$V \left. \frac{\partial P}{\partial V} \right|_T = -\frac{Nk_B T}{V} = -P \quad (6.3.24)$$

That is, $T_i = T_f$ for the classical case. Compared with this case, fermionic ideal gas should be harder to compress, so $(\partial E/\partial V)_T < 0$, which implies $(\partial T/\partial V)_E > 0$. We could use an explicit energy formula as you can see in the following discussion.

(3F)

$$E = \frac{3}{5} N \mu(0) + \zeta(2) \frac{3}{2\mu(0)} N (k_B T)^2 + \dots, \quad (6.3.25)$$

where

$$\mu(0) = \frac{h^2}{2m} \left(\frac{3N/V}{4\pi} \right)^{2/3}. \quad (6.3.26)$$

If V is increased, the Fermi energy $\mu(0)$ goes down, so the first term of the above formula decreases. Therefore, to keep E constant, we must increase the second term. That is, T goes up. The Fermi temperature after expansion of the volume is Ferm $(1/1.1)^{2/3} T_F = 0.938 T_F$, so approximately

$$T^2 \simeq \frac{4}{3\pi^2} 0.062 (\mu(0)/k_B)^2 = \frac{4}{3\pi^2} 0.062 T_F^2 = 0.00838 T_F^2, \quad (6.3.27)$$

or $T = 0.092 T_F$.

(1B) This is the same as (1F).

(2B) This is due to $E \propto VT^{5/2}$. $T_f = 1.1^{-0.4} T_i \simeq 0.962 T_i$, so $T_f < T_i$. In this case as well the expansion makes the energy level packing denser, so consequently excitations become easier and the amount of condensate should decrease. However, this does not imply the increase of temperature, because the total energy can be maintained constant by occupying lower energy states with more particles.

(3B) (3.4.23) implies that the T_c before expansion is (here, m is the mass of the particle)

$$T_c = \frac{h^2}{2\pi k_B m} \left(\frac{n}{\zeta(3/2)} \right)^{2/3} \quad (6.3.28)$$

Therefore, $1.1(T_c^*)^{5/2} = T_i^{5/2}$, where T_c^* is the critical temperature after expansion. Hence,

$$1.1^{-2/5} T_i = T_c^* = \frac{h^2}{2\pi k_B m} \left(\frac{n/1.1}{\zeta(3/2)} \right)^{2/3}, \quad (6.3.29)$$

where n is the number density before expansion. In terms of T_c

$$1.1^{-2/5+2/3}T_i = T_c \Rightarrow T_i = 1.1^{-4/15}T_c = 0.975T_c \quad (6.3.30)$$

3.5 [Basic problem for quantum ideal gas: adiabatic quasistatic expansion]

In a thermally isolated cylinder with a piston is an ideal gas, whose initial temperature is T_i and initial pressure is P_i . The piston is pulled slowly to double the volume.

The fermion case: Suppose the ideal gas is fermionic.

(1F) Obtain the final pressure P_f in terms of P_i .

(2F) What is the final temperature T_f , if $T_i = 0$?

(3F) More generally, obtain T_f in terms of T_i .

The boson case: Suppose the ideal gas is fermionic.

(1B) Obtain the final pressure P_f in terms of P_i .

(2B) Obtain T_f in terms of T_i , assuming that the condensate does not disappear.

(4B) Let N_{0i} be the initial number of particles in the condensate. Does the final number of particles N_{0f} in the condensate increase or decrease?

Solution

(1F) In this case, entropy does not change, so $dE = -PdV$. For any ideal gas $PV = (2/3)E$, so

$$dE = -\frac{2}{3}\frac{E}{V}dV. \quad (6.3.31)$$

This implies that $EV^{2/3}$ is constant. As can be seen from this derivation, the ratio is independent of statistics. Since $E_iV^{2/3} = E_f(2V)^{2/3}$, we get $E_f = 2^{-2/3}E_i$. That is,

$$P_f(2V) = \frac{2}{3}E_f = \frac{2}{3}2^{-2/3}E_i = 2^{-2/3}P_iV, \quad (6.3.32)$$

or

$$P_f = \frac{1}{2^{5/3}}P_i. \quad (6.3.33)$$

(2F) We can expect $T_f = 0$. Indeed, at $T = 0$

$$E = \int_0^{\mu(0)} d\varepsilon D_t(\varepsilon)\varepsilon = \frac{3}{4}\mu(0)N \propto N^{5/3}V^{-2/3}. \quad (6.3.34)$$

That is, $EV^{2/3}$ is kept constant (adiabatic and isothermal processes can agree only at $T = 0$). This result is an example of the general rule that the gas temperature never goes up through quasistatic expansion.

(3F) This can be solved with the aid of (6.3.25).

(1B) Exactly the same as (1F).

(2B) Since BCE occurs, $\mu = 0$ and

$$E = \int_0^\infty d\varepsilon D_t(\varepsilon) \frac{\varepsilon}{e^{\beta\varepsilon} - 1} \propto VT^{5/2}. \quad (6.335)$$

We know $EV^{2/3}$ is maintained constant irrespective of statistics, $V^{5/3}T^{5/2}$ is invariant. That is, $V^{2/3}T$ is constant. Hence, $T_f = 2^{-2/3}T_i$; the system temperature goes down.

Notice, however, that if we admit that the pressure increases with temperature, thermodynamics can tell this:

$$\left. \frac{\partial T}{\partial V} \right|_S = -\frac{T}{C_V} \left. \frac{\partial S}{\partial V} \right|_T = -\frac{T}{C_V} \left. \frac{\partial P}{\partial T} \right|_V < 0. \quad (6.336)$$

(4B) Since the process we are interested in is quasistatic and adiabatic, the average occupation number of the one-particle ground state should not change. If you realize this no calculation is needed, but if you wish to confirm this by computation, use $N_{0i} = N - N_{1i}$ and $N_{1i} = cVT_i^{3/2}$:

$$N_{1f} = c(2V)T_f^{3/2} = cVT_i^{3/2} = N_{1i}. \quad (6.337)$$

Hence, N_0 cannot change.

3.6 [Basic problem for quantum ideal gas: compression under constant internal energy]

In a cylinder with a piston is an ideal gas consisting of N particles, whose initial temperature is T_i . The piston is pushed in slowly to halve the volume while removing thermal energy appropriately to keep the internal energy constant. Let T_f be the final temperature.

I. The case of spinless bosons: assume that there is a Bose-Einstein condensate initially.

(1) Find the number of particles N_0 in the condensate before compression. You may use the critical temperature T_c .

(2) Which is true, $T_f < T_i$, $T_f = T_i$ or $T_f > T_i$?

(3) Does the number of particles in the condensate increase or decrease?

II. The case of spin 1/2 fermions.

(4) Find the final pressure P_f .

(5) Is there a minimum temperature (> 0) below which this process becomes impossible?

(6) Which is true, $T_f < T_i$, $T_f = T_i$ or $T_f > T_i$?

Solution

(1)

$$N_0 = N(1 - (T/T_c)^{3/2}), \quad (6.3.38)$$

where $T_c \propto n^{2/3}$.

(2) Below T_c we know $E \propto VT^{5/2}$. Therefore,

$$VT_i^{5/2} = (V/2)T_f^{5/2}. \quad (6.3.39)$$

That is, $T_f = 2^{2/5}T_i$ or $T_f > T_i$.

(3) Since $T_c \propto n^{2/3}$, $T_{cf} = T_{ci}2^{2/3}$ and $T_f = 2^{2/5}T_i$ hold. Therefore,

$$T_f/T_{cf} = 2^{2/5-2/3}T_i/T_{ci} < T_i/T_{ci}. \quad (6.3.40)$$

Consequently, the ration in (6.3.38) decreases and N_0 increases. This is also understandable from the widening of the energy level spacings.

(4) Since

$$P_iV = 2E/3 = P_f(V/2), \quad (6.3.41)$$

we get $P_f = 2P_i = 4E/3V$.

(5) At $T = 0$, we know $E \propto n^{2/3}$, so E increases if the system is compressed; this should be intuitively obvious because the level spacings increase. We cannot cool the system further if T is very low. Therefore, quasiequilibrium constant energy process becomes impossible at some low but positive temperature.

(6) We can generally write

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial P}{\partial T} \right|_V - P = \frac{2}{3V} \left[T \left. \frac{\partial E}{\partial T} \right|_V - E \right]. \quad (6.3.42)$$

For ideal Fermi gases the graph of $E(T)$ (Fig. 3.3.3) implies

$$\frac{E}{T} > \left. \frac{\partial E}{\partial T} \right|_V. \quad (6.3.43)$$

The difference converges to zero in the high temperature limit; the inequality is not due to thermodynamics. This inequality combined with (6.3.42) implies that $(\partial E/\partial V)_T < 0$. That is, if T were kept constant and the system volume decreased, then E would increase. Therefore, to maintain E , heat would have to be discarded. Thus, the final temperature must be smaller: $T_i > T_f$. This conclusion can also be obtained by noting that the energy level spacing increases upon compression.

3.7 [Qualitative properties of quantum ideal gases]

Assume the particles do not interact. Answer the following qualitative questions and give your justification for your answers. All the processes are quasistatic.

The boson case: there are N bosons in a volume V .

(1B) The volume is increased under constant energy. Does the temperature decrease?

(2B) The volume is increased under constant entropy. Does the temperature decrease?

(3B) Can we decrease the volume while keeping the internal energy?

The fermion case: there are N fermions in a volume V .

(1F) The volume is increased under constant energy. Does the temperature decrease?

(2F) The volume is increased under constant entropy. Does the temperature decrease?

(3F) Can we decrease the volume while keeping the internal energy?

Solution

(1B) Below T_c we can write explicitly as $E \propto VT^{5/2}$ ($5/2 = d/\alpha + 1$), so we immediately see that T decreases. If the volume is increased, the energy level spacing decreases, so excitations become easier (consequently T_c goes down), so the number of particles occupying the one-particle ground state decreases. If you wish to keep the system energy despite this, you have to decrease the system temperature. What could happen above T_c is subtle, as can be seen from the behavior of C_V . If the temperature is sufficiently high, then the system is close to a classical ideal gas, so the temperature dependence diminishes.

(2B) If S is kept, the particles must follow the behavior of the energy levels. The level spacings decrease, so this is possible only by decreasing the temperature.

(3B) This is possible, if heat is supplied appropriately to warm up the system.

(1F) The energy level spacings decrease, so the total energy cannot be maintained without increasingly occupying the excited states. Hence, the temperature goes up.

(2F) To keep S , the shape of the ‘cliff’ of the fermi distribution, but since the Fermi energy goes down, this is possible only through cooling the system.

(3F) This is generally impossible.

3.8 [Conversion of fermion into bosons]

There is an ideal Fermi gas with the total energy 10 eV in an adiabatic container. The fermion particles are actually metastable and turn into bosons without adding any energy. Assume that the conversion is done quasistatically and adiabatically. Does the container explode? [UIUC qual]

Solution

Irrespective of statistics $PV = 2E/3$. Since E and V are constant, the pressure does not change.

We know, if N and T are identical $P_{FD} > P_{MB} > P_{BE}$ (\rightarrow (3.1.17)). Since E is an increasing function of T , the pressure of the gas is an increasing function of T (however, $(\partial P/\partial T)_V > 0$ is NOT a thermodynamic inequality; think of counter examples). Therefore, we must conclude $T_{FD} < T_{MB} < T_{BE}$. This suggests that we may handle the boson system as a classical ideal gas system; we can easily guess $T \sim T_F$. Indeed, we can estimate the system temperature after conversion as

$$E = (3/5)\mu_0 n = (3/2)nk_B T \Rightarrow T = 2T_F/5. \quad (6.3.44)$$

This is an extreme high temperature, so the container melts away, and there is an explosion.

3.9 [Equation of state of ideal gases]

We know the relation between PV and the internal energy does not depend on particle statistics.

- (1) Is this still true for ideal gas mixtures?
- (2) Compute PV/E in d -space (this is already mentioned in the text).

Solution

- (1) You may use the law of partial pressure. Let P_i be the partial pressure due to chemical species i . If its internal energy is E_i , $P_i V = (2/3)E_i$ holds for all i . Since the internal energy is additive $PV = (2/3)E$ must also hold for the ideal gas mixtures.
- (2) You have only to trace the proof of $PV = 2E/3$. See up to (3.1.24). Let $D_t(\varepsilon)$ be the density of translational states in d -space. The key element of the derivation of (3.1.24) is the relation between $d(\varepsilon D(\varepsilon))/d\varepsilon$ and $D(\varepsilon)$. In d -space we can write $D(\varepsilon) = A\varepsilon^{d/2-1}$ with an appropriate numerical factor A , so

$$\frac{d}{d\varepsilon}\{\varepsilon D(\varepsilon)\} = \frac{d}{2}D(\varepsilon). \quad (6.3.45)$$

Hence, we get $PV/E = 2/d$.

3.10 [Effective interaction due to statistics]

Fig. 3.1.1 illustrates how we can intuitively understand the effective interactions between particles: compared with classical particles, between bosons there is an effective attraction, and between fermions there is an effective repulsion. Let us make this understanding slightly quantitative. Here, we proceed step by small step, reviewing elementary quantum mechanics.

We wish to consider a two-particle system in terms of canonical ensemble theory.

The system Hamiltonian reads

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m}, \quad (6.3.46)$$

and the canonical partition function is

$$Z = \text{Tr} e^{-\beta H}, \quad (6.3.47)$$

where the trace is with respect to the microstates specified by two momenta $|\mathbf{p}, \mathbf{p}'\rangle$. To compute this trace semi-classically, we introduce a single-particle momentum state $|\mathbf{p}\rangle$.

(1) Express $|\mathbf{p}, \mathbf{p}'\rangle$ both for the boson and fermion cases in terms of single particle kets $|\mathbf{p}\rangle$. You may regard two momenta are distinct, but the obtained states must be properly normalized.

(2) Assuming that the system is in a sufficiently big box of volume V , find the position representation $\langle \mathbf{r} | \mathbf{p} \rangle$ (i.e., the wave function) of the momentum ket $|\mathbf{p}\rangle$.

(3) Let \mathbf{r}_i be the position vector of the i -th particle. Find the position representation of $|\mathbf{p}, \mathbf{p}'\rangle$. [This is of course virtually the same question as (1).]

(4) For an N -particle system in the semi-classical limit, the calculation of trace in Z may be performed as follows:

$$\text{Tr} \rightarrow \frac{1}{N!} \int_{V^N} d\{\mathbf{r}_k\} \prod_{k=1}^N \langle \mathbf{r}_k | \cdots \prod_{k=1}^N | \mathbf{r}_k \rangle \quad (6.3.48)$$

$$= \frac{1}{N!} \int_{V^N} d\{\mathbf{r}_k\} \prod_{k=1}^N \langle \mathbf{r}_k | \left[\left(\sum_{\{\mathbf{p}_i\}} |\{\mathbf{p}_i\}\rangle \langle \{\mathbf{p}_i\}| \right) \cdots \left(\sum_{\{\mathbf{p}_i\}} |\{\mathbf{p}_i\}\rangle \langle \{\mathbf{p}_i\}| \right) \right] \prod_{k=1}^N | \mathbf{r}_k \rangle \quad (6.3.49)$$

If the volume is big enough, we should be able to replace the summation over momenta by integration over them. The replacement rule is

$$\sum_{\{\mathbf{p}_i\}} \rightarrow \frac{V^N}{h^{3N}} \int d\{\mathbf{p}_i\}. \quad (6.3.50)$$

Justify this for $N = 1$ in 1-space.

(5) Write Z down using $h^{-3/2} e^{i\mathbf{r}\cdot\mathbf{p}/\hbar} = \langle \mathbf{r}_i | \mathbf{p} \rangle$. Beyond this point, let us simplify formulas by taking the $V \rightarrow \infty$ limit. You need not perform the integration.

(6) The outcome of (5) must have the following form:

$$\frac{1}{2h^6} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p} d\mathbf{p}' e^{-\beta(\mathbf{p}^2 + \mathbf{p}'^2)/2m} [\dots]. \quad (6.3.51)$$

Perform the integral in this expression and find F in the following formula:

$$Z = \frac{1}{2h^6} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p} d\mathbf{p}' e^{-\beta(\mathbf{p}^2 + \mathbf{p}'^2)/2m} F \quad (6.3.52)$$

(7) F may be interpreted as the Boltzmann factor coming from the effective interaction originating from particle statistics. Sketch the potential ($\times\beta$) of this effective interaction for bosons and fermions.

Solution

(1) The ket $|\mathbf{p}\rangle|\mathbf{p}'\rangle$ must be correctly symmetrized; + is for bosons and – for fermions:

$$|\mathbf{p}, \mathbf{p}'\rangle = \frac{1}{\sqrt{2}}(|\mathbf{p}\rangle|\mathbf{p}'\rangle \pm |\mathbf{p}'\rangle|\mathbf{p}\rangle). \quad (6.3.53)$$

(2) $|\mathbf{p}\rangle$ describes a plane wave of wave vector $\mathbf{k} = \mathbf{p}/\hbar$:

$$\langle \mathbf{r} | \mathbf{p} \rangle \propto e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \quad (6.3.54)$$

The normalization condition is

$$\delta_{\mathbf{p}\mathbf{p}'} = \frac{1}{\hbar} \int_V d^3\mathbf{r} \langle \mathbf{p}' | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{p} \rangle. \quad (6.3.55)$$

Therefore,

$$\langle \mathbf{r} | \mathbf{p} \rangle = \sqrt{\frac{\hbar}{V}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \quad (6.3.56)$$

(3)

$$(\langle \mathbf{r}_1 | \langle \mathbf{r}_2 |) |\mathbf{p}, \mathbf{p}'\rangle = \frac{1}{\sqrt{2}} (\langle \mathbf{r}_1 | \mathbf{p} \rangle \langle \mathbf{r}_2 | \mathbf{p}' \rangle \pm \langle \mathbf{r}_1 | \mathbf{p}' \rangle \langle \mathbf{r}_2 | \mathbf{p} \rangle). \quad (6.3.57)$$

(4) The left-hand side is the sum over all the states in the volume V . If we adopt a periodic boundary condition $k = (2\pi/L)n$ ($n \in \mathbf{Z}$).

$$\sum_{n=-\infty}^{\infty} n \simeq \int_{-\infty}^{\infty} dn = \frac{L}{2\pi} \int \frac{2\pi}{L} dn = \frac{L}{2\pi} \int dk = \frac{L}{\hbar} \int dp. \quad (6.3.58)$$

The 3-dimensional version reads

$$\sum_{\mathbf{p}} \simeq \frac{V}{h^3} \int d\mathbf{p}. \quad (6.3.59)$$

If you do not like the periodic boundary condition, $k = (\pi/L)n$ ($n \in \mathbf{N}$) and

$$\sum_{n=1}^{\infty} \simeq \int_1^{\infty} dn = \frac{L}{\pi} \int_1^{\infty} \frac{\pi}{L} dn = \frac{L}{\pi} \int_0^{\infty} dk = \frac{L}{h} \int_{-\infty}^{\infty} dp. \quad (6.3.60)$$

(5) Using the results of (2) and (3), we get (the overall factor 1/2 comes from 1/N! in the definition of trace)

$$Z = \text{Tr} e^{-\beta H} = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \langle \mathbf{r}_1 | \langle \mathbf{r}_2 | e^{-\beta H} | \mathbf{r}_1 \rangle | \mathbf{r}_2 \rangle, \quad (6.3.61)$$

$$= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \sum_{\mathbf{p}, \mathbf{p}'} e^{-\beta(\mathbf{p}^2 + \mathbf{p}'^2)/2m} |(\langle \mathbf{r}_1 | \langle \mathbf{r}_2 |) | \mathbf{p}, \mathbf{p}' \rangle|^2, \quad (6.3.62)$$

$$= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \sum_{\mathbf{p}, \mathbf{p}'} e^{-\beta(\mathbf{p}^2 + \mathbf{p}'^2)/2m} |(\langle \mathbf{r}_1 | \langle \mathbf{r}_2 |) | \mathbf{p}, \mathbf{p}' \rangle|^2, \quad (6.3.63)$$

$$= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \sum_{\mathbf{p}, \mathbf{p}'} e^{-\beta(\mathbf{p}^2 + \mathbf{p}'^2)/2m} \frac{1}{2} |\langle \mathbf{r}_1 | \mathbf{p} \rangle \langle \mathbf{r}_2 | \mathbf{p}' \rangle \pm \langle \mathbf{r}_1 | \mathbf{p}' \rangle \langle \mathbf{r}_2 | \mathbf{p} \rangle|^2 \quad (6.3.64)$$

If we write the matrix elements explicitly,

$$Z = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \sum_{\mathbf{p}, \mathbf{p}'} e^{-\beta(\mathbf{p}^2 + \mathbf{p}'^2)/2m} \frac{1}{V^2} [1 \pm \text{Re} \exp(i(\mathbf{p} - \mathbf{p}') \cdot (\mathbf{r}_1 - \mathbf{r}_2)/\hbar)], \quad (6.3.65)$$

$$= \frac{1}{2h^6} \int d\mathbf{r}_1 d\mathbf{r}_2 \int d\mathbf{p} d\mathbf{p}' e^{-\beta(\mathbf{p}^2 + \mathbf{p}'^2)/2m} [1 \pm \text{Re} \exp(i(\mathbf{p} - \mathbf{p}') \cdot (\mathbf{r}_1 - \mathbf{r}_2)/\hbar)]. \quad (6.3.66)$$

(6) To obtain F we compute

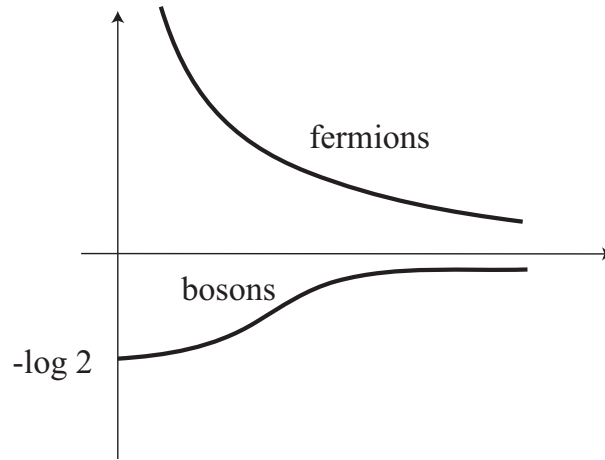
$$\frac{\int d\mathbf{p} e^{-\beta(p^2/2m) + i\mathbf{p} \cdot \mathbf{r}/\hbar}}{\int d\mathbf{p} e^{-\beta(p^2/2m)}} = e^{-mk_B T r^2 / 2\hbar^2}. \quad (6.3.67)$$

Hence,

$$F = 1 \pm e^{-mk_B T (\mathbf{r}_1 - \mathbf{r}_2)^2 / \hbar^2}. \quad (6.3.68)$$

(7) If we introduce the effective potential ϕ by $F = e^{-\beta\phi}$, we get

$$\beta\phi(\mathbf{r}) = -\log[1 \pm e^{-mk_B T (\mathbf{r}_1 - \mathbf{r}_2)^2 / \hbar^2}]. \quad (6.3.69)$$



The sketches of the potential are given in the attached figure.

