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.)

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).

1.3 [The fourth law of thermodynamics]
(1) For 0.5 moles of a certain substance the equation of state is obtained as:

$$E = \kappa T V^{1/2}, \tag{1.P.1}$$

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 extensive quantities per mole (or molecule).

1-XX [Elementary thermodynamics]
The following equations of state cannot be realized, because they violate some general rules of thermodynamics. State explicitly the reason why they are impossible. Notations are standard ones (e.g., E is the internal energy, etc.) and α is a positive constant.

(1) $S = \alpha[N^2 E/V]^{1/3}$
(2) $S = \alpha V^3/(NE)$
(3) $S = \alpha(NE)^{1/2} e^{-EV/N}$
(4) $S = N \log(V/N)$.

1-XX [Elementary Thermodynamics]
(1) A substance undergoes a melting phase transition at temperature T_m under pressure p. The latent heat is ΔH(cal/mol). The specific heat (in cal/molK) in the solid phase is C_S and in the liquid phase C_L; they are insensitive to temperature. Let $T_0 < T_m < T_1$. Find the entropy difference between the solid at T_0 and liquid at T_1.
(2) Find the excess entropy the supercooled liquid at T_0 has relative to the solid at the same temperature.[136]

1-xx [The most general expression of Maxwell's relations]
Demonstrate that all the Maxwell's relations are unified into the following form:

$$\frac{\partial(x, X)}{\partial(y, Y)} + 1 = 0. \tag{1.P.2}$$

Here, X and Y are generic extensive quantities, and x and y are the corresponding conjugate intensive variables (wrt internal energy).

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 get \$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 demonstrate[137] the law of large numbers and the central limit theorem.

1-XX [Elementary probability]
Monty problem.

1-XX [Uncorrelatedness and independence]
Let X be a Gaussian stochastic variable, and $Y = \pm X$ depending on the coin tossing (e.g., choose + for head). Show that X and Y are uncorrelated, but not statitically

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[136]Assume that equilibrium thermodynamics applies to metastable states. This assumption is practically always all right.

[137]Need not be mathematical; quite a theoretical physicist's way is OK!

independent.[138]

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 the head 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 are needed?

1-xx [Insufficiency of weak law of large numbers] Let $\{X_n\}$ be iid with

$$P(|X| > t) = e/t \log t \tag{1.P.3}$$

for $t > e$. Show that **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 geometrical centers. 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%?

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

$$p(x) = \frac{1}{\pi} \frac{a}{x^2 + a^2} \tag{1.P.4}$$

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

$$E_n = \frac{X_1 + \cdots + X_n}{n} \tag{1.P.5}$$

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.

1.8 [St. Petersburg Paradox by Daniel Bernoulli]
Let $\{X_i\}$ be iid with

$$P(X_1 = 2^n) = 2^{-n} \tag{1.P.6}$$

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[138]4.16 of J. P. Romano and A. F. Siegel, *Counterexamples in Probability and Statistics*(Wadsworth & Brooks/Cole 1986).

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

$$P\left(|E_n/\log_2 n - 1| > \varepsilon\right) \to 0 