As expected, the effective interaction is attractive for bosons, and repulsive for fermions.

3.11 [Elementary low temperature formulas for fermions]

The following questions ask for standard elementary calculations, but you should do them once in your life.

- (1) Obtain the chemical potential (the Fermi level) to order T^2 around $T = 0$.
- (2) Obtain the pressure P to order T^2 around $T = 0$.

Solution

- (1) Let us **apply**

$$\int_0^{+\infty} d\varepsilon \phi(\varepsilon) f(\varepsilon) = \int_0^{\mu(T)} \phi(x) dx + (k_B T)^2 \zeta(2) \phi'(\mu) + \dots \quad (6.3.70)$$

to the following calculation:

$$N = \int_0^{\infty} d\varepsilon g D_t(\varepsilon) f(\varepsilon) = \int_0^{\mu(T)} dx g D_t(x) + \zeta(2) \left. \frac{dg D_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu} (k_B T)^2 + \dots \quad (6.3.71)$$

We know the $T = 0$ result:

$$N = \int_0^{\mu(0)} d\varepsilon g D_t(\varepsilon). \quad (6.3.72)$$

This determines the Fermi energy $\mu(0)$.

$$\int_0^{\mu(0)} d\varepsilon gD_t(\varepsilon) = \int_0^\infty d\varepsilon gD_t(\varepsilon)f(\varepsilon) = \int_0^{\mu(T)} dx gD_t(x) + \zeta(2) \left. \frac{dgD_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu(T)} (k_B T)^2 + \dots, \quad (6.3.73)$$

so we can expect $\mu(T) = \mu(0) + aT^2 + o[T^2]$:

$$\int_0^{\mu(T)} dx gD_t(x) = \int_0^{\mu(0)+aT^2} dx gD_t(x) = \int_0^{\mu(0)} dx gD_t(x) + aT^2 gD_t(\mu(0)). \quad (6.3.74)$$

Now, combining (6.3.73) and (6.3.74), we obtain

$$\int_0^{\mu(0)} d\varepsilon gD_t(\varepsilon) = \int_0^{\mu(0)} dx gD_t(x) + aT^2 gD_t(\mu(0)) + \zeta(2) \left. \frac{dgD_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu(0)} (k_B T)^2 + \dots, \quad (6.3.75)$$

or

$$aT^2 gD_t(\mu(0)) + \zeta(2) \left. \frac{dgD_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu(0)} (k_B T)^2 = 0. \quad (6.3.76)$$

Therefore,

$$a = -\zeta(2) \left. \frac{d \log D_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu(0)} k_B^2 = -\frac{\pi^2}{6} \left. \frac{d \log D_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu(0)} k_B^2. \quad (6.3.77)$$

Thus, the final result is

$$\mu(T) = \mu(0) - \frac{\pi^2}{6} \left. \frac{d}{d\varepsilon} \log D_t(\varepsilon) \right|_{\varepsilon=\mu(0)} (k_B T)^2 + \dots \quad (6.3.78)$$

(2) P is required, but it is easier to compute E . Utilizing (6.3.70), we get

$$E(T) = \int d\varepsilon gD_t(\varepsilon)\varepsilon f(\varepsilon), \quad (6.3.79)$$

$$= \int_0^\mu d\varepsilon gD_t(\varepsilon)\varepsilon + \zeta(2)(k_B T)^2 \left. \frac{dgD_t(\varepsilon)\varepsilon}{d\varepsilon} \right|_\mu + \dots \quad (6.3.80)$$

We must expand $\mu(T)$ using the result of (1):

$$\int_0^{\mu(T)} d\varepsilon gD_t(\varepsilon)\varepsilon = \int_0^{\mu(0)} d\varepsilon gD_t(\varepsilon)\varepsilon - \frac{\pi^2}{6} \left. \frac{d \log D_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu(0)} gD_t(\mu(0))\mu(0)(k_B T)^2, \quad (6.3.81)$$

$$= E(0) - \frac{\pi^2}{6} gD_t'(\mu(0))\mu(0)(k_B T)^2 \quad (6.3.82)$$

Comparing this with (6.3.80), we can write

$$E(T) = E(0) - \frac{\pi^2}{6} g D'_t(\mu(0)) \mu(0) (k_B T)^2 + \zeta(2) (k_B T)^2 \left. \frac{dg D_t(\varepsilon) \varepsilon}{d\varepsilon} \right|_{\mu} + \dots, \quad (6.3.83)$$

$$= E(0) + \frac{\pi^2}{6} g D_t(\mu(0)) (k_B T)^2. \quad (6.3.84)$$

Since $P = 2E/3V$

$$P(T) = P(0) + \frac{\pi^2}{9V} g D_t(\mu(0)) (k_B T)^2. \quad (6.3.85)$$

3.12 [Derivation of Maxwell's distribution]

Maxwell derived in his *Illustrations of the Dynamical Theory of Gases* (1860) the density distribution function $f(\mathbf{v})$ of the gas particle velocity.

Maxwell assumed that orthogonal components of the velocity are statistically independent. This implies that we may write

$$f(\mathbf{v}) = \phi_x(v_x) \phi_y(v_y) \phi_z(v_z), \quad (6.3.86)$$

where ϕ_x , etc., are density distribution function for each component. Maxwell also assumed isotropy. Hence, f is a function of $v^2 \equiv |\mathbf{v}|^2$, so we may regard $f(\mathbf{v}) \equiv F(v^2)$, and ϕ_x 's do not depend on suffixes. Let us introduce $\psi(s^2) \equiv \phi_x(s)$. Then, the above functional equation reads

$$F(x + y + z) = \psi(x) \psi(y) \psi(z). \quad (6.3.87)$$

If F and ψ are both once differentiable, we obtain

$$F'(x + y + z) = \psi(x) \psi(y) \psi'(z). \quad (6.3.88)$$

Setting $y = z = 0$, we have

$$F(x) = \psi(x) \psi(0) \psi(0), \quad F'(x) = \psi(x) \psi(0) \psi'(0), \quad (6.3.89)$$

so $F'(x)/F(x)$ must be a constant. This implies that the distribution is Gaussian.

(1) Is there any other solution? If we do not assume the differentiability of F (that is, if we assume only the continuity of F), what do you get?²³

(2) Since we know the result of equilibrium statistical mechanics, if the particle

²³If we do not assume the continuity of F , there would be uncountably many solutions.

energy is E , then the distribution function is proportional to $e^{-\beta E}$. This is derived from the consistency of mechanics and thermodynamics. On the other hand, the above derivation of the Maxwell distribution uses only the statistical independence of the orthogonal components and its isotropy, and mechanics is never used. Then, this seems to imply that Maxwell's logic determines the form of the kinetic energy K in terms of velocity from statistically natural assumption + thermodynamics; at least $K \propto \mathbf{v}^2$ is concluded. This sounds incredible, even if thermodynamics is great. What is wrong? [Hint: think of relativistic case.]

[Comment] Maxwell himself did not like the above derivation we criticize here,²⁴ so he rederived the distribution a few years later. He this time used the detailed balance argument (as explained in the [text](#)). Pay due respect to Maxwell's sound instinct.

Solution

(1) Needless to say, if we assume differentiability there is no other solution. Maxwell was correct.

Let us try to solve the problem assuming only continuity (and isotropy). Let us introduce $g = \log F$ and $\phi = \log \psi$; this is admissible because F and ψ are positive. We have

$$g(x + y) = \phi(x) + \phi(y) + \phi(0) = \phi(x + y) + 2\phi(0). \quad (6.3.90)$$

Therefore, if we define $f(x) = \phi(x) - \phi(0)$, then we get

$$f(x) + f(y) = f(x + y). \quad (6.3.91)$$

Since we assume f to be continuous, the solution is $f(x) = cx$ for some constant c . Thus, we can get only a Gaussian form.

(2) If we consider the relativistic case, the velocity distribution function reads

$$P(\mathbf{v}) \propto \exp(mc^2/\sqrt{1 - v^2/c^2}). \quad (6.3.92)$$

Obviously, it does not have the structure (6.3.86). That is, orthogonal components are not statistically independent, although isotropy is still correct.

3.13 [2-dimensional neutron system]

10^{18} neutrons are confined in a square of edge length 1 m. If we regard this as a 2-dimensional system, estimate the needed temperature required for this system to be regarded as a classical system.²⁵

Solution

²⁴However, even strict Pauli uncritically repeat the above argument in W. Pauli, *Thermodynamics and the Kinetic Theory of Gases* (edited by C. P. Enz), Section 25.

²⁵cf ProblWS p176.

Non-classical behavior is observed if the interparticle distance is comparable to the thermal wave length of the particle. This happens when the number density becomes comparable to the so-called **quantum number density** n_Q (the quantum density must be computed in 2-space):

$$n_Q = 2\pi m k_B T / h^2. \quad (6.3.93)$$

Since $m = 1.65 \times 10^{-27}$ kg, $k_B = 1.38 \times 10^{-23}$ J/K, $h = 6.63 \times 10^{-34}$ Js, $n/n_Q \sim 1$ implies $T \sim 3.1$ K. That is, if the temperature is as high as 30 K, the system behaves classically.

3.14 [2-dimensional fermion system]

The density of translational states of a 2D fermion system confined in a volume (area) V may be written as $c D(\varepsilon) = cV$ with a positive constant c .

- (1) Find the chemical potential μ in terms of the number density ρ and (inverse) temperature β .
- (2) In the high density limit, we have $\mu \propto \rho$. Explain why this form is plausible.
- (3) What is the classical limit? Does the obtained result consistent with the classical ideal gas result?

Solution

- (1) We can write

$$\rho = c \int_0^\infty d\varepsilon \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}. \quad (6.3.94)$$

To integrate this, recall:

$$\frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = \frac{d}{d(\beta\mu)} \log[1 + e^{-\beta(\varepsilon-\mu)}]. \quad (6.3.95)$$

Therefore,

$$\rho = c \int_0^\infty d\varepsilon \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = -c \int_0^\infty d\varepsilon \frac{d}{d(\beta\varepsilon)} \log[1 + e^{-\beta(\varepsilon-\mu)}] = (c/\beta) \log[1 + e^{\beta\mu}]. \quad (6.3.96)$$

That is,

$$\mu = \beta^{-1} \log(e^{\beta\rho/c} - 1). \quad (6.3.97)$$

In the high density limit, $\mu \simeq \rho/c$.

- (2) The high density limit implies high degeneracy for a Fermi gas.²⁶D We may

²⁶The slope of the cliff of the Fermi distribution in the present case is $4/k_B T$, so you might think it is not sharp. However, the width of the cliff ($\sim 5k_B T$) must be compared with the width of the plateau $\mu(0) = k_B T_F$, which becomes indefinitely large as the density increases, so the distribution is after all close to a step function of the low temperature limit.

approximate the distribution as a step function going from 1 to 0 around the Fermi level μ . Therefore, the integration range of (6.3.94) is essentially from 0 to μ . Hence, $\rho = c\mu$ is very plausible.

(3) We certainly have

$$\mu \rightarrow k_B T \log(\beta\rho/c); \quad (6.3.98)$$

consistent!

3.15 [Quantum gas with internal degrees of freedom]

Let us consider a quantum gas consisting of N particles. Individual particles have internal states consisting of two levels: the ground state and the non-degenerate excited state with energy ε (> 0).

(1) Suppose the particles are fermions. How does the Fermi energy μ_F (i.e., the chemical potential) behave as a function of ε ?

(2) Suppose the particles are bosons. How does the Bose-Einstein critical temperature T_c depends on ε ? Give a clear argument even if it is qualitative.

Solution

(1) The Fermi energy μ is determined by

$$N = \int dE \mathcal{D}(E) \frac{1}{e^{\beta(E-\mu)} + 1}. \quad (6.3.99)$$

If ε is increase, then the occupation number of the one-particle states with internal excitation. If the number of particles is constant, then to accommodate these internally non-excited particles, the Fermi level must be increased. Therefore, μ is an increasing function of ε .

(2) Consider the total number of internally excited particles (note that $\mu = 0$):

$$N_1 = \int dE \mathcal{D}(E) \frac{1}{e^{\beta E} - 1}. \quad (6.3.100)$$

If ε is increased, N_1 decreases, so this favors the formation of condensate. That is, T_c increases with ε .

3.16 [Zeemann splitting]

The outer shell of an ion has a magnetic moment μ_B of 1 Bohr magneton. In a magnetic field B this outer shell state splits into two energy states with energies $E = E_0 \pm \mu_B B$. Let n_u (resp., n_d) be the occupancy number of up-spin (resp., down-spin) states. Then the magnetization reads $M = \mu_B(n_u - n_d)$. You may ignore the electron-electron interactions.

(1) Find $\langle M \rangle$ and $\langle N \rangle$ ($N = n_u + n_d$) with the aid of the grand canonical formalism.

(2) Find the magnetization when the outer shell has one electron for each ion. Compare the result with the result of (1) for $\mu = E_0$.²⁷

Solution

(1) Since

$$n_u = \frac{1}{e^{\beta(E_0 + \mu_B B - \mu)} + 1}, \quad n_d = \frac{1}{e^{\beta(E_0 - \mu_B B - \mu)} + 1}, \quad (6.3.101)$$

$\langle M \rangle$ and $\langle N \rangle$ can be written down immediately.

(2) Define $x = e^{\beta(\varepsilon - \mu)}$ and $y = e^{\beta\mu_B H}$. Then, $\langle N \rangle = 1$ can be written as

$$1 = n_u + n_d = \frac{2 + x(y + 1/y)}{1 + x(y + 1/y) + x^2}. \quad (6.3.102)$$

If we set $x = 1$, this equality holds for any y . Therefore, $E_0 = \mu$ is the condition, and

$$\langle M \rangle = \mu_B \left(\frac{1}{1 + xy} - \frac{1}{1 + x/y} \right) = \mu_B \frac{1 - y^2}{1 + y^2}. \quad (6.3.103)$$

3.17 [Electron paramagnetism]

Due to the spin, each electron in a magnetic field B (assumed to be pointing the z -direction) has the potential energy $\pm \tilde{\mu} B$. Let $D_t(\varepsilon)$ be the one-particle translational density of states (however, the electrons may be in a crystal field, so we do not specify its form).

(1) The magnetization M of this system M is the expectation of the magnetic moment due to electron spins. Express M in terms of $D_t(\varepsilon \pm \tilde{\mu} B)$.

(2) Express the magnetic susceptibility χ in terms of $D_t'(\varepsilon)$, assuming that $\tilde{\mu} B$ is not too large.

(3) Obtain χ to order T^2 around $T = 0$ with the aid of $\log D_t(\varepsilon)$.

Solution

(1) The contribution of the up-spin electrons to the magnetization is

$$M_+ = \tilde{\mu} \int d\varepsilon D_t(\varepsilon) \frac{1}{e^{\beta(\varepsilon - \tilde{\mu} B - \mu)} + 1} = \tilde{\mu} \int d\varepsilon D_t(\varepsilon + \tilde{\mu} B) \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}. \quad (6.3.104)$$

We can easily obtain the analogous formula for down-spin electron, so we get

$$M = M_+ + M_- = \tilde{\mu} \int d\varepsilon [D_t(\varepsilon + \tilde{\mu} B) - D_t(\varepsilon - \tilde{\mu} B)] \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}. \quad (6.3.105)$$

²⁷UIUC QualFall 95

(2) $\tilde{\mu}B$ is assumed to be not too large, we may Taylor expand as

$$M = \tilde{\mu} \int d\varepsilon [D_t(\varepsilon + \tilde{\mu}B) - D_t(\varepsilon - \tilde{\mu}B)] \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = 2\tilde{\mu}^2 B \int d\varepsilon D'_t(\varepsilon) \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}. \quad (6.3.106)$$

(3) From the definition

$$\chi = \left. \frac{\partial M}{\partial B} \right|_T = 2\tilde{\mu}^2 \int_0^\infty d\varepsilon D'_t(\varepsilon) \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}. \quad (6.3.107)$$

To expand this around $T = 0$ we use, setting $\phi = 2\tilde{\mu}^2 D'_t(\varepsilon)$,

$$\int_0^\infty d\varepsilon \phi(\varepsilon) \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = \int_0^\mu d\varepsilon \phi(\varepsilon) + (k_B T)^2 \zeta(2) \phi'(\mu). \quad (6.3.108)$$

That is,

$$\chi = 2\tilde{\mu}^2 D_t(\mu) + 2\tilde{\mu}^2 (k_B T)^2 \zeta(2) D_t''(\mu). \quad (6.3.109)$$

This is, however, not yet the final result. Since

$$\mu = \mu_0 - \zeta(2) \left. \frac{d}{d\varepsilon} \log D_t(\varepsilon) \right|_{\varepsilon=\mu_0}, \quad (6.3.110)$$

(6.3.109) reads

$$\chi = 2\tilde{\mu}^2 D_t(\mu_0) - 2\tilde{\mu}^2 (k_B T)^2 \zeta(2) D_t'(\mu_0) \left. \frac{d}{d\varepsilon} \log D_t(\varepsilon) \right|_{\varepsilon=\mu_0} + 2\tilde{\mu}^2 (k_B T)^2 \zeta(2) D_t''(\mu). \quad (6.3.111)$$

This can be streamlined to the following form:

$$\begin{aligned} \chi &= 2\tilde{\mu}^2 D_t(\mu_0) + 2\tilde{\mu}^2 (k_B T)^2 \zeta(2) D_t(\mu_0) \left. \frac{d^2}{d\varepsilon^2} \log D_t(\varepsilon) \right|_{\varepsilon=\mu_0} \\ &= 2\tilde{\mu}^2 D_t(\mu_0) \left[1 + \zeta(2) (k_B T)^2 \left. \frac{d^2}{d\varepsilon^2} \log D_t(\varepsilon) \right|_{\varepsilon=\mu_0} \right]. \end{aligned} \quad (6.3.112)$$

3.18 [Do we have only to treat the ground state special below T_c ?]

For a Bose gas in 3-space we know the following integral expression is not always correct:

$$\langle N \rangle = \sum_{i=0}^{\infty} \langle \hat{n}_i \rangle = \int_0^{\infty} d\varepsilon D_t(\varepsilon). \quad (6.3.113)$$

It is because the expression ignores a large number of particles in the one-particle ground state. Thus, we are taught that if we count the number N_0 of the particles occupying the one-particle ground state and if we add this to N_1 , then the number of particles in the system may be expressed correctly. However, there may be the people who are not so convinced yet: why only ground state? Don't we have to consider the first excited state? Don't we actually have to perform the following calculation ...:

$$\frac{\langle N \rangle}{V} = \frac{1}{V} \langle \hat{n}_0 \rangle + \frac{1}{V} \langle \hat{n}_1 \rangle + \frac{1}{V} \int_0^{\infty} d\varepsilon D_t(\varepsilon). \quad (6.3.114)$$

Let us perform a slightly more honest calculation (to recognize clearly that Einstein is always correct!):

(1) Our energy coordinate convention is that the ground state is always 0: $\varepsilon_0 = 0$. Let us assume that the system is a cube of edge length L : $V = L^3$. The lowest excited one-particle state energy ε_1 as a function of V .

(2) Compare the occupation number of the one-particle ground state and the one-particle first excited states (which is triply degenerate). That is, compute the ratio $(\langle \hat{n}_0 \rangle / (\langle \hat{n}_1 \rangle + \langle \hat{n}_2 \rangle + \langle \hat{n}_3 \rangle)) = \langle \hat{n}_0 \rangle / 3\langle \hat{n}_1 \rangle$ for a very small negative **chemical potential** μ ²⁸ required by the Bose-Einstein condensation. How big is it as a function of V ?

(3) We just saw in (2) except for $\langle \hat{n}_0 \rangle$ other expectation values are not extensive. That is, the ground state is really special. Excited states cannot contribute an extensive quantity unless infinitely many of them are collected. Explain that the contribution of all the excited states may be obtained accurately by replacing the summation with integration (as usual).

Solution

(1) This calculation is just as we did in **Chapter 1**:

$$\varepsilon_{\mathbf{n}} = \frac{h^2}{8mV^{2/3}}(n_x^2 + n_y^2 + n_z^2), \quad (6.3.115)$$

where n 's are positive integer quantum numbers. Therefore, the energy difference between the ground state and the first excited state is

$$\Delta\varepsilon = 3 \frac{h^2}{8mV^{2/3}}. \quad (6.3.116)$$

²⁸which is not zero, because the system is finite.

This is ε_1 according to our convention.

(2) We have

$$\frac{\langle \hat{n}_0 \rangle}{3\langle \hat{n}_1 \rangle} = \frac{e^{\beta(\varepsilon_1 - \mu)} - 1}{e^{-\beta\mu} - 1}. \quad (6.3.117)$$

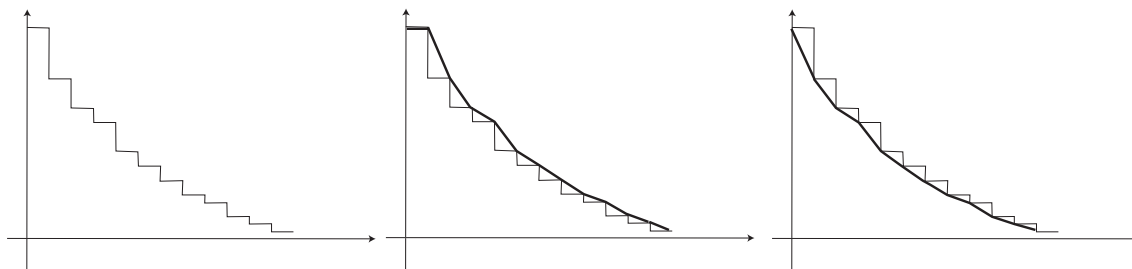
We know below T_c $\beta\mu = O[N^{-1}] (< 0)$. Furthermore, we know $\varepsilon_1 = O[V^{-2/3}]$. Since $T > 0$ is a fixed temperature, however small it is (or however large β is), if we take a sufficiently large V , we may regard $\beta\varepsilon_1$ to be sufficiently small ($\beta\mu$ is much smaller than this), so we may expand as

$$\frac{\langle \hat{n}_0 \rangle}{3\langle \hat{n}_1 \rangle} = \frac{\varepsilon_1 - \mu}{-3\mu} = \frac{1}{3}(1 - \varepsilon_1/\mu) = O[N^{1/3}] \gg 1. \quad (6.3.118)$$

Thus, we see that only the one-particle ground state is occupied by an extensive number of particles; any finite some of the occupation numbers of one-particle excited states is far less than N_0 for large systems.

(3) Let $\{f(i)\}$ be a monotone decreasing sequence of positive integers and assume $\sum f(i)$ converge. Define monotone decreasing (piecewise linear) functions $f_L(x)$ as $f_L(i-1) = f(i)$ for $i = 1, 2, \dots$ and $f_U(x)$ as $f_U(i) = f(i)$ for $i = 1, 2, \dots$ and $f_U(0) = f_U(1)$ (see the graphs below). Then,

$$\int_0^\infty f_L(x) dx \leq \sum_{i=1}^\infty f(i) \leq \int_0^\infty f_U(x) dx. \quad (6.3.119)$$



The thick curve in the center is f_U ; that in the right is f_L .

As can easily be seen from the figure

$$\int_0^\infty f_U(x) dx - \int_0^\infty f_L(x) dx < f(\varepsilon_1). \quad (6.3.120)$$

Therefore, the difference divided by V is extremely small.

3.19 [Ideal boson gas slightly warmer than T_c]

Fig. 3.4.2 illustrates that the specific heat C_v of the ideal Bose gas has a cusp. Let us demonstrate this. To compute C_v we need the internal energy of the system. Let us compute it.

(1) What is the internal energy below T_c ? (This is an easy question.)

(2) If we compute the internal energy assuming $\mu = 0$ and write its value as E_0 , show

$$\frac{\partial E_0}{\partial \mu} \simeq \frac{3}{2} N_0(T), \quad (6.3.121)$$

where

$$N_0(T) \equiv N(T, 0) = \frac{V}{h^3} \int_0^\infty \frac{1}{e^{\beta p^2/2m} - 1} 4\pi p^2 dp. \quad (6.3.122)$$

Therefore, for $T (> T_c)$ we could approximate the true internal energy at T as $E(T) = E_0 + (3/2)N_0(T)\mu$. This implies that to obtain E as a function of T , we need μ as a function of T . To this end let us write the number of particles for $T > T_c$ ($\mu < 0$) as

$$N = N_0(T) + \frac{V}{h^3} \int_0^\infty \left\{ \frac{1}{e^{\beta(p^2/2m - \mu)} - 1} - \frac{1}{e^{\beta p^2/2m} - 1} \right\} 4\pi p^2 dp. \quad (6.3.123)$$

(3) Show that we may approximate the second term of (6.3.123) as

$$\int_0^\infty \left\{ \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} - \frac{1}{e^{\beta\varepsilon} - 1} \right\} \sqrt{\varepsilon} d\varepsilon \simeq k_B T \mu \int_0^\infty d\varepsilon \frac{1}{\sqrt{\varepsilon}(\varepsilon + |\mu|)} = -\pi k_B T \sqrt{|\mu|}. \quad (6.3.124)$$

Do not forget that $\mu < 0$. [This allows us to obtain μ in terms of $N_0(T)$ which is obtainable from (6.3.122) as a function of T .]

Solution

(1) Simply copy the formula:

$$E = \int d\varepsilon g D_t(\varepsilon) \frac{\varepsilon}{e^{\beta\varepsilon} - 1} = \frac{3}{2} k_B T V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \zeta(5/2) \propto V T^{5/2}, \quad (6.3.125)$$

(2) Since

$$E = \frac{V m^{3/2}}{2^{1/2} \pi^2 \hbar^3} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon - \mu)} - 1} d\varepsilon, \quad (6.3.126)$$

we have

$$\frac{\partial E}{\partial \mu} = \frac{V m^{3/2}}{2^{1/2} \pi^2 \hbar^3} \int_0^\infty \varepsilon^{3/2} \frac{\partial}{\partial \mu} \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} d\varepsilon, \quad (6.3.127)$$

$$= -\frac{Vm^{3/2}}{2^{1/2}\pi^2\hbar^3} \int_0^\infty \varepsilon^{3/2} \frac{\partial}{\partial \varepsilon} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon, \quad (6.3.128)$$

$$= \frac{Vm^{3/2}}{2^{1/2}\pi^2\hbar^3} \int_0^\infty \left(\frac{\partial}{\partial \varepsilon} \varepsilon^{3/2} \right) \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon, \quad (6.3.129)$$

$$= \frac{3}{2} \frac{Vm^{3/2}}{2^{1/2}\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{1/2}}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon. \quad (6.3.130)$$

Comparing this with (6.3.122), we get (6.3.121).

(3) The first approximate relation in (6.3.124) is due to simple Taylor expansion. The integral in the second formula could be computed with the aid of complex analysis (you must respect the branching due to $\sqrt{\varepsilon}$), but an easier way may be to set $\sqrt{\varepsilon} = x$:

$$\int_0^\infty d\varepsilon \frac{1}{\sqrt{\varepsilon}(\varepsilon + |\mu|)} = 2 \int_0^\infty dx \frac{1}{x^2 + |\mu|} = \int_{-\infty}^\infty \frac{dx}{x^2 + |\mu|}. \quad (6.3.131)$$

3.20 [Bose-Einstein condensation in a harmonic trap]

Let us consider an ideal Bose gas consisting of N particles confined in a 3D harmonic potential.²⁹ It is hard to treat this in terms of the canonical ensemble, so we discuss this with the aid of the grand canonical theory; if N is larger than 10^3 , then $\log N/N$ ³⁰ is not large, so this approach must not be bad.

(1) Suppose the angular frequency of the trapped boson is ω_t . Find the density $D(\varepsilon)$ of one-particle state as a function of energy ε . Measure the energy from the ground state and ignore the zero-point energy.

(2) Find the number of particles N_1 in the non-condensate as a function of the chemical potential. Show that the integral (or N_1) is bounded from above in 3-space (no explicit integration required). Thus, Bose-Einstein condensation is possible in this system.

(3) The number of particles occupying the one-particle ground state approaches zero as

$$N_0(T) = N \left(1 - \left(\frac{T}{T_c} \right)^\gamma \right), \quad (6.3.132)$$

when $T \nearrow T_c$. Find γ .

(4) Find T_c as a function of N . For $N = 3000$, and $\omega_t = 10^3$ rad/s estimate T_c . (Use $\zeta(3) = 1.2020569031595 \dots$)

²⁹Actually, BEC is observed in a collection of Rb atoms confined in a (not spherically symmetric) 3D harmonic potential.

³⁰It is emphasized again that the error is not of order $\sqrt{N}/N = 1/\sqrt{N}$, but $\log N/N$.

(5) If a 2D harmonic potential can trap 2D Bose gas,³¹ can we observe Bose-Einstein condensation?

Solution

(1) The one particle energy in a 3D harmonic potential may be written as $\varepsilon = \hbar\omega_t(n_x + n_y + n_z)$, where n_x are nonnegative integers. The number of energy levels up to energy ε is the volume of a cone $x + y + z \in [0, \varepsilon/\hbar\omega_t]$ within the first octant, we get

$$\int_0^\varepsilon D(\varepsilon') d\varepsilon' = \frac{1}{3!} \left(\frac{\varepsilon}{\hbar\omega_t} \right)^3. \quad (6.3.133)$$

That is,

$$D(\varepsilon) = \frac{\varepsilon^2}{2(\hbar\omega_t)^3}. \quad (6.3.134)$$

(2) By using D obtained in (1), the number of particles in the excited states is given by

$$N_1 = \int_0^\infty d\varepsilon D(\varepsilon) \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} = \int_0^\infty d\varepsilon' \frac{\varepsilon'^2}{2(\hbar\omega_t)^3} \frac{1}{e^{\beta(\varepsilon'-\mu)} - 1}. \quad (6.3.135)$$

This is an increasing function of μ , so by setting $\mu = 0$ an upper bound of N_1 may be obtained:

$$N_1 \leq \frac{1}{2} \left(\frac{k_B T}{\hbar\omega_t} \right)^3 \int_0^\infty dx \frac{x^2}{e^x - 1}. \quad (6.3.136)$$

This integral from 1 to ∞ converges and

$$\int_0^1 dx \frac{x^2}{e^x - 1} \leq \int_0^1 x dx = \frac{1}{2}. \quad (6.3.137)$$

Therefore, N_1 is bounded from above. We may estimate it as

$$N_1(T) \leq AT^3, \quad (6.3.138)$$

where $A (> 0)$ is an appropriate constant. Hence, BEC must occur.

(3) If $\mu = 0$, we know from (2) that $N_1(T) \propto T^3$. Therefore, $\gamma = 3$.

(4) To estimate T_c we need the value of A in $N_1 = AT_c^3$: at T_c

$$N = N_1 = \int_0^\infty d\varepsilon' \frac{\varepsilon'^2}{2(\hbar\omega_t)^3} \frac{1}{e^{\beta\varepsilon'} - 1} = \frac{1}{2} \left(\frac{k_B T}{\hbar\omega_t} \right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx = \zeta(3) \left(\frac{k_B T}{\hbar\omega_t} \right)^3. \quad (6.3.139)$$

³¹This is virtually realized on graphene.

Therefore, we conclude

$$T_c = (1.2)^{-1/3} \frac{\hbar\omega_t}{k_B} N^{1/3} = 9.02 \times 10^{-8} \text{ K.} \quad (6.3.140)$$

(5) For 2D harmonic potential

$$D(\varepsilon) = \varepsilon / (\hbar\omega_t)^2. \quad (6.3.141)$$

Therefore, N_1 is computed as

$$N_1 = \int_0^\infty d\varepsilon' \frac{\varepsilon'}{(\hbar\omega_t)^2} \frac{1}{e^{\beta(\varepsilon' - \mu)} - 1} \leq \int_0^\infty d\varepsilon' \frac{\varepsilon'}{(\hbar\omega_t)^2} \frac{1}{e^{\beta\varepsilon'} - 1}, \quad (6.3.142)$$

which is bounded from above (bounded by some AT^2). Therefore, BEC can occur in 2D if harmonically bound (quite different from the free space).

3.21 [Expanding universe]

At present, the cosmic background radiation is at 3 K. Suppose the volume of the universe doubles adiabatically. What is the temperature of the cosmic background radiation after this expansion?

Solution

We know the entropy of the radiation field is $S \propto VT^3$. If the system expand quasistatically, the entropy is constant, so $(2V)T^3 = V3^3$. That is, $T = 3/2^{1/3}$ K. Actually, the process may not be quasistatic, so this estimate must be the lower bound.³²

3.22 [Specific heat of hydrogens]

Consider a 1 mole of ideal gas at 10 K consisting of pure HD, pure HT or pure DT. Whose specific heat C_V is the largest? Give your answer without detailed computation. You may assume that the length of the chemical bonds are all the same.

Solution

We may totally ignore the the contribution of oscillations. There is no difference in the contribution of translational motions. These are all heteronuclear molecules, so we need not worry about **spin-rotation coupling**. Therefore, we have only to pay attention to the rotational contributions. The molecules with the largest moment of inertia is the easiest to excite, so their rotational specific heat is the largest (notice that the **peak** of the rotational specific heat occurs around 40 K or above). Therefore,

³²This is virtually a monatomic ideal gas problem, but do not forget that the particles are superrelativistic.

the specific heat of DT must be the largest around 10K. This is indeed the case.

3.23 [Internal degree of freedom of heavy hydrogen]

The potential energy function describing the chemical bond in a heavy hydrogen D_2 may be approximately described as

$$\phi(r) = \varepsilon [e^{-2(r-d)/a} - 2e^{-(r-d)/a}], \quad (6.3.143)$$

where $\varepsilon = 7 \times 10^{-19}$ J, $d = 8 \times 10^{-11}$ m and $a = 5 \times 10^{-11}$ m.

(1) Evaluate the smallest energy required to excite the rotational motion, and estimate the temperature T_r for which the rotation starts to contribute significantly.

(2) Evaluate the smallest energy required to excite the vibrational motion, and estimate the temperature $T_r v$ for which the vibration starts to contribute significantly.

Solution

(1) The moment of inertia is

$$I = \frac{1}{2} m d^2 = (1/2) \times (1.66 \times 10^{-27}) \times (8 \times 10^{-11})^2, \quad (6.3.144)$$

so $\Theta_r = \hbar^2 / 2k_B I \simeq 150$ K.

(2) The vibrational quantum is $\hbar\omega / k_B \simeq 6300$ K.

3.24 [Computation of inertial moment tensor]

Obtain the moment of inertia tensor for CH_3D around its center of mass, and compute its rotational partition function **classically**. [You have only to state your strategy without actually estimating the components of the tensor.]

Solution

The inertial moment tensor around the center of mass A_{CM} and that A_O around an arbitrary point O is related as

$$A = A_O - A_{CM}, \quad (6.3.145)$$

where

$$A_{CM} = M [r_{CM}^2 I - \mathbf{r}_{CM} \mathbf{r}_{CM}^T]. \quad (6.3.146)$$

Here, M is the total mass, \mathbf{r}_{CM} is the CM coordinate vector relative to O . A_O is computed as

$$A_O = \sum_i m_i [r_i^2 I - \mathbf{r}_i \mathbf{r}_i^T], \quad (6.3.147)$$

where m_i is the mass of atom i , \mathbf{r}_i its position vector relative to O .

Let us compute the inertial moment tensor of CH_3D . The molecule may be considered to be a regular tetrahedron, so it is convenient to compute the inertial moment

tensor around the central carbon. H and D sits at the apices of the tetrahedron and the cC is at its geometrical center. Take the position of the carbon as O . Let us write the length of the CH (or CD) bond as r_0 . Let us take $r_0/\sqrt{3}$ as the length unit. Three H's are placed at $(1, -1, -1)$, $(-1, -1, 1)$ and $(-1, 1, -1)$, and D at $(1, 1, 1)$. Then, we have

$$A_O = \begin{pmatrix} 10 & -1 & -1 \\ -1 & 10 & -1 \\ -1 & -1 & 10 \end{pmatrix} m_H^2 (r_0^2/3). \quad (6.3.148)$$

The position of the center of mass is $\mathbf{r}_{CM} = (1, 1, 1)/17$, so

$$A_{CM} = \frac{1}{17} \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} m_H^2 (r_0^2/3). \quad (6.3.149)$$

Combining these results, we have

$$A = \begin{pmatrix} 10 - 2/17 & -16/17 & -16/17 \\ -16/17 & 10 - 2/17 & -16/17 \\ -16/17 & -16/17 & 10 - 2/17 \end{pmatrix} m_H^2 (r_0^2/3). \quad (6.3.150)$$

To compute the rotational partition function, we have only to compute the determinant of this matrix.

6.4 Problems for Chapter 4

4.1. [Kac potential]

There is an imperfect classical gas with a binary potential ϕ given by

$$\phi(|\mathbf{r}|) = \begin{cases} \infty & \text{if } |\mathbf{r}| < a, \\ -\varepsilon/l^3 & \text{if } a \leq |\mathbf{r}| < l, \\ 0 & \text{otherwise.} \end{cases} \quad (6.4.1)$$

Here, $\varepsilon > 0$, a is a length scale of atom size, and the $l \rightarrow \infty$ limit is taken. (This is an example of the [Kac potential](#).)

(1) Compute the [second virial coefficient](#) (in the $l \rightarrow \infty$ limit).

(2) Compute the Joule-Thomson coefficient $(\partial T/\partial P)_H$, where H is enthalpy. The reader may assume that the heat capacity C_P under constant pressure is a constant and is known.

Solution

Since

$$B(T) = \frac{1}{2} \int_0^\infty [1 - e^{-\beta\phi(r)}] 4\pi r^2 dr, \quad (6.4.2)$$

we have

$$2B(T) = \int_0^a 4\pi r^2 dr + \int_a^l (1 - e^{-\beta\varepsilon/l^3}) 4\pi r^2 dr, \quad (6.4.3)$$

$$\rightarrow \frac{4}{3}\pi a^3 - \frac{4}{3}\pi\beta\varepsilon. \quad (6.4.4)$$

That is,

$$B(T) = \frac{2\pi}{3}(a^3 - \beta\varepsilon). \quad (6.4.5)$$

(2)

$$\left. \frac{\partial T}{\partial P} \right|_H = \frac{\partial(T, H)}{\partial(T, P)} \frac{\partial(T, P)}{\partial(P, H)} = - \left. \frac{\partial H}{\partial P} \right|_T \bigg/ \left. \frac{\partial H}{\partial T} \right|_P. \quad (6.4.6)$$

$(\partial H/\partial T)_P = C_P$ and

$$\left. \frac{\partial H}{\partial P} \right|_T = T \left. \frac{\partial S}{\partial P} \right|_T + V = -T \left. \frac{\partial V}{\partial T} \right|_P + V. \quad (6.4.7)$$

Since the equation of state is

$$PV = Nk_B T \left(1 + B(T) \frac{N}{V} + \dots \right), \quad (6.4.8)$$

we obtain

$$\frac{V}{N} = \frac{k_B T}{P} + B + O[\rho], \quad (6.4.9)$$

where ρ is the number density, and

$$\left. \frac{\partial V}{\partial T} \right|_P = \frac{N k_B}{P} + N B' + \dots \quad (6.4.10)$$

Therefore, (again higher order terms in ρ are ignored)

$$T \left. \frac{\partial V}{\partial T} \right|_P = V + T N B' + \dots, \quad (6.4.11)$$

so the Joule-Thomson coefficient reads

$$\left. \frac{\partial T}{\partial P} \right|_H = \frac{N}{C_P} \left(T \frac{dB(T)}{dT} - B \right). \quad (6.4.12)$$

Now, introduce B obtained in (1) and we get

$$\left. \frac{\partial T}{\partial P} \right|_H = \frac{2\pi N}{3C_P} \left(2 \frac{\varepsilon}{k_B T} - a^3 \right). \quad (6.4.13)$$

From this we see that if the temperature is sufficiently low, we can cool the gas using the Joule-Thomson effect (as the ordinary gases).

4.2 [van der Waals equation of state]

(1) Show that the critical point is defined by

$$\left. \frac{\partial P}{\partial V} \right|_T = \left. \frac{\partial^2 P}{\partial V^2} \right|_T = 0. \quad (6.4.14)$$

(2) For the van der Waals equation of state, find the universal ratio $P_c V_c / k_B T_c$.

(3) Obtain the reduced equation of state $P_r = f(V_r, T_r)$ for the van der Waals gas. Here, $P_r = P/P_c$, $V_r = V/V_c$ and $T_r = T/T_c$ are reduced variables. [The reader can work with a 1 mole gas.]

(4) Near the critical point $P_r - 1$ may be expanded in powers of $T_r - 1$ and $n_r - 1$, where $n_r = 1/V_r$ is the reduced number density. Find the coefficients $A - C$ (we will see a close relation of this to the Landau theory of phase transition later).

$$P_r - 1 = A(T_r - 1) + B(T_r - 1)(n_r - 1) + C(n_r - 1)^3 + \dots \quad (6.4.15)$$

(5) For hydrogen gas H_2 , $b = 26.61 \text{ cm}^3/\text{mol}$. This volume can be interpreted as the smallest volume that the molecules can be squeezed into. Assuming that Avogadro's constant is known, estimate Planck's constant (use dimensional analysis to guess the atom size in terms of electron charge e , mass m , h and $4\pi\epsilon_0$).

Solution

(1) The condition for the criticality is for the van der Waals loop to become a single point. Therefore, the critical point corresponds to the inflection point of the PV -curve (the point where the local max and min points coalesce). This implies the two conditions stated in the problem.

(2) The equation of state we start with is

$$P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}, \quad (6.4.16)$$

and the two conditions in (1) read

$$-\frac{Nk_B T_c}{(V_c - Nb)^2} + 2\frac{aN^2}{V_c^3} = 0, \quad (6.4.17)$$

$$2\frac{Nk_B T_c}{(V_c - Nb)^3} - 6\frac{aN^2}{V_c^4} = 0. \quad (6.4.18)$$

Taking the ratio of these two equations, we get $V_c - Nb = 2V_c/3$. That is, $V_c = 3Nb$. From the first equality (6.4.17)

$$\frac{k_B T_c}{(2bN)^2} = 2\frac{aN}{(3bN)^3} \Rightarrow k_B T_c = \frac{8a}{27b}. \quad (6.4.19)$$

Now, with the aid of the equation of state, we get

$$P_c = \frac{N(8a/27b)}{2Nb} - \frac{aN^2}{9N^2b^2} = \frac{a}{27b^2}. \quad (6.4.20)$$

Combining all the results, we get

$$\frac{P_c V_c}{Nk_B T_c} = \frac{(a/27b^2)(3Nb)}{N(8a/27b)} = \frac{3}{8}. \quad (6.4.21)$$

That is, unless the ratio is $3/8$, a gas does not obey the van der Waals equation of state.

(3) Introducing $P = (a/27b^2)P_r$, $k_B T = k_B T_r(8a/27b)$ and $V = (3b)V_r$ into the van der Waals equation of state, we get

$$P_r \frac{a}{27b^2} = \frac{NT_r(8a/27b)}{3bNV_r - Nb} - \frac{aN^2}{9N^2b^2V_r^2}, \quad (6.4.22)$$

that is,

$$P_r = \frac{(8/3)T_r}{V_r - (1/3)} - \frac{3}{V_r^2}. \quad (6.4.23)$$

(4) If you are confident about your analytical muscle, you may leave all the following calculation to, e.g., Mathematica.

Using $P_r = \pi + 1$, $T_r = \tau + 1$, and $V_r = 1/(1+n)$, we can rewrite (6.4.23) as

$$\pi + 1 = \frac{(8/3)(1+\tau)}{1/(n+1) - 1/3} - 3(1+n)^2 = \frac{8(1+\tau)(1+n)}{2-n} - 3(1+n)^2, \quad (6.4.24)$$

$$= 4(1+\tau)(1+n) \left(1 + \frac{n}{2} + \frac{n^2}{4} + \dots \right) - 3(1+n)^2, \quad (6.4.25)$$

$$= 4(1+\tau+n+n\tau) \left(1 + \frac{n}{2} + \frac{n^2}{4} + \frac{n^3}{8} + \dots \right) + (3+6n+3n^2), \quad (6.4.26)$$

$$= 4 \left(1 + \tau + \frac{3n}{2} + \frac{3}{2}n\tau + \frac{3}{4}n^2 + \frac{3}{4}n^2\tau + \frac{3}{8}n^3 + \dots \right) - 3 - 6n - 3n^2, \quad (6.4.27)$$

$$= 1 + 4\tau + 6n\tau + \frac{3}{2}n^3 + 3n^2\tau + \dots. \quad (6.4.28)$$

That is,

$$\pi = 4\tau + 6n\tau + \frac{3}{2}n^3 + \dots. \quad (6.4.29)$$

This implies that $A = 4$, $B = 6$ and $C = 3/2$.

(5) The radius of the atom may be dimensional-analytically estimated as follows: $[m] = M$, $[e^2/4\pi\epsilon_0] = ML^3T^{-2}$ and $[h] = ML^2T^{-1}$, so the quantity with the dimension of length that can be constructed from these quantities is

$$[(h/m)^2/(e^2/4\pi m\epsilon_0)] = (L^2T^{-1})^2/(L^3/T^{-2}) = L. \quad (6.4.30)$$

That is, the radius of an atom may be evaluated as $a = 4\pi\epsilon_0 h^2/me^2$. This a is something like $(b/N_A)^{1/3}$. Therefore,

$$h = \sqrt{\frac{me^2}{4\pi\epsilon_0} \left(\frac{b}{N_A} \right)^{1/3}} = 2.2 \times 10^{-34} \text{ Js}. \quad (6.4.31)$$

This is not very bad (taking the crudeness of the argument into account, it is not at all bad).

4.3 [The free energy of the van der Waals gas]

The Helmholtz free energy of the van der Waals gas may be expressed as

$$A = -Nk_B T \left\{ \log \left[\frac{n_Q}{N} (V - Nb) \right] + 1 \right\} - \frac{aN^2}{V}. \quad (6.4.32)$$

(1) Comparing this with the free energy formula for the ideal gas, explain why this form is natural.

(2) Compute the internal energy and the entropy of the van der Waals gas.

Solution

(1) If we forget about the effect of the attractive forces, the fundamental idea of the van der Waals gas is the ideal gas in the effective volume (= free volume) $V - Nb$, that is, the actual space – the excluded volume due to molecules. The first term of A is, as you can see by comparing it with the ideal gas formula, just the term for such an ideal gas. The second term is the effect of attractive forces: since $\partial A / \partial V = -P$, the effect of the attractive forces may be computed as (integrating $-PdV$)

$$- \int_{\infty}^V \left[-\frac{aN^2}{V^2} \right] = -\frac{aN^2}{V}. \quad (6.4.33)$$

(2)

$$S = -\frac{A}{T} = N \left\{ \log \left[\frac{n_Q}{N} (V - Nb) \right] + \frac{5}{2} \right\}. \quad (6.4.34)$$

$E = A + ST$ is

$$E = \frac{3}{2} Nk_B T - \frac{aN^2}{V}. \quad (6.4.35)$$

They are very natural expressions.

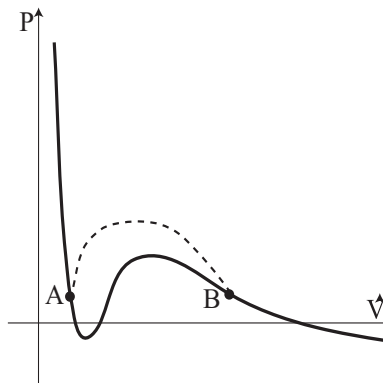
4.4 [Thermodynamically respectable derivation of Maxwell's rule]

If the temperature is sufficiently low, the PV -curve given by the van der Waals equation of state implies

$$\frac{\partial P}{\partial V} = -\frac{Nk_B T}{(V - N\sigma)^2} + a\frac{N^2}{V^3} > 0. \quad (6.4.36)$$

That is, it is thermodynamically unrealizable. Actually, gas-liquid coexistence occurs when this ‘unphysical behavior’ happens, and the coexistence temperature T is determined by the Maxwell rule. This is what Maxwell proposed and an ‘explanation’ was given in the [text](#) but was with a remark that the argument is an abuse of thermodynamics. Many textbooks argue that Maxwell's rule cannot be derived

thermodynamically properly, because the argument in the text (the usual one) utilizes thermodynamics where the states are unstable. However, it is possible to avoid this abuse and still we can thermodynamically demonstrate Maxwell's rule. The coexistence condition for phase A and phase B is the agreement of P , T and μ . $\mu_B(T, P) - \mu_A(T, P)$ of the difference of the Gibbs free energy must be computable along the path in the phase diagram through only stable phases (that is, the broken curve in the following figure).



Since

$$G = E - ST + PV, \quad (6.4.37)$$

if we compute $E_B - E_A$ and $S_B - S_A$, then $G_A = G_B$ allows us to compute the difference of PV , that is, $P(V_A - V_B)$.

- (1) Compute $E_B - E_A$.
- (2) Compute $S_B - S_A$.
- (3) Since $G_B - G_A = 0$, these results allow us to compute $P(V_B - V_A)$. Confirm that this and the result obtained by the naive abuse of thermodynamics:

$$\int_A^B P dV \quad (6.4.38)$$

agree.

Solution

- (1) We compute the internal energy difference as

$$E_B - E_A = \int_A^B dE = \int_A^B \left[\left. \frac{\partial E}{\partial V} \right|_T dV + \left. \frac{\partial E}{\partial T} \right|_V dT \right], \quad (6.4.39)$$

where the temperatures at A and at B are identical. To compute the second term we need the constant volume specific heat C_V . C_V for the van der Waals gas is identical with that for a (monatomic) ideal gas (the effect of the attractive interaction depends

only on the density, so it does not contribute to C_V as can explicitly be seen from (6.4.35)). Since $T_A = T_B$, the second term is always zero. From $dE = TdS - PdV$ we get

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial S}{\partial V} \right|_T - P = T \left. \frac{\partial P}{\partial T} \right|_V - P = \frac{1}{2}a \left(\frac{N}{V} \right)^2. \quad (6.4.40)$$

Therefore,

$$E_B - E_A = \int_A^B \frac{1}{2}a \left(\frac{N}{V} \right)^2 dV = \frac{aN^2}{2} \left(\frac{1}{V_A} - \frac{1}{V_B} \right). \quad (6.4.41)$$

(2) This can also be obtained, if we note $T_A = T_B$. The temperature derivative gives $(C_V/T)dT$, but this is a function of T only, so if the initial and the final temperatures are the same, it cannot contribute to the integral. Therefore,

$$S_B - S_A = \int_A^B dS = \int_A^B \left. \frac{\partial S}{\partial V} \right|_T dV. \quad (6.4.42)$$

Thus, we get

$$T(S_B - S_A) = T \int_A^B \left. \frac{\partial P}{\partial T} \right|_V dV = \int_A^B \frac{Nk_B T}{V - N\sigma} dV = Nk_B T \log \frac{V_B - N\sigma}{V_A - N\sigma}. \quad (6.4.43)$$

(3) Since $G_B - G_A = 0$ and since the initial and the final T and P are the same,

$$P(V_B - V_A) = T(S_B - S_A) - (E_B - E_A). \quad (6.4.44)$$

If we introduce (6.4.43) and (6.4.41) into this, along the broken curve in the above figure

$$P(V_B - V_A) = Nk_B T \log \frac{V_B - N\sigma}{V_A - N\sigma} - \frac{aN^2}{2} \left(\frac{1}{V_A} - \frac{1}{V_B} \right). \quad (6.4.45)$$

The RHS of this formula agrees exactly with the naive computation of (6.4.38) along the van der Waals curve. Therefore, Maxwell's rule has been justified thermodynamically. Notice that this happy consequence depends on a peculiar feature of the van der Waals gas that its specific heat is not volume dependent at all.

4.5 [Grand canonical approach to 1D van der Waals gas]

Let us study the 1D Kac model with the aid of the grand canonical approach.

(1) If there are N particles in the container of volume V , the canonical partition function reads

$$Z_N(V) = \int_{(N-1)\sigma}^{V-\sigma} dx_N \cdots \int_{\sigma}^{x_3-\sigma} dx_2 \int_0^{x_2-\sigma} dx_1 \int dp_1 \cdots dp_n e^{-\sum_{i=1}^N p_i^2/2mk_B T + aN^2/k_B TV}. \quad (6.4.46)$$

After checking the formula is correct, actually compute this.

(2) Using the result of (1) write down the grand partition function (you cannot perform the summation in a closed form).

(3) The grand partition function written down in (2) has the following structure:

$$\Xi = \sum_{N=0}^M e^{VA(N/V)}, \quad (6.4.47)$$

where M is the maximum number of particles we can push into the volume V . Show that if the temperature is sufficiently high, there is only one $n = N/V$ that maximizes $A(n)$. Also demonstrate that if the temperature is sufficiently low, there can be three extrema for $A(n)$.

(4) What do you expect the grand partition function looks like, if n that maximizes $A(n)$ are not unique?

(5) There is a text book which writes explicitly as follows:

$$\Xi = e^{\beta PV} + e^{\beta P'V}. \quad (6.4.48)$$

Here, we have assumed that $A(n)$ have two maxima, and the two terms correspond respectively to the two maxima. Is this correct?

Solution

(1) Let us start with the $N = 2$ case:

$$Z_2(V) = \frac{1}{h^2} \int_{\sigma}^{V-\sigma} dx_2 \int_0^{x_2-\sigma} dx_1 \int dp_1 dp_2 e^{-\sum_{i=1}^2 p_i^2/2mk_B T + aN^2/2k_B TV} \quad (6.4.49)$$

$$= \left(\frac{2\pi mk_B T}{h^2} \right)^{2/2} \int_0^{V-2\sigma} dy_2 \int_0^{y_2} dy_1 e^{2aV k_B T} \quad (6.4.50)$$

$$= \left(\frac{2\pi mk_B T}{h^2} \right)^{2/2} \frac{1}{2} (V - 2\sigma)^2 e^{2aV k_B T}. \quad (6.4.51)$$

In the above calculation the interparticle distances $y_2 = x_2 - x_1$ and $y_1 = x_1 - 0$ have been introduced.

For $N = 3$, introducing $y_3 = x_3 - x_2$ as well we get

$$Z_3(V) = \frac{1}{h^3} \int_{2\sigma}^{V-\sigma} dx_3 \int_{\sigma}^{x_3-\sigma} dx_2 \int_0^{x_2-\sigma} dx_1 \int dp_1 dp_2 dp_3 e^{-\sum_{i=1}^3 p_i^2/2mk_B T + aN^2/k_B TV} \quad (6.4.52)$$

$$= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \int_0^{V-3\sigma} dy_3 \int_0^{y_3} dy_2 \int_0^{y_2} dy_1 e^{9a/2V k_B T} \quad (6.4.53)$$

$$= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{1}{3!} (V - 3\sigma)^3 e^{9a/2V k_B T}. \quad (6.4.54)$$

Now, it is easy to guess the following general formula:

$$Z_N(V) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{N/2} (V - N\sigma)^N e^{aN^2/2V k_B T}. \quad (6.4.55)$$

It is not hard to show that this is correct in 1D if you plot possible trajectories of particles as a function of time.

(2)

$$\Xi = \sum_{N=0}^M \frac{1}{N!} (V - N\sigma)^N (2\pi m k_B T / h^2)^{N/2} e^{aN^2/2V k_B T} e^{\mu N / k_B T}. \quad (6.4.56)$$

(3) From (6.4.56) we obtain

$$A(N) = N \log(V - N\sigma) - N \log N + N + \frac{N}{2} \log(2\pi m k_B T / h^2) + aN^2/2V k_B T + \mu N / k_B T, \quad (6.4.57)$$

so

$$A(n) = V[n \log(1/n - \sigma) + n + \frac{n}{2} \log(2\pi m k_B T / h^2) + an^2/2k_B T + \mu n / k_B T] \quad (6.4.58)$$

$$= V[n \log(1/n - \sigma) + n\Lambda + an^2/2k_B T], \quad (6.4.59)$$

where $\Lambda = 1 + (1/2) \log(2\pi m k_B T / h^2) + \mu / k_B T$. Differentiating this wrt to n , we get the condition for a maximum:

$$\frac{\partial A(n)}{\partial n} = V \left[\log \left(\frac{1}{n} - \sigma \right) - \frac{1}{1 - n\sigma} + \Lambda + an/k_B T \right] = 0. \quad (6.4.60)$$

The first two terms in the brackets are

$$\log(1/n) + \log(1 - n\sigma) - \frac{1}{1 - n\sigma}. \quad (6.4.61)$$

This is a monotone decreasing function from $+\infty$ (at $n = 0$) to $-\infty$ (at $n = 1/\sigma$, the maximum packing density). Therefore, if T is sufficiently large, then there is only one solution to (6.4.60). Also we see there could be three solutions for this equation

if T is sufficiently small; they correspond to two maxima and one minimum between them of $A(n)$.

(4) At high temperatures there is only one maximum for $A(n)$, so we may use the maximum term to estimate (6.4.56). This is just as we have seen in the proof of ensemble equivalence in the text.

$$\Xi \simeq e^{PV/k_B T}. \quad (6.4.62)$$

If T is sufficiently low (with an appropriate chemical potential), as noted in (3) there are two maxima. If the heights of these maxima are different, then thanks to the multiplicative V in the exponent of (6.4.56) only one maximum can contribute. Only when these two maxima have exactly the same heights can they both contribute to the grand partition function, and this corresponds to the phase coexistence temperature.

(5) As already explained in (4) this form holds only at the phase transition temperature. At other temperatures one term is overwhelmingly smaller than the other, and around the taller maximum are numerous higher $A(n)$'s than the secondary maximum, so if we do not pay attention to the former, there is no point to keep the secondary maximum contribution. Thus, if we interpret $e^{\beta PV}$ as representative term(s) among the summands we cannot write such a formula. However, if you interpret each term to be the sum below or above some n (intermediate value of the two coexisting phases), you might be allowed to write such a formula symbolically.

4.6 [Hard sphere fluid]

The virial equation of state for a fluid interacting with 2-body potential reads

$$\frac{P}{nk_B T} = 1 - \frac{2\pi}{3}\beta n \int_0^\infty \phi'(r)g(r)r^3 dr. \quad (6.4.63)$$

Using this formula, derive the equation of state for the hard sphere fluid:

$$\frac{P_H}{nk_B T} = 1 + \frac{2\pi}{3}ng(\sigma)\sigma^3, \quad (6.4.64)$$

where σ is the diameter of the sphere. Strictly speaking, $g(\sigma)$ is $\lim_{r \searrow \sigma} g(r)$.

Solution

Notice that $\phi_H g$ is zero inside the sphere.

$$-\frac{2\pi}{3}n \int_0^\infty \beta \phi'_H(r)g(r)r^3 dr = \frac{2\pi}{3}n \int_0^\infty \frac{df(r)}{dr} e^{\beta\phi} g(r)r^3 dr \quad (6.4.65)$$

$$= \frac{2\pi}{3}n \int_0^\infty \delta(r - \sigma) e^{\beta\phi} g(r)r^3 dr \quad (6.4.66)$$

$$= \frac{2\pi}{3}ng(\sigma)\sigma^3 \quad (6.4.67)$$

4.7 [Internal energy of fluid interacting with binary forces]

- (1) Suppose the interactions among spherical particles can be expressed in terms of the two-body interaction potential $\phi(\mathbf{r}) = \phi(r)$. Write down its internal energy in terms of E , ϕ , the number density n and the radial distribution function $g(r)$.
- (2) Obtain the internal energy of the Kac fluid (i.e., the fluid interacting via the Kac potential). Set $\sigma = 1$.
- (3) Using the virial equation of state

$$P/nk_B T = 1 - \frac{2\pi}{3} n\beta \int_0^\infty \phi'(r)g(r)r^3 dr, \quad (6.4.68)$$

obtain the augmented van der Waals equation of state for a Kac fluid:

$$\beta P = \beta P_H + \frac{n^2}{2} \beta \int d^3\mathbf{r} \phi(\mathbf{r}). \quad (6.4.69)$$

Notice that the radial distribution function of the Kac fluid is the same as the hard sphere fluid with the same number density.³³

Solution

- (1) The internal energy is the expectation value of the system Hamiltonian. The expectation value of the kinetic energy is simple:

$$\left\langle \sum p^2/2m \right\rangle = (3/2)Nk_B T. \quad (6.4.70)$$

The expectation value of the potential energy is

$$\langle U \rangle = \left\langle \frac{1}{2} \sum_{i \neq j} \phi(|\mathbf{r}_i - \mathbf{r}_j|) \right\rangle = \int d\mathbf{x} d\mathbf{y} \phi(|\mathbf{x} - \mathbf{y}|) \left\langle \frac{1}{2} \sum_{i \neq j} \delta(\mathbf{x} - \mathbf{r}_i) \delta(\mathbf{y} - \mathbf{r}_j) \right\rangle \quad (6.4.71)$$

$$= \frac{1}{2} \int d\mathbf{x} d\mathbf{y} n^{(2)}(\mathbf{x}, \mathbf{y}) \phi(|\mathbf{x} - \mathbf{y}|). \quad (6.4.72)$$

Therefore,

$$E = \frac{3}{2}Nk_B T + 2\pi nN \int dr r^2 \phi(r)g(r). \quad (6.4.73)$$

³³However, we cannot derive the Maxwell's rule requirement.

(2) For the Kac potential case, the hard-core part of the potential does not contribute to the energy, so we have only to consider the attractive part in the $\gamma \rightarrow 0$ limit:

$$U = \frac{1}{2}nN4\pi \int_1^\infty \gamma^3 \phi(\gamma r)g(r)r^2 dr = \frac{1}{2}nN4\pi \int_\gamma^\infty \phi(y)g(y/\gamma)y^2 dy. \quad (6.4.74)$$

$g(y/\gamma) \rightarrow 1$ for any finite y in the $\gamma \rightarrow 0$ limit, so

$$U = \frac{1}{2}nN4\pi \int_0^\infty \phi(y)y^2 dy = \frac{1}{2}Nn\bar{\phi}. \quad (6.4.75)$$

Therefore,

$$E = \frac{3}{2}Nk_B T + \frac{1}{2}Nn\bar{\phi}. \quad (6.4.76)$$

(3) consider the contribution of the interaction potential to the pressure $\beta\Delta P$ (we perform the limit $\gamma \rightarrow 0$ at a convenient stage of calculation):

$$\beta\Delta P = -\beta\frac{2\pi}{3}n^2 \int_0^\infty \phi'(r)g(r)r^3 dr \quad (6.4.77)$$

$$= -\beta\frac{2\pi}{3}n^2 \int_0^\infty [\phi'_H(r) + \gamma^4\phi'(\gamma r)]g(r)r^3 dr. \quad (6.4.78)$$

We have already computed the contribution of the hard-core portion:

$$-\frac{2\pi}{3}n^2 \int_0^\infty \beta\phi'_H(r)g(r)r^3 dr = \frac{2\pi}{3}n^2 g(\sigma)\sigma^3. \quad (6.4.79)$$

The contribution from the foothill of the potential is

$$-\beta\frac{2\pi}{3}n^2 \int_1^\infty \gamma^4\phi'(\gamma r)g(r)r^3 dr = -\beta\frac{2\pi}{3}n^2 \int_\gamma^\infty \phi'(y)g(y/\gamma)y^3 dy \quad (6.4.80)$$

$$\rightarrow -\beta\frac{2\pi}{3}n^2 \int_0^\infty \phi'(y)y^3 dy, \quad (6.4.81)$$

where we have used $g \rightarrow 1$ at infinity. Therefore,

$$\beta\Delta P = +\frac{2\pi}{3}n^2 g(\sigma)\sigma^3 + 2\pi n^2 \beta \int_0^\infty \phi(y)y^2 dy. \quad (6.4.82)$$

4.8 [Functional differentiation]

Compute the following functional derivative.

$$\frac{\delta}{\delta\psi(\mathbf{x})} \int d^3\mathbf{r} \left[\frac{1}{2}(\nabla\psi(\mathbf{r}))^2 - \frac{1}{2}\tau\psi^2(\mathbf{r}) + \frac{1}{4}\psi^4(\mathbf{r}) \right], \quad (6.4.83)$$

where τ is a constant.

(2) [Green's function and functional differentiation] Consider a differential equation (partial or ordinary) $L\varphi = f$, where L is a linear differential operator acting on the functions of x .³⁴ Show that $\delta\varphi/\delta f$ is the Green's function for the initial boundary value problem defined by the linear operator L . (This is a problem immediately solved by inspection, but the fact is not meaningless. The method of Green's function is actually a method to solve a differential equation by the first order functional Taylor expansion approach explained in the text; in this case the problem is linear, so the method gives an exact solution.)

(3) Regard the entropy S of a fluid interacting with the binary potential ϕ as its functional, and express the functional derivative

$$\frac{\delta S}{\delta\phi(\mathbf{r})}, \quad (6.4.84)$$

in terms of the radial distribution function (and its appropriate partial derivatives). It may be easy to compute the corresponding functional derivative of the Helmholtz free energy.

Solution

(1)

$$\begin{aligned} & \frac{\delta}{\delta\psi(\mathbf{x})} \int d^3\mathbf{r} \left[\frac{1}{2}(\nabla\psi(\mathbf{r}))^2 - \frac{1}{2}\tau\psi^2(\mathbf{r}) + \frac{1}{4}\psi^4(\mathbf{r}) \right] \\ &= \int d^3\mathbf{r} [(\nabla\psi(\mathbf{r}))\nabla\delta(\mathbf{r}-\mathbf{x}) - \tau\psi(\mathbf{r})\delta(\mathbf{r}-\mathbf{x}) + \psi^3(\mathbf{r})\delta(\mathbf{r}-\mathbf{x})] = -\nabla^2\psi(\mathbf{x}) - \tau\psi(\mathbf{x}) + \psi^3(\mathbf{x}) \end{aligned} \quad (6.4.85)$$

(2) The first order Taylor expansion approximation reads

$$\delta\varphi = \int d\bullet \frac{\delta\varphi}{\delta f(\bullet)} \delta f(\bullet), \quad (6.4.86)$$

³⁴If $(Lf)(x)$ is determined by the value of f at x and the values of various derivatives of f at x , L is called a differential operator.

where dummy variables are expressed by \bullet . The integration wrt the dummy is written as \int . If the problem is linear, φ does not depend on f , so ‘integrating’ the above formula, we find

$$\varphi = \int d\bullet \frac{\delta\varphi}{\delta f(\bullet)} f(\bullet) \quad (6.4.87)$$

Functionally differentiating $L\varphi = f$ wrt f (recall that we may always exchange the order of functional calculus procedures and ordinary calculus procedures), we obtain (in the following L is written as L_x to emphasize that it acts on the functions of x)

$$L_x \frac{\delta\varphi(x)}{\delta f(y)} = \delta(x - y) \quad (6.4.88)$$

(under the same linear auxiliary conditions), Hence, we have $G(x|y) = \delta\varphi(x)/\delta f(y)$. Indeed,

$$\begin{aligned} L_x \int G(x|y) f(y) dy &= L_x \int d\bullet \frac{\delta\varphi(x)}{\delta f(\bullet)} f(\bullet) = \int d\bullet \frac{\delta(L\varphi)(x)}{\delta f(\bullet)} f(\bullet) \quad (6.4.89) \\ &= \int d\bullet \frac{\delta f(x)}{\delta f(\bullet)} f(\bullet) = \int d\bullet \delta(x - \bullet) f(\bullet) = f(x). \end{aligned} \quad (6.4.90)$$

(3) Let us write $d\Gamma_N = (1/h^{3N} N!)d(\text{phase volume})$ and differentiate the free energy first:

$$\frac{\delta A}{\delta\phi(\mathbf{r})} = \frac{\delta}{\delta\phi(\mathbf{r})} (-k_B T \log \int d\Gamma_N e^{-\beta(K + \sum \phi(x_i - x_j))}) \quad (6.4.91)$$

$$= \frac{1}{Z} \int d\Gamma_N \sum_{i < j} \delta(\mathbf{r} - (x_i - x_j)) e^{-\beta(K + \sum \phi(x_i - x_j))} = \left\langle \sum_{i < j} d(\mathbf{r} - (x_i - x_j)) \right\rangle \quad (6.4.92)$$

$$= \frac{1}{2} \left\langle \sum_{i \neq j} \int dy \delta(\mathbf{r} + \mathbf{y} - x_i) \delta(\mathbf{y} - x_j) \right\rangle = \frac{1}{2} \int dy n^{(2)}(\mathbf{r} + \mathbf{y}, \mathbf{y}). \quad (6.4.93)$$

Since the system is expected to be translationally symmetric and isotropic, we can simplify this as

$$\frac{\delta A}{\delta\phi(\mathbf{r})} = \frac{1}{2} V n^{(2)}(\mathbf{r}, 0) = \frac{1}{2} N n g(|\mathbf{r}|). \quad (6.4.94)$$

Incidentally, this formula gives a perturbative way to compute A .

Since $S = -\partial A / \partial T$ (notice that n is a constant)

$$\frac{\delta S}{\delta\phi(\mathbf{r})} = -\frac{1}{2} N n \frac{\partial}{\partial T} g(|\mathbf{r}|). \quad (6.4.95)$$

4.9 [Functional derivatives of canonical partition function]

Redo the calculations (4.4.26)-(4.4.28) using the canonical formalism; this is slightly easier than the grand canonical approach given in the text.

4.10 [Debye-Hückel theory]

Let us perform the functional Taylor approximation approach explained in [Section 4.4](#) with $A = n$ and $B = U$.

- (1) Within this approach find the equation governing the radial distribution function g .
- (2) Obtain the Fourier transform of the indirect correlation function in the present approximation.
- (3) Let ϕ be the Coulomb potential. Its Fourier transform may be written as $\phi_k = Q/k^2$. What is the functional form of the indirect correlation function $h(r)$?

Solution

- (1) From the formulas in the text, we can almost write down the solution as

$$h = -\beta(nh * \phi + \phi). \quad (6.4.96)$$

First, (4.4.31) tells us

$$\left(\frac{\delta n(x|U)}{\delta -\beta U(y)} \right)_{U=0} = n^2 h(x-y) + n\delta(x-y), \quad (6.4.97)$$

so the Taylor approximation reads

$$n(x|\phi) - n(x|0) = \int dy [n^2 h(x-y) + n\delta(x-y)](-\beta\phi(y) - 0). \quad (6.4.98)$$

That is,

$$nh(x) = -\beta n^2 \int dy h(x-y)\phi(y) - \beta n\phi(x). \quad (6.4.99)$$

This leads to the answer given above.

- (2) Fourier transforming (6.4.96), we get

$$h_k = \frac{-\beta\phi_k}{1 + \beta n\phi_k}. \quad (6.4.100)$$

- (3) For the Coulomb potential

$$h_k = \frac{-\beta Q}{k^2 + \beta n Q}. \quad (6.4.101)$$

Therefore,

$$h \propto \frac{1}{r} e^{-r\sqrt{\beta n Q}}. \quad (6.4.102)$$

This is a Yukawa potential. That is, the Coulomb force is shielded by many-body effects. Recall that $\log g \sim h$ is the **effective two-body** interaction.

4.11 [Toy integral equation for liquid]

Let us make a prototype closure for the radial distribution.

- (1) Make the first order approximation (i.e., the first order functional Taylor expansion approximation) of $n^{(1)}(\mathbf{x}|U)$ in terms of the Boltzmann factor $\exp[-\beta U(\mathbf{x})]$.
- (2) What is the direct correlation function?
- (3) Find the Fourier transform of the indirect correlation function.
- (4) Find the equation of state with our approximation with the aid of compressibility or its reciprocal. Assume that the diameter of the hard core is a .

Solution

Let $A = n^{(1)}(\mathbf{x}|U)$ and $B = \exp[-\beta U(\mathbf{x})]$. We need the following calculation:

$$\frac{\delta A(\mathbf{x}|U)}{\delta B(\mathbf{y}|U)} = -e^{\beta U(\mathbf{x})} \frac{\delta n^{(1)}(\mathbf{x}|U)}{\delta \beta U(\mathbf{y})} \quad (6.4.103)$$

$$= e^{\beta U(\mathbf{x})} [n^{(2)}(\mathbf{x}, \mathbf{y}|U) - n^{(1)}(\mathbf{x}|U)n^{(1)}(\mathbf{y}|U) + n^{(1)}(\mathbf{x}|U)\delta(\mathbf{x} - \mathbf{y})]. \quad (6.4.104)$$

Let us estimate this at $U = 0$:

$$\left. \frac{\delta A(\mathbf{x}|U)}{\delta B(\mathbf{y}|U)} \right|_{U=0} = n^2 g(\mathbf{x} - \mathbf{y}) - n^2 + n\delta(\mathbf{x} - \mathbf{y}). \quad (6.4.105)$$

Let ϕ be the potential created by the particle placed at the origin. Then, $A(\mathbf{x}|\phi) = n^{(1)}(\mathbf{x}|\phi) = ng(\mathbf{x})$, $A(\mathbf{x}|0) = n^{(1)}(\mathbf{x}|0) = n$, $B(\mathbf{x}|\phi) = \exp[-\beta\phi(\mathbf{x})]$ and $B(\mathbf{x}|0) = 1$. Using these formulas, the linear Taylor approximation reads

$$ng(\mathbf{x}) - n = n \int d\mathbf{y} [ng(\mathbf{x} - \mathbf{y}) - n + \delta(\mathbf{x} - \mathbf{y})] (\exp[-\beta\phi(\mathbf{y})] - 1). \quad (6.4.106)$$

Using h and Mayer's f , we have

$$h(\mathbf{x}) = \int d\mathbf{y} [nh(\mathbf{x} - \mathbf{y}) + \delta(\mathbf{x} - \mathbf{y})] f(\mathbf{y}), \quad (6.4.107)$$

or

$$h(\mathbf{x}) = f(\mathbf{x}) + n \int d\mathbf{y} h(\mathbf{x} - \mathbf{y}) f(\mathbf{y}). \quad (6.4.108)$$

This is our final result. This is already a closed equation for h .

(2) Comparing (6.4.108) and the Ornstein-Zernike equation, we immediately see $c = f$.

(3) (6.4.108) is linear in h , so we can solve it with the aid of Fourier transformation:

$$f(\mathbf{k}) = \int d^3\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}). \quad (6.4.109)$$

Its inverse is

$$f(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{k}). \quad (6.4.110)$$

The most important feature we use is that the convolution is converted into product:

$$(f * g)(\mathbf{k}) = f(\mathbf{k})g(\mathbf{k}). \quad (6.4.111)$$

Using this, we have

$$h(\mathbf{k}) = f(\mathbf{k}) + nh(\mathbf{k})f(\mathbf{k}). \quad (6.4.112)$$

That is,

$$h(\mathbf{k}) = f(\mathbf{k})/(1 - nf(\mathbf{k})). \quad (6.4.113)$$

(4) The compressibility equation gives $\partial P/\partial n$:

$$\beta \left. \frac{\partial P}{\partial n} \right|_{T,V} = 1 - n \int c d\mathbf{x} = 1 + n \frac{4\pi}{3} a^3. \quad (6.4.114)$$

Therefore,

$$\frac{P}{nk_B T} = 1 + \frac{2\pi}{3} a^3 n. \quad (6.4.115)$$

4.12. [Scaled particle theory of hard core fluid]³⁵

As we know well by now, for a spherical hard core fluid

$$P/nk_B T = 1 + \frac{2\pi}{3} n\sigma^3 g(\sigma), \quad (6.4.116)$$

where σ is the diameter of the spherical core. Therefore, to know the hard core equation of state we need g only at $r = \sigma$.

Let $p_0(r)$ be the probability of observing a bubble of radius r . Let $nG(r)$ be the expected number of the centers just outside the bubble ($nGdr$ is the expected

³⁵R. J. Baxter, in *Physical Chemistry an advanced treatise* volume VIIIA Liquid State (edited by H. Eyring, D. Henderson and W. Jost, Academic Press 1971) Chapter 4, Section VIII.

number of particle centers in the spherical shell between r and $r + dr$). When the bubble is of radius σ , it just behaves as the exclusion zone by the hard sphere at the origin. Therefore,

$$g(\sigma) = G(\sigma). \quad (6.4.117)$$

We have only to determine G to know the hard-core fluid pressure.

(1) Derive

$$p_0(r + dr) = p_0(r)[1 - 4\pi nr^2 G(r) dr]. \quad (6.4.118)$$

That is,

$$\frac{d}{dr} \log p_0(r) = -4\pi nr^2 G(r). \quad (6.4.119)$$

(2) We can determine G for very large r . According to the fluctuation theory, the probability of fluctuation that creates a bubble of radius r may be written in terms of the reversible work $W(r)$ required to make it. Therefore,

$$p_0(r) = e^{-\beta W(r)}. \quad (6.4.120)$$

Using this and the thermodynamic result for large r (i.e., for the usual macroscopic bubble!)

$$dW(r) = PdV + f[1 - (2\delta/r)]dA, \quad (6.4.121)$$

where A is the surface area of the bubble, and $f(1 - 2\delta/r)$ is the surface tension of the curved surface of mean curvature $1/r$. Using (6.4.119)-(6.4.121), find $G(r)$ as a function of r .

(3) If $r < \sigma/2$, only 1 particle center can come in the bubble. What is this probability? This must be $1 - p_0(r)$ for $r < \sigma/2$.

(4) Determine $G(r)$ for $r < \sigma/2$.

(5) Unfortunately, $G(r)$ is not a smooth function, but it is known that it is continuously differentiable at $r = \sigma/2$. Let us make an approximation that the unknown parameters f and δ may be determined by matching G obtained in (2) and in (4) at $r = \sigma/2$ smoothly (match G and G' there). Derive, under this approximation,

$$\frac{P}{nk_B T} = \frac{1 + \eta + \eta^3}{(1 - \eta)^3}, \quad (6.4.122)$$

where η is the packing density: $\eta = \pi\sigma^3 n/6$ as usual.

[This is identical to PY-C! Furthermore, f obtained is quite reasonable.]

Solution

(1) If we assume that there is no more than a single particle in a thin shell, then $4\pi r^2 dr \times nG(r)$ is the expectation value of the number of particles in the shell immediately outside the bubble of radius r . Poisson distribution tells us that the

probability to find no particle in the shell is $e^{-4\pi nr^2 G(r) dr} = 1 - 4\pi nr^2 G(r) dr$.

(2)

$$-\beta \frac{d}{dr} W(r) = -4\pi nr^2 G(r). \quad (6.4.123)$$

A and V must be expressed in terms of r : $V = (4\pi/3)r^3$, $A = 4\pi r^2$. Therefore,

$$\frac{dW}{dr} = 4\pi Pr^2 + 8\pi f[1 - (2\delta/r)]r = 4\pi k_B T nr^2 G(r). \quad (6.4.124)$$

That is,

$$G(r) = \frac{P + (2f/r) - (4f\delta/r^2)}{nk_B T}. \quad (6.4.125)$$

(3) $(4\pi/3)nr^3$ is the expectation value of the number of (the centers of the) particles. Here, the sphere of radius r does not contain any particle (with probability p_0) or contains only one particle (with probability $p_1 = 1 - p_0$), and the expectation value of the number of particle is equal to p_1 . Therefore,

$$p_0(r) = 1 - \frac{4}{3}\pi nr^3. \quad (6.4.126)$$

(4) If we use p_0 obtained in (3) in (6.4.119), we get

$$G(r) = \frac{1}{1 - (4\pi/3)r^3 n}. \quad (6.4.127)$$

(5) If we demand G just obtained and (6.4.125) agree at $r = \sigma/2$:

$$\frac{1}{1 - (4\pi/3)(\sigma/2)^3 n} = \frac{P + (4f/\sigma) - (16f\delta/\sigma^2)}{nk_B T}. \quad (6.4.128)$$

Introducing the following variable

$$X = P/nk_B T, \quad Y = 4f/n\sigma k_B T, \quad Z = 4\delta/\sigma, \quad (6.4.129)$$

the above equality reads

$$\frac{1}{1 - \eta} = X + Y - YZ. \quad (6.4.130)$$

If we further demand the agreement of G' there, we have

$$\frac{4\pi r^2 n}{(1 - (4\pi/3)r^3 n)^2} = \frac{-(2f/r^2) + 2(4f\delta/r^3)}{nk_B T}, \quad (6.4.131)$$

or

$$\frac{4\pi r^3 n}{(1 - (4\pi/3)r^3 n)^2} = \frac{-(2f/r) + 2(4f\delta/r^2)}{nk_B T}. \quad (6.4.132)$$

This can be rewritten as follows:

$$\frac{3\eta}{(1 - \eta)^2} = -Y + 2YZ. \quad (6.4.133)$$

We need one more relation. It is the expression of the pressure in terms of $G(\sigma)$:

$$X = 1 + 4\eta G(\sigma) = 1 + 4\eta(X + Y/2 - YZ/4), \quad (6.4.134)$$

where the second equality is obtained with the aid of (6.4.125).

From (6.4.130) and (6.4.133) we get

$$YZ = \frac{1}{1 - \eta} + \frac{3\eta}{(1 - \eta)^2} - X, \quad (6.4.135)$$

$$Y = \frac{2}{1 - \eta} + \frac{3\eta}{(1 - \eta)^2} - 2X. \quad (6.4.136)$$

Introducing these into (6.4.134) gives

$$X = 1 + 4\eta X + 2\eta Y - \eta YZ, \quad (6.4.137)$$

$$= 1 + 4\eta X + \frac{3\eta}{1 - \eta} + \frac{3\eta^2}{(1 - \eta)^2} - 3\eta X. \quad (6.4.138)$$

Therefore,

$$(1 - \eta)X = 1 + \frac{3\eta}{1 - \eta} + \frac{3\eta^2}{(1 - \eta)^2} = \frac{1 + \eta + \eta^2}{(1 - \eta)^2}. \quad (6.4.139)$$

We've done it!

4.13 [Quantum effect on the second virial coefficient]³⁶

The second virial coefficient for a spherical symmetrical particle is, classically,

$$B = 2\pi \int_0^\infty (1 - e^{-\beta\phi(r)})r^2 dr. \quad (6.4.140)$$

Its quantum version should be obtained by replacing the Boltzmann factor $e^{-\beta\phi}$ with the diagonal element of the 2-body density operator $\rho(r)$:

$$B = 2\pi \int_0^\infty (1 - \mathcal{N}\rho(r))r^2 dr, \quad (6.4.141)$$

³⁶This is based on T. Kihara, *Molecular forces*.

where \mathcal{N} is the normalization constant to make $\mathcal{N}\rho(r) \rightarrow 1$ in the $r \rightarrow \infty$ limit.³⁷

Thus, the calculation has been reduced to that of ρ . Let us perform this through small steps. The difference of fermions and bosons can be ignored except for helium below 25 K. Therefore, we totally ignore the effect of particle symmetry on the wave function. The following calculation was done for the first time by E. Wigner in the 1930s. For ${}^4\text{He}$, below 50 K the quantum correction increases the classical value by about 50%, but by about 10% around 100 K, so the quantum correction is not very small.

(1) Let us assume that two-body Hamiltonian to be

$$H = -\frac{\hbar^2}{2m}(\Delta_1 + \Delta_2) + \phi(|\mathbf{r}_1 - \mathbf{r}_2|), \quad (6.4.142)$$

where Δ_i is the Laplacian wrt the position coordinates of the i -particle. The two-body density operator is given by $\rho = e^{-\beta H}$. Show that the matrix element $\langle \mathbf{r}_1, \mathbf{r}_2 | \rho | \mathbf{r}'_1, \mathbf{r}'_2 \rangle$ of the 2-body density operator satisfies the following equation:

$$\frac{\partial}{\partial \beta} \langle \mathbf{r}_1, \mathbf{r}_2 | \rho | \mathbf{r}'_1, \mathbf{r}'_2 \rangle = -H \langle \mathbf{r}_1, \mathbf{r}_2 | \rho | \mathbf{r}'_1, \mathbf{r}'_2 \rangle. \quad (6.4.143)$$

If we use the normalized eigenket $|i\rangle$ ($H|i\rangle = E_i|i\rangle$) of H , we can write

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \rho | \mathbf{r}'_1, \mathbf{r}'_2 \rangle = \sum_i \langle \mathbf{r}_1, \mathbf{r}_2 | i \rangle e^{-\beta E_i} \langle i | \mathbf{r}'_1, \mathbf{r}'_2 \rangle. \quad (6.4.144)$$

Here, the summation may include integration.

(2) For the case with $\phi = 0$ (i.e., for the ideal gas case) obtain $\langle \mathbf{r}_1, \mathbf{r}_2 | \rho | \mathbf{r}'_1, \mathbf{r}'_2 \rangle$. As already noted, you can totally forget about the particle exchange symmetry. You must specify the initial and the boundary conditions correctly to solve the above parabolic equation.

(3) Let us introduce the deviation Ψ from the case without interactions as

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \rho | \mathbf{r}'_1, \mathbf{r}'_2 \rangle = \left(\frac{2\pi\hbar^2\beta}{m} \right)^{-3} \exp \left[-\frac{m}{2\hbar^2\beta} [(\mathbf{r}_1 - \mathbf{r}'_1)^2 + (\mathbf{r}_2 - \mathbf{r}'_2)^2] + \Psi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \right]. \quad (6.4.145)$$

Note that $-k_B T \Psi$ corresponds to the ‘quantum-corrected two-body interaction. Ψ satisfies the following equation:

$$\phi + \frac{\partial \Psi}{\partial \beta} + k_B T [(\mathbf{r}_1 - \mathbf{r}'_1) \cdot \nabla_1 + (\mathbf{r}_2 - \mathbf{r}'_2) \cdot \nabla_2] \Psi = \frac{\hbar^2}{2m} [(\nabla_1 \Psi)^2 + \Delta_1 \Psi + (\nabla_2 \Psi)^2 + \Delta_2 \Psi]. \quad (6.4.146)$$

³⁷As we will see below, the diagonal element of the position representation of the density operator is proportional to the probability of finding particles, so it is proportional to the Boltzmann factor semi-classically. Therefore, normalizing the density operator appropriately, we can interpret it as a quantum statistical extension of the spatial Boltzmann factor.

This equation can be obtained from (6.4.143) by substituting (6.4.145); nothing special has not been done at all.

To obtain the quantum correction we expand Ψ as

$$\Psi = \Psi_0 + \frac{\hbar^2}{2m}\Psi_1 + \dots \quad (6.4.147)$$

and then introduce this into (6.4.146). Requiring the order by order agreement of the substituted result, we get

$$\phi + \frac{\partial}{\partial\beta}\Psi_0 + k_B T [(\mathbf{r}_1 - \mathbf{r}'_1) \cdot \nabla_1 + (\mathbf{r}_2 - \mathbf{r}'_2) \cdot \nabla_2] \Psi_0 = 0, \quad (6.4.148)$$

$$\frac{\partial}{\partial\beta}\Psi_1 + k_B T [(\mathbf{r}_1 - \mathbf{r}'_1) \cdot \nabla_1 + (\mathbf{r}_2 - \mathbf{r}'_2) \cdot \nabla_2] \Psi_1 = (\nabla_1 \Psi_0)^2 + \Delta_1 \Psi_0 + (\nabla_2 \Psi_0)^2 + \Delta_2 \Psi_0, \quad (6.4.149)$$

etc. First, we must solve the zeroth order equation. Show that the diagonal element of the only meaningful solution is $\Psi_0(\beta, \mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = -\beta\phi(|\mathbf{r}_1 - \mathbf{r}_2|)$.

(4) We have only to obtain the diagonal element of Ψ_1 . Solve the simplified equation that can be obtained by taking the diagonal limit of (6.4.149):

$$\frac{\partial}{\partial\beta}\Psi_1 = \lim_{\{\mathbf{r}'_i\} \rightarrow \{\mathbf{r}_i\}} [(\nabla_1 \Psi_0)^2 + \Delta_1 \Psi_0 + (\nabla_2 \Psi_0)^2 + \Delta_2 \Psi_0]. \quad (6.4.150)$$

As can immediately be seen, to compute the RHS of this equation, we cannot use $\Psi_0(\beta, \mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = -\beta\phi(|\mathbf{r}_1 - \mathbf{r}_2|)$ that is already in the diagonal limit. The derivative must be computed from the original expression of Ψ_0 . Find $\lim_{\{\mathbf{r}'_i\} \rightarrow \{\mathbf{r}_i\}} \nabla_1 \Psi_0$ and $\lim_{\{\mathbf{r}'_i\} \rightarrow \{\mathbf{r}_i\}} \nabla_2 \Psi_0$.

(5) To obtain $\Delta_1 \Psi_0$ we could perform a similar calculation. However, our purpose is not to practice calculation (although this practice is also meaningful), the needed result is provided:

$$\Delta_i \Psi_0 = -\frac{1}{3}\beta \Delta_i \phi, \quad (6.4.151)$$

where $i = 1, 2$.

Obtain the diagonal element $\langle \mathbf{r}_1, \mathbf{r}_2 | \Psi_1 | \mathbf{r}_1, \mathbf{r}_2 \rangle$. Then compute the quantum correction to the second virial coefficient to order \hbar^2 . Show that the correction is positive for any T (as stated for helium, quantum correction always increases the second virial coefficient).

(6) The quantum correction starts with the term of $O[\hbar^2]$. Why, or why isn't there any correction of odd order in \hbar ?

Solution

(1) Obviously,

$$\frac{d}{d\beta} e^{-\beta H} = -H e^{-\beta H}. \quad (6.4.152)$$

If we position represent this, we get the desired equation. The result is a parabolic partial differential equation.

(2) We must solve the following partial differential equation:

$$\frac{d}{d\beta} f(\beta, \{\mathbf{r}_i\}, \{\mathbf{r}'_i\}) = \frac{\hbar^2}{2m} (\Delta_1 + \Delta_2) f(\beta, \{\mathbf{r}_i\}, \{\mathbf{r}'_i\}), \quad (6.4.153)$$

where the primed vector variables are regarded as constant parameters in this equation. The initial condition at $\beta = 0$ can be obtained immediately from the definition of the density matrix:

$$f(0, \{\mathbf{r}_i\}, \{\mathbf{r}'_i\}) = \sum_i \langle \mathbf{r}_1, \mathbf{r}_2 | i \rangle \langle i | \mathbf{r}'_1, \mathbf{r}'_2 \rangle = \langle \mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}'_1, \mathbf{r}'_2 \rangle = \delta(\mathbf{r}_1 - \mathbf{r}'_1) \delta(\mathbf{r}_2 - \mathbf{r}'_2). \quad (6.4.154)$$

The boundary condition is that the solution goes to zero if $\{\mathbf{r}_i\}$ and $\{\mathbf{r}'_i\}$ are far apart.

This equation can be totally separated for different particles (as can be guessed from physics), so we have only to solve

$$\frac{\partial}{\partial \beta} \varphi(\beta, \mathbf{r}, \mathbf{r}') = \frac{\hbar^2}{2m} \Delta \varphi(\beta, \mathbf{r}, \mathbf{r}'). \quad (6.4.155)$$

This is an elementary diffusion equation (the simplest way to solve it is to use Fourier transformation):

$$\varphi(\beta, \mathbf{r}, \mathbf{r}') = \left(\frac{2\pi\hbar^2\beta}{m} \right)^{-3/2} \exp \left[-\frac{m}{2\hbar^2\beta} (\mathbf{r} - \mathbf{r}')^2 \right]. \quad (6.4.156)$$

Therefore, the answer is (6.4.145) without Ψ . We immediately see that \mathcal{N} can be chosen to cancel the numerical factor in front of the exponential function.

(3) The characteristic equation of this linear first order partial differential equation is

$$\frac{d\beta}{1} = -\frac{d\Psi_0}{\phi} = \frac{\beta dx_1}{x_1 - x'_1} = \frac{\beta dy_1}{y_1 - y'_1} = \dots, \quad (6.4.157)$$

where \dots denote similar equations for all the remaining particles. From this we see that the diagonal element is $\Psi_0 = -\beta\phi + \text{const}$. The answer must agree with the

ideal case in the $\beta\phi \rightarrow 0$ limit, the constant must be zero.

(4) If we apply ∇_1 to the zeroth order equation (6.4.148), we get

$$\nabla_1\phi + \frac{\partial}{\partial\beta}\nabla_1\Psi_0 + \frac{1}{\beta}\nabla_1\Psi_0 + k_B T [(\mathbf{r}_1 - \mathbf{r}'_1) \cdot \nabla_1 + (\mathbf{r}_2 - \mathbf{r}'_2) \cdot \nabla_2] \nabla_1\Psi_0 = 0. \quad (6.4.158)$$

Its diagonal element is

$$\nabla_1\phi + \frac{\partial}{\partial\beta}\nabla_1\Psi_0 + \frac{1}{\beta}\nabla_1\Psi_0 = 0. \quad (6.4.159)$$

This is an ordinary differential equation, so its general solution reads

$$\nabla_1\Psi_0 = -\frac{1}{2}\beta\nabla_1\phi + k_B T c, \quad (6.4.160)$$

where c is an arbitrary function of \mathbf{r} . However, we know that both Ψ and Ψ_0 must vanish in the $\beta \rightarrow 0$ limit, $c = 0$. Similarly,

$$\nabla_2\Psi_0 = -\frac{1}{2}\beta\nabla_2\phi. \quad (6.4.161)$$

(5) Since

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \Psi_1 | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{\beta^3}{6}(\nabla\phi)^2 - \frac{\beta^2}{3}\Delta\phi, \quad (6.4.162)$$

we now know the ‘quantum-corrected’ two-body potential. Therefore, we can write

$$B(T) = \frac{1}{2} \int_V d\mathbf{r} (1 - e^\Psi) = B_c(T) - \frac{\hbar^2}{4m} \int_V \left(\frac{\beta^3}{6}(\nabla\phi)^2 - \frac{\beta^2}{3}\Delta\phi \right) e^{-\beta\phi} d^3\mathbf{r}, \quad (6.4.163)$$

where B_c is the classic value. If we perform integration by parts, the result becomes cleaner. Using Gauss’ theorem, we have

$$(\Delta\phi)e^{-\beta\phi} = \nabla \cdot ((\nabla\phi)e^{-\beta\phi}) - \nabla\phi \cdot \nabla e^{-\beta\phi}, \quad (6.4.164)$$

so

$$\int (\Delta\phi)e^{-\beta\phi} = \int_S e^{-\beta\phi} \nabla\phi \cdot d\mathbf{S} - \int d^3\mathbf{r} \nabla\phi \cdot \nabla e^{-\beta\phi} = +\beta \int d^3\mathbf{r} (\nabla\phi \cdot \nabla\phi) e^{-\beta\phi}. \quad (6.4.165)$$

Thus, we have arrived at the desired result:

$$B(T) = B_c(T) + \frac{\hbar^2}{4m} \int_V \frac{\beta^3}{6} (\nabla\phi)^2 e^{-\beta\phi} d^3\mathbf{r}. \quad (6.4.166)$$

Thanks to the spherical symmetry $\nabla\phi(r) = (\mathbf{r}/r)\phi'(r)$ (the chain rule!), we can further rewrite this as

$$B(T) = B_c(T) + \frac{\pi\beta^3\hbar^2}{6m} \int_0^\infty (\phi')^2 e^{-\beta\phi} r^2 dr. \quad (6.4.167)$$

The correction term is clearly positive for any T .

(6) Perform $\hbar \rightarrow -\hbar$ in quantum mechanics. For the system with spatial inversion symmetry, this corresponds to the time reversal operation. We are discussing equilibrium states, so the situation should not be affected by time reversal. Therefore, quantum correction must be even in \hbar . [What if the system is chiral?]

6.5 Problems for Chapter 5

5.1 [Phase transition and analyticity]

If there is no phase transition in a range of fugacity $z = e^{\beta\mu}$, $P/k_B T$ is, by definition, holomorphic in z , so we may expand it as

$$\frac{P}{k_B T} = \sum_{\ell=1}^{\infty} b_{\ell} z^{\ell}, \quad (6.5.1)$$

where b_{ℓ} is called the ℓ -body cluster coefficient. They are smooth (actually real analytic) functions of T and positive for lower temperatures, so each b_{ℓ} has the smallest real positive zero T_{ℓ} . It is known that $\{T_{\ell}\}$ is a monotone decreasing sequence of ℓ . It is demonstrated³⁸ that

- (i) $b_{\ell}(T_c) > 0$ if ℓ is sufficiently large.
- (ii) There are infinitely many T_{ℓ} between any $T (> T_c)$ and T_c .

Let T_a be the accumulation point of $\{T_{\ell}\}$. Show $T_c = T_a$.³⁹

Solution

(ii) implies that T_c is an accumulation point of $\{T_{\ell}\}$. Needless to say, $\{T_{\ell}\}$ is bounded from below and monotone decreasing, its accumulation point is unique. Therefore, $T_c = T_a$. (i) is unnecessary.

5.2 [Crude version of rigorous Peierls' argument]

Let us impose an all up spin boundary condition to the 2-Ising model on the finite square. Then, we wish to take a thermodynamic limit. If the spin at the center of the square is more likely to be up than to be down, we may conclude that there is a long-range order.

Let γ be a closed Bloch wall (i.e., the boundary between up and down spin domains; this does not mean that the domain enclosed by γ is a totally up or down domain (lakes can contain islands with ponds with islets, etc.; the wall corresponds to the shore lines.) The probability $P_V(\gamma)$ to find such a wall in the system with volume V has the following estimate (we used this in our discussion on [Peierls' argument](#)):

$$P_V(\gamma) \leq e^{-2\beta J|\gamma|}, \quad (6.5.2)$$

where $|\gamma|$ is the total length of the contour γ , $\beta = 1/k_B T$, and J is the usual ferromagnetic coupling constant. [This naturally looking inequality needs a proof; it

³⁸T. Kihara and J. Okutani, Chem. Phys. Lett., **8**, 63 (1971).

³⁹This problem asks a mathematically trivial question, but the main point is the fact stated here.

is not trivial.]

(1) Since the outside boundary is all up, there must be a Bloch wall encircling the origin for the spin at the origin to be down. Therefore, the probability P_V^0 of the spin at the origin to be down must be smaller than the probability of the occurrence of at least one contour encircling the origin. Show

$$P_V^0 \leq \sum_{\gamma} e^{-2\beta J|\gamma|}, \quad (6.5.3)$$

where the summation is over all the possible contours surrounding the origin. [Hint: Don't think too much. If event A occurs when at least one of B and C occurs, then $A \subset B \cup C$.]

(2) Estimate the number of contours with circumference $|\gamma|$ crudely as the total number of random walks of length $|\gamma|$ starting from appropriate neighborhood points of the origin. Use this crude estimate and show that if β is sufficiently large, $P_V^0 < 1/2$ for large V .

Solution

The argument here is, although simplified, almost rigorous.

(1) The event that the spin at the origin is down occurs only if at least one Bloch wall surrounds the origin. Let $P(\gamma)$ be the probability that there is a closed Bloch wall γ surrounding the origin. Then,

$$P_V^0 \leq P(\text{at least there is one Bloch wall surrounding the origin}) = P(\cup_{\gamma} \{\exists \gamma\}) \leq \sum_{\gamma} P(\gamma), \quad (6.5.4)$$

where $\cup\{\exists \gamma\}$ is the event that there is at least one closed wall around the origin irrespective of its shape. The left-most inequality is due to $P(A \cup B) \leq P(A) + P(B)$. The sum is over all the closed curves around the origin. We use (6.5.2) to get (6.5.3).

(2) Again we perform extremely excessive estimate: to draw a closed curve surrounding the origin of length $|\gamma|$, we must start at some point. Let the starting point be the closest point on γ to the origin. The number of candidate points for this cannot exceed $|\gamma|^2$. Let us start a random walk of length $|\gamma|$. There is no guarantee that the walk makes a closed curve, but all the curves satisfying the desired condition can be drawn in this fashion. Since the number of distinct walks is $4 \times 3^{|\gamma|-1}$, we have

$$P_V^0 \leq \sum_{\gamma} e^{-2\beta J|\gamma|} \leq \sum_{|\gamma|=4}^{\infty} |\gamma|^2 3^{|\gamma|} e^{-2\beta J|\gamma|}. \quad (6.5.5)$$

Here, we have used the fact that the smallest closed curve on the lattice surrounding the origin has length 4 (the smallest square on the dual lattice; notice that the wall

is a curve on the dual lattice). Therefore, if β is sufficiently large, for any V we can make $P_V^0 < 1/2$. The key point of the argument is that $[\log C_{|\gamma|}]/|\gamma|$ is uniformly bounded from above, where C_n is the total number of closed curves of length n surrounding the origin.

(6.5.5) tells us that the spin at the origin points upward more likely than downward. The required β is unrealistically large due to the crudeness of the estimation, but still it is finite (that is, $T > 0$). Thus, we have shown that the system orders at some low but positive temperature.

Now, we demonstrate (6.5.2).⁴⁰ This is called Peierls' inequality. The statement of the proposition is:

Let V be a finite domain. On its boundary all the spins are fixed to point upward. Under this condition the probability $P_V(\gamma)$ of formation of a Bloch wall γ is bounded from above as

$$P_V(\gamma) \leq e^{-\beta 2J|\gamma|}, \quad (6.5.6)$$

where $|\gamma|$ is the total length of γ .

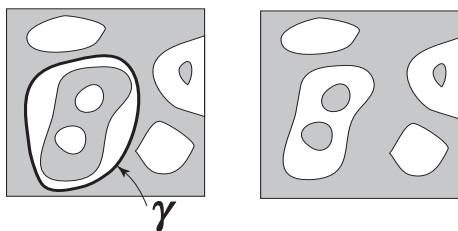
To demonstrate this, the energy in the volume V is estimated (let us denote the number of lattice points in V by the same symbol V):

$$\mathcal{H}_V(\phi) = -2JV + 2J|\partial\phi(V)|, \quad (6.5.7)$$

where $\partial\phi$ denotes the totality of the Bloch walls appearing in the spin configuration ϕ . We may write

$$P_V(\gamma) = \frac{\sum_{\phi(V): \gamma \subset \partial\phi(V)} e^{-\beta\mathcal{H}_V(\phi)}}{\sum_{\phi(V)} e^{-\beta\mathcal{H}_V(\phi)}}. \quad (6.5.8)$$

Here, in the numerator the sum is over all the spin configurations containing the Bloch wall γ . Next, the spin configurations on V is divided into the ones including γ denoted by Φ_γ and the rest denoted by Φ_γ^- . Let us define a one-to-one map $\chi: \Phi_\gamma \rightarrow \Phi_\gamma^-$ that flips all the spins inside γ (see the figure below).



Configurations with and without γ .
This correspondence is one-to-one.

⁴⁰Chapter 2 Section 1 of Ya G Sinai, *Theory of Phase Transitions: Rigorous Results* (Pergamon Press, 1982).

The map χ reduce the number of adjacent up-down spin pairs by $|\gamma|$, so the Boltzmann factor must be multiplied by $e^{2\beta|\gamma|}$. Therefore, if we replace every element in Φ_γ with the corresponding element in Φ_γ^- , we must multiply $e^{-2\beta|\gamma|}$ to cancel this Boltzmann factor:

$$P_V^+(\gamma) = \frac{\sum_{\Phi_\gamma} e^{-\beta\mathcal{H}_V(\phi)}}{\sum_{\phi(V)} e^{-\beta\mathcal{H}_V(\phi)}}. \quad (6.5.9)$$

$$= e^{-2\beta|\gamma|} \frac{\sum_{\Phi_\gamma^-} e^{-\beta\mathcal{H}_V(\phi)}}{\sum_{\phi(V)} e^{-\beta\mathcal{H}_V(\phi)}} \leq e^{-2\beta J|\gamma|}. \quad (6.5.10)$$

5.3 [Phase transition in 1D long-range system]

Using Peierls' argument, discuss the phase transition in a 1d spin system whose coupling constant behaves as r^{-q} ($q < 2$) beyond some distance r_0 (you may assume that the coupling constant for $r < r_0$ is J , constant). No rigorous argument is wanted.

Solution

Assume initially all the spins are up. Then, we flip L contiguous spins. The required energy is estimated as

$$\Delta E = 2 \int_{L/2+\delta}^{\infty} dx \int_{-L/2}^{L/2} dy \frac{1}{(x-y)^q}. \quad (6.5.11)$$

The contribution of the short-range interactions is $\sim 2J\delta$, so it is ignored. It is easy to see

$$\int_L^{\infty} dx \int_{-L/2}^{L/2} dy \frac{1}{(x-y)^q} = O[L^{2-q}]. \quad (6.5.12)$$

This energy increases indefinitely with L if $q < 2$. As we have seen for the nearest neighbor interaction system in the [text](#), the contribution of entropy that fatally cripple system ordering is of order $\log L$, so the entropy effect cannot destroy the order even at finite temperatures.

According to a rigorous argument even for $q = 2$ phase transition occurs at a finite temperature.

5.4 [Griffiths' inequality]

Empirically, it is known that there is the following relation among critical exponents:

$$\alpha + \beta(1 + \delta) = 2. \quad (6.5.13)$$

(1) Thermodynamically, demonstrate the following inequality (Griffiths' inequality)

$$\alpha + \beta(1 + \delta) \geq 2. \quad (6.5.14)$$

[Hint: You may proceed just as the case of **Rushbrooke's inequality**, but use $m \sim h^{1/\delta}$ (at $T = T_c$) to differentiate wrt H under constant temperature. At $\tau = 0$ and $h = 0$ the (vertical) line $T = T_c$ is tangent to $m = m(\tau, h = 0)$, so m may be parameterized by τ .]

(2) Using the scaling relation or Kadanoff's argument (that is, using the **expression** of the magnetization as a generalized homogeneous function of h and τ), show that the equality actually holds. [Hint: the wisest approach may be to use $\beta\delta = \beta + 1$. You may use such as $\alpha + 2\beta + \gamma = 2$ we have already discussed.]

Solution

(1) We start with the following inequality (just as in the case of Rushbrooke's inequality):

$$\left. \frac{\partial S}{\partial T} \right|_H \left. \frac{\partial M}{\partial H} \right|_T \geq \left. \frac{\partial S}{\partial H} \right|_T \left. \frac{\partial M}{\partial T} \right|_H = \left. \frac{\partial M}{\partial T} \right|_H^2. \quad (6.5.15)$$

Using $m \sim h^{1/\delta}$ at T_c , very close to T_c we have

$$T^{-1} |\tau|^{-\alpha} h^{1/\delta-1} = |\tau|^{-\alpha} m^{1-\delta} \geq |\tau|^{2(\beta-1)}, \quad (6.5.16)$$

where the T in the LHS is almost T_c , so we may ignore it. Using the hint, we have

$$|\tau|^{-\alpha} |\tau|^{\beta(1-\delta)} \geq |\tau|^{2(\beta-1)}. \quad (6.5.17)$$

This requires that the LHS of the following formula must be larger than some constant:

$$|\tau|^{-(\alpha+\beta(1+\delta)-2)} \geq \text{const}, \quad (6.5.18)$$

which implies $\alpha + \beta(1 + \delta) - 2 \geq 0$.

(2) Using the following result we have obtained in the text:

$$\beta = (d - y_2)/y_1, \delta = y_2/(d - y_2), \gamma = (2y_2 - d)/y_1, \quad (6.5.19)$$

we get

$$\beta\delta = y_2/y_1 = \beta + \gamma. \quad (6.5.20)$$

This with $\alpha + 2\beta + \gamma = 2$ gives what we want.

[In Griffiths' original (PRL **14** 623 (1965)), primed and unprimed quantities are undistinguished. This distinction corresponds the values below and above T_c . Now, we believe this distinction is not needed, so in the present exposition, primes were

removed.]

5.5 [A toy illustration of Lee-Yang theory]⁴¹

Suppose the grand partition function of a fluid in a volume V is given by

$$\Xi_V = (1+z)^V \frac{1-z^V}{1-z}, \quad (6.5.21)$$

where z is the fugacity.

- (1) Find the zeros of Ξ_V . How does the distribution of the zeros change as $V \rightarrow \infty$?
- (2) Obtain P for real positive z and locate the phase transition.
- (3) Find the volume v per particle as a function of z .
- (4) Find the P - v relation, and demonstrate that phase coexistence does happen.

Solution

- (1) Zeros are -1 and $e^{-2\pi ik/V}$ ($k = 1, 2, \dots, V$). Therefore, as $V \rightarrow \infty$, the density of zeros on the unit circle increases. In particular on the real positive axis, $z = 1$ is an accumulation point of zeros. Therefore, $z = 1$ must be a phase transition point.
- (2) Let us take the thermodynamic limit. If $|z| < 1$,

$$\beta P_V = \frac{1}{V} \log \left[(1+z)^V \frac{1-z^V}{1-z} \right] \rightarrow \log(1+z). \quad (6.5.22)$$

If $|z| > 1$,

$$\beta P_V = \frac{1}{V} \log \left[(1+z)^V \frac{1-z^V}{1-z} \right] = \frac{1}{V} \log \left[(1+z)^V z^V \frac{z^{-V} - 1}{1-z} \right] \rightarrow \log z + \log(1+z). \quad (6.5.23)$$

Therefore,

$$\beta P = \begin{cases} \log(1+z) & z < 1, \\ \log z + \log(1+z) & z > 1. \end{cases} \quad (6.5.24)$$

As expected, $z = 1$ is a singularity and phase transition occurs there.

(3) Since

$$\frac{\partial \beta P_V}{\partial \log z} = \frac{z}{1+z} - \frac{z^V}{1-z^V} + \frac{1}{V} \frac{z}{1-z}, \quad (6.5.25)$$

we have

$$\frac{1}{v} = \lim_{V \rightarrow \infty} \frac{\partial \beta P_V}{\partial \log z} = \begin{cases} z/(1+z) & z < 1, \\ (2z+1)/(1+z) & z > 1. \end{cases} \quad (6.5.26)$$

⁴¹S similar question can be found in Reichl

Notice that for $z > 1$ and for $z < 1$ the number densities (or the specific volumes) are distinct; of course, the smaller z corresponds to gas.

(4) For $z < 1$, we have $v = 1 + 1/z$, so $v > 2$, and

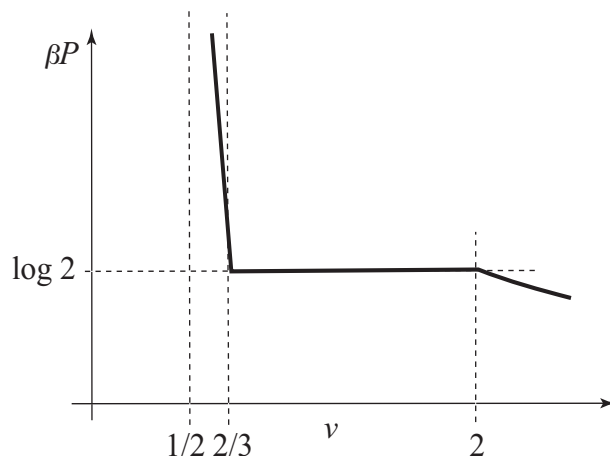
$$\beta P = \log \frac{v}{v-1}. \quad (6.5.27)$$

Notice that this is equal to $\log 2$ at $v = 2$.

For $z > 1$ since $z = (1-v)/(2v-1)$, $1/2 < v < 2/3$ and

$$\beta P = \log \frac{v(1-v)}{(2v-1)^2}. \quad (6.5.28)$$

This gives $\log 2$ at $v = 2/3$. Therefore, in the interval $v \in [2/3, 2]$ the pressure is constant: $\beta P = \log 2$; we expect a phase coexistence. The equation of state can be plotted as



5.6 [The Lee-Yang circle theorem illustrated

The theorem is proved in Supplementary Pages. Here, let us check its content for simple cases.

(1) According to the theorem the root of $p(z) = 1 + 2az + z^2$ must be on the unit circle as long as $a \in [-1, 1]$. Confirm this.

(2) On the apices of a triangle are spins interacting with each other. For this system construct the polynomial of z , and confirm that as long as the interactions are ferromagnetic, all the zeros are on the unit circle.

Solution

(1) This is the circle theorem for the two spin system. The roots can be computed

explicitly and $-a \pm i\sqrt{1-a^2}$, so they are on the unit circle.

(2) The polynomial in the theorem reads

$$p(z) = 1 + 3az + 3az^2 + z^3, \quad (6.5.29)$$

where $a = e^{-2\beta J}$ (even if the interactions are different for different spin pairs, the modification of the following argument is easy and no different argument is needed), which is less than 1 for ferromagnetic interactions. This polynomial is a real positive coefficient polynomial, so according to the theorem -1 must be a root. It is indeed the case: we can factorize the polynomial as

$$p(z) = (z + 1)(z^2 + (3a - 1)z + 1). \quad (6.5.30)$$

The complex roots are

$$\frac{1}{2} \left\{ (1 - 3a) \pm i\sqrt{4 - (1 - 3a)^2} \right\}, \quad (6.5.31)$$

which are actually on the unit circle. Very interestingly, as soon as the interaction ceases to be ferromagnetic, the theorem breaks down.

5.7 [A derivation of mean field theory]

A mean field approach may be obtained with the aid of a variational principle for free energy. If the (density) distribution function of microstates is f (we consider classical case) the Helmholtz free energy may be written as:

$$A = \langle H \rangle + k_B T \int d\Gamma f(\Gamma) \log f(\Gamma). \quad (6.5.32)$$

Here, the integration is over the whole phase space. $\langle H \rangle$ is the expectation value of the system Hamiltonian with respect to f . Let us apply this to the Ising model on a $N \times N$ square lattice. Its Hamiltonian is as usual

$$H = -J \sum_{\langle i,j \rangle} S_i S_j. \quad (6.5.33)$$

If we could vary f unconditionally and minimize A , then the minimum must be the correct free energy, but this is in many cases extremely hard or plainly impossible. Therefore, we assume an approximate form for f and the range of variation is narrowed. For example, we could introduce a ‘single-body’ approximation:

$$f = \phi(S_1)\phi(S_2)\cdots\phi(S_N), \quad (6.5.34)$$

where ϕ is a single-spin (density) distribution function.

(1) Under this approximation write down A in terms of ϕ . That is, find X_1 and X_2 in the following formula:

$$A = X_1 \left[\sum_S \phi(S)S \right]^2 + X_2 \sum_S \phi(S) \log \phi(S), \quad (6.5.35)$$

where N and $N \pm 1$ need not be distinguished.

(2) Minimize A wrt ϕ . ϕ must be normalized. What is the equation determining ϕ ?

(3) Using the obtained formula, write down the magnetization per spin. The used Lagrange's multiplier must be determined.

Solution

(1) We have only to compute each term honestly:

$$\langle H \rangle = -J \sum_{\langle i,j \rangle} \sum_{S_k = \pm 1} S_i S_j \prod_k \phi(S_k) \quad (6.5.36)$$

$$= -J \sum_{\langle i,j \rangle} \langle S_i \rangle \langle S_j \rangle = -2JN^2 \langle S \rangle^2. \quad (6.5.37)$$

Hence, $X_1 = 2JN$.

The entropy part reads

$$k_B T \sum_{S_i = \pm 1} \prod_k \phi(S_k) \sum_k \log \phi(S_k) = N^2 k_B T \sum_{s = \pm 1} \phi(s) \log \phi(s). \quad (6.5.38)$$

Therefore, $X_2 = N^2 k_B T$.

(2) Introducing a Lagrange's multiplier λ to impose the normalization condition, we must minimize

$$A + \lambda \sum_{S = \pm 1} \phi(S) = -2N^2 J \left[\sum_{S = \pm 1} \phi(S) S \right]^2 + N^2 k_B T \sum_{S = \pm 1} \phi(S) \log \phi(S) + \lambda \sum_{S = \pm 1} \phi(S). \quad (6.5.39)$$

The minimization condition reads

$$-4N^2 J S \langle S \rangle + N^2 k_B T (1 + \log \phi(S)) + \lambda = 0, \quad (6.5.40)$$

so we see

$$\phi(S) \propto \exp(-4\beta J m S), \quad (6.5.41)$$

where $\langle S \rangle = m$.

(3) We can get rid of λ from the formula for m with the aid of $\langle S \rangle = m$:

$$m = \tanh 4J\beta m. \quad (6.5.42)$$

This is nothing but the self-consistency equation.

5.8 [Gibbs-Bogoliubov' inequality and mean field]

(1) Derive the following inequality (called the Gibbs-Bogoliubov inequality) with the aid of **Jensen's inequality** for classical systems [This question has already been asked in Chapter 2, but is reproduced here]:

$$A \leq A_0 + \langle H - H_0 \rangle_0. \quad (6.5.43)$$

Here, A is the free energy of the system with the Hamiltonian H , A_0 is the free energy of the system with the Hamiltonian H_0 , $\langle \cdot \rangle_0$ is the average over the canonical distribution wrt H_0 . [Hint: compute $\langle e^{-(H-H_0)} \rangle_0$; the temperature may be absorbed or we could use the unit system with $k_B = 1$.]

All the variational approximations for statistical thermodynamics are applications of this inequality.⁴² Let H be the Hamiltonian of the system we are interested in, and H_0 be the Hamiltonian of a system whose free energy A_0 we can compute exactly. We introduce variational parameters in H_0 and then try to make the RHS of (6.5.43) as small as possible.

(2) As H we adopt the $N \times N$ 2-Ising model Hamiltonian (without a magnetic field; even with it there is almost no change), and

$$H_0 = \sum_i h s_i. \quad (6.5.44)$$

Derive the equation for h that minimizes the RHS of (6.5.43).

Solution

(1) See the solution to 2.22.

(2) Let us first compute A_0 and $m = \langle s_i \rangle_0$:

$$A_0 = -k_B T \log[2 \cosh \beta h]^{N^2}, \quad (6.5.45)$$

$$m = -\tanh \beta h. \quad (6.5.46)$$

⁴²See, for example, M. D. Girardeau and R. M. Mazur, "Variational methods in statistical mechanics," Adv. Chem. Phys. XXIV, eds. I. Prigogine and S.A. Rice (Academic, New York, 1974), p187-255.

Consequently, since the number of nearest neighbor pairs is $2N^2$,

$$\langle H \rangle_0 = -J(2N^2) \tanh^2 \beta h. \quad (6.5.47)$$

Also we have

$$\langle H_0 \rangle_0 = -N^2 h \tanh \beta h. \quad (6.5.48)$$

Combining all the results, we can write the Gibbs-Bogoliubov inequality as

$$A \leq -N^2 k_B T \log[2 \cosh \beta h] - J(2N^2) \tanh^2 \beta h + N^2 h \tanh \beta h. \quad (6.5.49)$$

Differentiating the RHS wrt h , we have

$$-N^2 \frac{\sinh \beta h}{\cosh \beta h} - 4JN^2 \tanh \beta h \frac{\sinh \beta h}{\cosh^2 \beta h} + N^2 \tanh \beta h + N^2 h \frac{\sinh \beta h}{\cosh^2 \beta h} = 0, \quad (6.5.50)$$

so we obtain

$$4J \tanh \beta h = h. \quad (6.5.51)$$

If we multiply β to the both sides and taking their tanh, we get

$$\tanh(4\beta J \tanh \beta h) = \tanh \beta h, \quad (6.5.52)$$

but if we use (6.5.46), this turns out to be our familiar formula:

$$m = \tanh 4\beta J m. \quad (6.5.53)$$

5.9 [Exact mean field for 1-Ising model]

The starting point of the mean-field theory can be the following [exact relation](#) for the 1-Ising model:

$$\langle s_0 \rangle = \langle \tanh \beta J (s_{-1} + s_1) \rangle, \quad (6.5.54)$$

where $\langle \rangle$ is the equilibrium expectation. Utilizing $s^2 = 1$ and translational symmetry of the system, write down a closed equation for $m = \langle s \rangle$, and then discuss the possible phase transitions.

Solution

The odd powers of s_1 and s_{-1} are identical to the original s_1 and s_{-1} , respectively, we can write

$$\tanh \beta J (s_{-1} + s_1) = A(s_{-1} + s_1), \quad (6.5.55)$$

where A is a numerical constant. If we set $s_1 = s_{-1} = 1$, we have $\tanh 2\beta J = 2A$, which fixes A , and we get the following identity:

$$m = (\tanh 2\beta J) m. \quad (6.5.56)$$

Unless $\beta = \infty$, $\tanh 2\beta J < 1$, so $m = 0$ for any positive temperature; we know there is no phase transition for $T > 0$. If $\beta \rightarrow \infty$, the equation reads $m = m$, so the theory does not exclude the possibility of $T_c = 0$, but it seems we cannot say anything further.

5.10 [2-Ising model on the honeycomb lattice]

Let us consider a 2-Ising model on the honeycomb lattice whose coupling constant is J . Assume there is no magnetic field.

- (1) Find the equation corresponding to (5.8.4).
- (2) Find T_c with the aid of the approximation corresponding to (5.8.6).
- (3) Then, using a more accurate mean field theory corresponding to (5.8.13) compute T_c . Which T_c obtained by (2) or this question should be lower? Is your result consistent with your expectation?

Solution

- (1) The coordination number of the honeycomb lattice is 3, so

$$\langle s_0 \rangle = \langle \tanh[\beta J(s_1 + s_2 + s_3)] \rangle. \quad (6.5.57)$$

- (2) The approximation gives

$$m = \tanh 3\beta J m. \quad (6.5.58)$$

That is,

$$x = 3\beta J \tanh x. \quad (6.5.59)$$

This gives $3\beta_c J = 1$ or $T_c = 3J/k_B$.

- (3) The equation corresponding to (5.8.10) is

$$\tanh \beta J(s_1 + s_2 + s_3) = a(s_1 + s_2 + s_3) + bs_1 s_2 s_3, \quad (6.5.60)$$

and the coefficients are determined by the following simultaneous equation

$$\tanh 3\beta J = 3a + b, \quad (6.5.61)$$

$$\tan \beta J = a - b. \quad (6.5.62)$$

We get

$$a = \frac{1}{4}(\tanh \beta J + \tanh 3\beta J), \quad b = \frac{1}{4}(\tanh 3\beta J - 3 \tanh \beta J). \quad (6.5.63)$$

Thus, the mean-field equation reads

$$m = 3am + bm^3, \quad (6.5.64)$$

or

$$m = \sqrt{\frac{1-3a}{b}}. \quad (6.5.65)$$

This implies T_c is determined by $a = 1/3$:

$$\tanh \beta J + \tanh 3\beta J = 4/3. \quad (6.5.66)$$

A more accurate calculation is expected to take the effect of fluctuations more accurately into account. Fluctuations oppose ordering, so better approximation should give lower T_c . That is, we can expect that the T_c from the current approximation method is lower than that obtained in (3), i.e., $T_c = 3J/k_B$.

It is not hard to prove that the T_c according to the ‘better’ approximation is indeed lower than $3J/k_B$, but here let us use a numerical result: $\beta_c J = .47$ or $T_c = 2.13J/k_B$. The exact answer is known to be $T_c = 1.52J/k_B$; the improvement is considerable.

5.11 [1-Gaussian model]

At each lattice point i of a one-dimensional lattice lives a real variable q_i , and the system Hamiltonian is given by

$$H = \sum_j \left[\frac{1}{2} q_j^2 - K q_j q_{j+1} \right]. \quad (6.5.67)$$

The partition function reads

$$Z = \left(\prod_j \int_{-\infty}^{\infty} dq_j \right) \prod_{j=1}^{N-1} \exp[w(q_j, q_{j+1})], \quad (6.5.68)$$

where

$$w(x, y) = -\frac{1}{4}(x^2 + y^2) + Kxy. \quad (6.5.69)$$

The partition function should be evaluated just as the 1-Ising model with the aid of the eigenvalue problem:

$$\lambda f(x) = \int_{-\infty}^{\infty} dy f(y) \exp \left[-\frac{1}{4}(x^2 + y^2) + Kxy \right]. \quad (6.5.70)$$

The integral kernel is Gaussian, so the eigenfunction belonging to the largest eigenvalue should be of constant sign [Hint: you can see a correspondence to the [transfer matrix](#) approach; actually, there is a counterpart of [Perron-Frobenius theorem](#) for positive definite integral kernels]. Therefore, we may assume that f is also Gaussian.

- (1) Find $f(x)$ (its multiplicative numerical coefficient may be ignored).
 (2) Find the free energy per lattice point. Is there any phase transition? **y**

Solution

(1) Since the integral kernel is L^2 (square integrable), the integral operator is compact (a Hilbert-Schmidt operator), so the spectrum is discrete.⁴³ The integral kernel is positive definite, so the largest eigenvalue is positive and non-degenerate (a counterpart of the Perron-Frobenius theorem holds for compact operators). We are discussing an integral operator, so there are infinitely many eigenvalues, but they accumulate at 0. We have only to consider the eigenvalue corresponding to the Perron-Frobenius eigenvalue. Assume

$$f(x) = e^{-ax^2/2}. \quad (6.5.71)$$

Then, we have

$$\int dy e^{-ay^2/2} \exp \left[-\frac{1}{4}(x^2 + y^2) + Kxy \right] = \sqrt{\frac{2\pi}{a + 1/2}} \exp \left(-\frac{1}{2} + \frac{K^2}{a + 1/2} \right) x^2. \quad (6.5.72)$$

If we choose a as

$$a = \frac{1}{2} - \frac{K^2}{a + 1/2}, \quad (6.5.73)$$

or

$$a = \sqrt{(1/4) - K^2}, \quad (6.5.74)$$

f becomes an eigenfunction belonging to the following eigenvalue:

$$\lambda = \sqrt{\frac{4\pi}{1 + \sqrt{1 - 4K^2}}} \quad (6.5.75)$$

(2) The problem is quite parallel to the ordinary spin problems; the free energy per lattice is given by

$$f = -\frac{1}{2} k_B T \log \frac{4\pi}{1 + \sqrt{1 - 4K^2}}. \quad (6.5.76)$$

If f is holomorphic wrt K , there is no phase transition. A candidate singularity is at $K = \pm 1/2$, and it is a branching point. In the current problem, the system loses stability for $|K| > 1/2$ (the free energy is not bounded from below), so we conclude that there is no phase transition in the range of parameters where the model is meaningful.

⁴³Kolmogorov-Fomin, *Introductory Functional Analysis* (Dover) is an excellent textbook to review such common-sense knowledge.

5.12 [Correlation function by mean field theory, or mean field for nonuniform space]

(1) Let us assume that the coupling constant and the magnetic field depend on spatial position:

$$H = - \sum_{\langle i,j \rangle} J_{ij} s_i s_j - \sum_i h_i s_i. \quad (6.5.77)$$

Derive the basic equation for the mean-field theory for a square lattice:

$$\langle s_i \rangle = \left\langle \tanh\left(\beta \sum_j J_{ij} s_j + \beta h_i\right) \right\rangle. \quad (6.5.78)$$

If we introduce the crude approximation like (5.8.6), we obtain

$$\langle s_i \rangle = \tanh\left(\beta \sum_j J_{ij} \langle s_j \rangle + \beta h_i\right). \quad (6.5.79)$$

(2) We wish to compute the spatial correlation $\langle s_i s_j \rangle$. First, demonstrate that

$$\frac{\partial \langle s_i \rangle}{\partial h_k} = k_B T \langle s_i s_k \rangle \quad (6.5.80)$$

without any approximation.

(3) Applying this to the following form of (6.5.79), obtain the equation for $\{\langle s_i s_k \rangle\}$:

$$\text{Arctanh} \langle s_i \rangle = \beta \sum_j J_{ij} \langle s_j \rangle + \beta h_i. \quad (6.5.81)$$

(4) Now, let us go over to the continuum limit, assuming that the system has a translational symmetry. If we write the correlation as g , the equation obtained in (3) becomes

$$\int dy \left(\frac{\delta(x-y)}{1-m^2} - \beta J(x-y) \right) g(y-z) = \delta(x-z). \quad (6.5.82)$$

We have already assumed the spatial translational symmetry and set $m(x) = m$. The Fourier transform of the coupling constant reads

$$J(k) = \sum_j e^{ik \cdot r_j} J(r_j) = 2^d J \cos k_x \cos k_y \cdots. \quad (6.5.83)$$

Find the Fourier transform $G(k)$ of the correlation function g .

(5) If we are interested in global features, we have only to pay attention to small k . Determine the coefficients A and B in the following formula (you may assume $T > T_c$):

$$G(k) \simeq \frac{1}{A + Bk^2}. \quad (6.5.84)$$

(6) Determine the critical exponent ν .

Solution

(1) no explanation should be needed.

(2) This is an exact relation without any approximation.

$$\frac{\partial}{\partial h_k} \langle s_i \rangle = \frac{\partial}{\partial h_k} \frac{\sum s_i \exp(\beta J \sum s_j s_k + \beta \sum h_k s_k)}{\sum \exp(\beta J \sum s_j s_k + \beta \sum h_k s_k)} \quad (6.5.85)$$

$$= \beta \frac{\sum s_i s_k \exp(\beta J \sum s_j s_k + \beta \sum h_k s_k)}{\sum \exp(\beta J \sum s_j s_k + \beta \sum h_k s_k)} - \beta \langle s_i \rangle \langle s_k \rangle. \quad (6.5.86)$$

(3) Differentiating (6.5.81) with h_k , we obtain

$$\beta \frac{1}{1 - \langle s_i \rangle^2} \langle s_i s_k \rangle = \beta^2 \sum_j J_{ij} \langle s_j s_k \rangle + \beta \delta_{ik}. \quad (6.5.87)$$

That is,

$$\frac{1}{1 - \langle s_i \rangle^2} \langle s_i s_k \rangle = \beta \sum_j J_{ij} \langle s_j s_k \rangle + \delta_{ik}. \quad (6.5.88)$$

(4) Fourier transformation is defined as follows:

$$G(k) = \int dx e^{ikx} g(x). \quad (6.5.89)$$

(6.5.88) becomes

$$\left(\frac{1}{1 - m^2} - \beta J(k) \right) G(k) = 1, \quad (6.5.90)$$

so we obtain

$$G(k) = \frac{1}{1/(1 - m^2) - \beta J(k)}. \quad (6.5.91)$$

(5) Since we may assume $T > T_c$, $m = 0$. An approximation of $J(k)$ for small k is obtained from (6.5.83) as

$$J(k) = 2^d J \left(1 - \frac{1}{2} \mathbf{k}^2 + \dots \right), \quad (6.5.92)$$

so

$$G(k) \simeq \frac{1}{1 - 2^d \beta J + 2^{d-1} \beta J \sum k_i^2}. \quad (6.5.93)$$

Therefore,

$$A = 1 - 2^d \beta J, \quad B = 2^{d-1} \beta J. \quad (6.5.94)$$

(6) The mean-field critical point is determined by $2^d \beta J = 1$ so we may write $A \propto (T - T_c)$. On the other hand B is almost a constant, so taking positive constants a and b , the Fourier transform of the correlation function reads

$$G(k) = \frac{1}{a(T - T_c) + bk^2}. \quad (6.5.95)$$

Therefore, the critical exponent for the correlation length is $\nu = 1/2$.

5.13 [Lattice gas on honeycomb lattice]

Let us relate the 2-Ising model on the honeycomb lattice and the lattice gas on the same lattice. The Ising Hamiltonian H and the lattice gas Hamiltonian H_L as just as given in the [text](#):

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i, \quad (6.5.96)$$

$$H_L = -J' \sum_{\langle i,j \rangle} n_i n_j. \quad (6.5.97)$$

Let $V (\gg 1)$ be the total number of lattice points and down spins are regarded particles.

(1) Following the procedure around [p260](#), rewrite the canonical partition function of the Ising model in terms of the number of down spins $[D]$ and that of down spin pairs $[DD]$.

(2) Express the lattice gas pressure in terms of magnetic field h and the free energy per spin f .

(3) Demonstrate that the lattice gas pressure P is a continuous function of h .

(4) Sketch the free energy $Vf = -k_B T \log Z^{44}$ of the Ising model for a few representative temperatures. Next, sketch the pressure of the lattice gas as a function of $\log z$ (this is essentially the chemical potential) for a few representative temperatures. Then, explain their noteworthy features succinctly.

Solution

(1) $V = [U] + [D]$ so

$$\sum_i s_i = -[D] + [U] = V - 2[D]. \quad (6.5.98)$$

⁴⁴Notice that this free energy is G rather than A , since h is on.

The total energy is

$$-J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i = J([UD] - [UU] - [DD]) + h(2[D] - V). \quad (6.5.99)$$

Since

$$2[UU] + [UD] = 6[U], \quad 2[DD] + [UD] = 6[D], \quad (6.5.100)$$

we have

$$[UD] - [UU] - [DD] = [UD] - \left(3[U] - \frac{1}{2}[UD]\right) - \left(3[D] - \frac{1}{2}[UD]\right) = 2[UD] - 3V. \quad (6.5.101)$$

Therefore (subtracting the energy $-J$ from each spin energy),

$$H = 2J[UD] + h(2[D] - V) = -hV + (12J + 2h)[D] + 4J[DD]. \quad (6.5.102)$$

This equation happens to be identical to (5.3.14). The canonical partition function for the spin system reads

$$Z = \sum_C \exp\{-\beta(-hV + (2h + 12J)[D] - 4J[DD])\}, \quad (6.5.103)$$

where \sum_C implies the sum over all the spin configurations.

(2) since $[D]$ is the total number of particles, $e^{-\beta(2h+12J)} = z$ is the fugacity. $H_L = -4J[DD]$ and

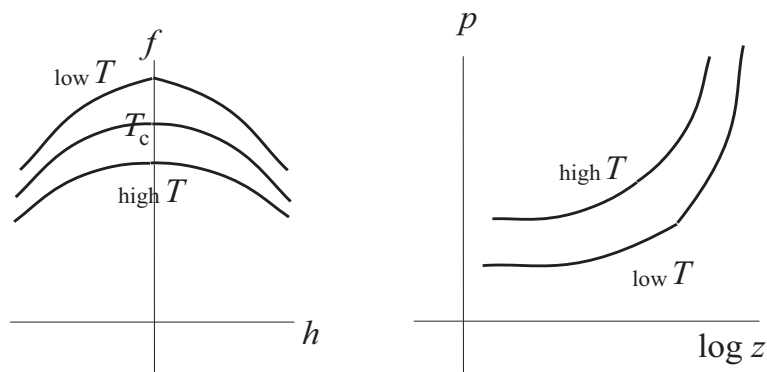
$$Z e^{-\beta hV} = e^{-\beta V(h+f)} = \sum z^{[D]} e^{4\beta J[DD]}. \quad (6.5.104)$$

That is, the Pressure of the lattice gas is given by $P = -h - f$.

(3) We know from the result of the Ising model that f is a continuous function of h . Therefore, P is continuous. Even if we lack such knowledge about the Ising model, we may use the logic explained below (5.3.5). Needless to say, the number density is bounded from above. If V is finite, then P is differentiable, and its derivative is uniformly bounded from above. Therefore, P in the thermodynamic limit must be continuous.

(4) If the temperature T is very high, there is no phase transition, so f is a smooth function (actually a holomorphic function) of h . If $|h|$ is increased, f decreases. f is an even function of h . If we lower T , eventually we encounter a second-order phase transition, and then first order phase transitions. This happens for $h = 0$, so f starts to have a kink at $h = 0$. Thus, the sketch of f is as in the left of the following figure.

As a function of $\log z$ $P = -h - f$ may be guessed easily, since $\log z$ is essentially $-h$. The crucial point is that the P - $\log z$ curve exhibits a kink corresponding to the



gas-liquid phase transition.

See Fig. 2 of the first paper by Lee and Yang: Phys. Rev., **87**, 404 (1952).

5.14 [RG by Migdal approximation⁴⁵]

When we discussed ‘decimation’, we have realized that the procedure is not very good in the space higher than 1D. For example, if we apply the method to the 2-Ising model (taking $\ell = 2$, i.e., thin half of spins), we obtain

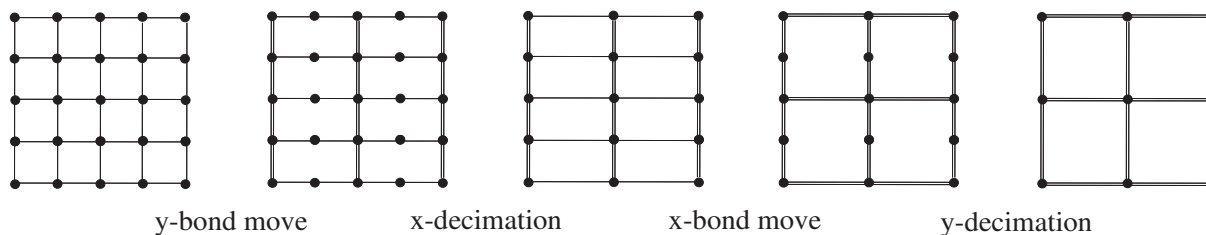
$$K' = \frac{1}{4} \log \cosh 4K, \quad (6.5.105)$$

where the Hamiltonian is written in the following form:

$$H = - \sum K s_i s_j \quad (6.5.106)$$

and the temperature is absorbed in the parameter. The fixed point of this transformation is $K = 0$ (i.e., the high temperature limit), so there is no ordering.

Migdal proposed to remedy the defect of underestimating the interactions as follows (see the figure below).



(i) [*y*-bond moving step] Every other vertical bonds (*y*-bonds) are combined with their right-neighboring bonds. If the coupling constant in the *y*-direction is K_y , the coupling constant due to the new bonds made by combining two vertical couplings is $2K_y$.

(ii) [*x*-decimation step] For the *x*-direction, one dimensional thinning is performed. For the new *x*-directional coupling constant is computed by the 1D thinning result we obtained (5.10.10).

(iii) [*x*-bond moving step] Next, every other *x*-bonds are merged with their lower neighbor *x*-bonds.

(iv) [*y*-decimation step] Apply one-dimensional decimation in the *y*-direction. Thus, we have arrived at the square lattice with the lattice spacings doubled (i.e., $\ell = 2$). If we halve the spatial scale we can complete a renormalization group transformation.

(1) Let us put ' to the parameters after the procedure (i)-(iv). Show that

$$K'_x = \log \cosh(2K_x), \quad (6.5.107)$$

$$K'_y = \frac{1}{2} \log \cosh(4K_y). \quad (6.5.108)$$

Here, the 'initial values' are K for both the *x* and *y* couplings. Notice that in two different directions, the step-cycle of the procedure is 'out of phase,' so to speak. In the *x*-direction, the decimation is applied first and then the bond are moved, while in the *y*-direction the bonds are merged first, and then decimation follows. Consequently, the fixed points of these two equations have different fixed points (marked with *): $K_x^* = 2K_y^*$.⁴⁶

(2) Find all the fixed points K_x^* . Which corresponds to the critical fixed point?

(3) **Linearizing** the renormalization transformation around the fixed point, we can calculate critical exponents; we have only to compute $d \log \cosh(2K_x)/dK_x$. This corresponds to ℓ^{y_1} . Determine ν . We cannot say the result is impressive, but still there is an improvement from the mean-field approach.

Solution

(1) These formula should be obvious, if you understand the 1D decimation.

(2) 0 and ∞ are stable fixed points and they correspond to the high and low temperature limits, respectively. If you draw the graph of the LHS, there is one more fixed point, which is unstable. This must be the most interesting fixed point. This is determined by $(1/2)\text{Arc cosh } e^x = x$ (iterative substitution could solve this): we have $K^* = 0.609$.

(3) The derivative is $2 \tanh 2K$, which is 1.678 at K^* . Therefore, $1.678 = 2^{1/\nu}$ or

⁴⁶This might be remedied by changing the ordering every other RG step; that is, with obvious abbreviations: $M_y \rightarrow D_x \rightarrow M_x \rightarrow D_y \rightarrow M_x \rightarrow D_y \rightarrow M_y \rightarrow D_x$.

$1/\nu = 0.746$, that is, $\nu = 1.339$. The mean field result is $1/2$, and the exact result is 1.

5.15 [Finite size effect]

The specific heat of a certain magnetic system behaves $C \sim |\tau|^{-\alpha}$ near its critical point without external magnetic field, if the specimen is sufficiently large. If the magnet is not very large, or more concretely, if it is a sphere of radius R , near its critical point, its maximum specific heat is $C(R)$. Compute the ratio $C(2R)/C(R)$ in terms of critical indices.

Solution

We expect that C would depend on R , but the dependence must be only through a dimensionless parameter. The most natural dimensionless quantity near T_c must be its ratio against the correlation length. Thus, $C = \tau^{-\alpha} f(R/\xi)$. Since $\xi \sim \tau^{-\nu}$, we have

$$C = \tau^{-\alpha} f(\tau^\nu R). \quad (6.5.109)$$

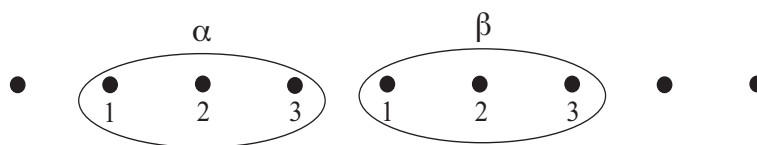
If we are sufficiently close to the critical point, the effect of the size (i.e., R) becomes prominent, and the temperature effect should be masked: in the $\tau \rightarrow 0$ limit C must not depend on τ . To this end, the function $f(x)$ around $x = 0$ must be a power: $f(x) \propto x^q$. $\tau^{-\alpha}(\tau^\nu)^q \sim 1$ implies $q = \alpha/\nu$. Consequently, we see

$$C \sim R^{\alpha/\nu}. \quad (6.5.110)$$

Hence, $C(2R)/C(R) \simeq 2^{\alpha/\nu}$.

5.16 [Use of block spins in 1-Ising model]

Let us construct an RG transformation for a 1-Ising model with a similar approach as is applied to the triangle lattice 1-Ising model. We start with (5.10.12). The figure corresponding to Fig. 5.10.2 is as shown below:



The equation corresponding to (5.10.13) is

$$K' s'_\alpha s'_\beta = K s_{\alpha 3} s_{\beta 1}, \quad (6.5.111)$$

and s' is the block spin of ± 1 determined by the majority rule. This relation cannot literally be realized, so just as in the triangle lattice case, we need an analogue of (5.10.14).

(1) Write down $\phi(K)$ corresponding to (5.10.16).

- (2) Write down the RG equation corresponding to (5.10.19) and (5.10.21).
 (3) Find the fixed points.
 (4) What can you conclude from these calculations?

Solution

- (1) We wish to demand that

$$K' s'_\alpha s'_\beta = K s_{\alpha 3} s_{\beta 1} \quad (6.5.112)$$

is an identity, but this is impossible, so we demand that the identity holds on the average. Therefore, we demand

$$K' s'_\alpha s'_\beta = K \langle s_{\alpha 3} \rangle_{s'_\alpha} \langle s_{\beta 1} \rangle_{s'_\beta}, \quad (6.5.113)$$

where $\langle s_{\alpha 3} \rangle_{s'_\alpha}$ is the conditional expectation value of $s_{\alpha 3}$ under the condition $s'_\alpha = 1$ or -1 . The up-down symmetry of the spin system (for simplicity we consider the case with $h \simeq 0$, so you may assume $h = 0$), so if we understand the $s'_\alpha = 1$ case, the rest is obvious. We can trace what we have done for the triangle lattice. The table corresponding to the one just above (5.10.16) reads

	+++	++-	+-+	-++	
$s_{\alpha 2}$	+1	+1	-1	+1	
$s_{\alpha 3}$	+1	-1	+1	+1	
E	$-2J$	0	$+2J$	0	(6.5.114)

Following the logic in the text, we have

$$\langle s_{\alpha 3} \rangle_{s'_\alpha} = \frac{e^{2K} + e^{-2K}}{2 + e^{2K} + e^{-2K}} s'_\alpha = \frac{\cosh 2K}{1 + \cosh 2K} s'_\alpha. \quad (6.5.115)$$

$\langle s_{\alpha 1} \rangle_{s'_\alpha}$ is quite the same.

- (2) From the above result, we get

$$K' = K \left(\frac{\cosh 2K}{1 + \cosh 2K} \right)^2. \quad (6.5.116)$$

Actually, we also need $\langle s_{\alpha 2} \rangle_{s'_\alpha}$:

$$\langle s_{\alpha 2} \rangle_{s'_\alpha} = \frac{e^{2K} - e^{-2K} + 2}{2 + e^{2K} + e^{-2K}} = \frac{1 + \sinh 2K}{1 + \cosh 2K}. \quad (6.5.117)$$

This gives

$$h' = h \frac{1 + \sinh 2K + 2 \cosh 2K}{1 + \cosh 2K}. \quad (6.5.118)$$

(3) We have to solve

$$K_F = K_F \left(\frac{\cosh 2K_F}{1 + \cosh 2K_F} \right)^2. \quad (6.5.119)$$

$K_F = 0$ and $\cosh 2K_F = +\infty$ that is $K_F = +\infty$ are the fixed points. $h_F = 0$ is obvious. Hence, $(0, 0)$ is a stable fixed point and $(+\infty, 0)$ an unstable fixed point.⁴⁷

(4) Obviously, $(0, 0)$ corresponds to the high temperature limit. $(\infty, 0)$ corresponds to $T \searrow 0$. Since it is a repeller, we expect that the fixed point corresponds to a critical point at $T = 0$.

5.17 [‘Democracy’]⁴⁸

Let us consider a hierarchical organization in which the decision at the k th level depends on the decisions of the s cells of the $k - 1$ st level. Assume that the 0th level corresponds to individual members of the organization, and the decision at level F is the decision of the organization. If there are sufficiently many levels (actually 5 levels are enough), the system may be understood as a system to coarse-grain individual opinions. To be frank, any political organization is a coarse-graining mechanism of opinions, and it is usually the case that conscientious subtle voices do not reach the top.

In the following, we assume there are two options A and B that must be chosen. Consider the fraction p_n of the cells at level n that support B.

(1) Suppose $s = 3$ and strict majority rule is applied. Find all the fixed points of this system and study their stability.

(2) Suppose $s = 4$. Majority rule is applied but if two opinions A and B are equally supported, A is always selected. For B to be the decision of the organization, at least how many % of the people should support B? In the extreme case, if $s = 2$, what happens?

(3) Suppose $s = 5$. Majority rule is applied, but due to the organizational propaganda at every level there is always at least one cell that supports A. For B to win despite this arrangement, what is the minimum % of the supporters of B?

Solution

(1) If 3 or 2 cells vote for B, the choice of the cell is B, so if p_n is the fraction of B-supporter at the n th level,

$$p_{n+1} = p_n^3 + 3p_n^2(1 - p_n). \quad (6.5.120)$$

⁴⁷Here, $K_F = -\infty$ is also a fixed point, and this corresponds to the antiferromagnetic case. However, we ignore this, because, if the initial system (the actual system we wish to study) is ferromagnetic and $K > 0$ the RG flow never go into the $K < 0$ region.

⁴⁸cf. S. Galam and S. Woczek, “Dictatorship from majority rule voting,” *Eur. Phys. J. B* **18**, 183 (2000). The paper contains some trivial calculation errors, so trust your own result.

The fixed point f obeys

$$f = f^3 + 3f^2(1 - f), \quad (6.5.121)$$

or

$$f(1 - f)(2f - 1) = 0. \quad (6.5.122)$$

Therefore, $f = 0, 1$ and $1/2$. 0 and 1 are stable fixed points, and $1/2$ is unstable. This scheme is fair in the sense that the the majority (whose fraction is $1/2 +$ infinitesimal number) regulated the whole organization, and can change the regime. [Really? Of course, voting or democracy can decide only not very serious questions; you cannot nationalize foreign companies only by voting.]

(2) In this case to choose B 4 or 3 cells must choose B:

$$p_{n+1} = p_n^4 + 4p_n^3(1 - p_n). \quad (6.5.123)$$

This case is discussed in the quoted paper. The fixed point fractions f obey

$$f(1 - f)(1 + f - 3f^2) = 0, \quad (6.5.124)$$

so $0, 1$ and $(1 + \sqrt{13})/6 = 0.76759$ are the fixed points. It is very hard (77% support required) to change the regime.

If $s = 2$, then

$$p_{n+1} = p_n^2, \quad (6.5.125)$$

so it is impossible to change the regime.

As you have already realized, the problem is a caricature of constructing block spins or Kadanoff transformation \mathcal{K} . What if we choose a coarse-graining procedure that destroys the system Hamiltonian? In this case, automatically the field appears that tries to restore the system symmetry.

(3) This is exactly the case of (2).

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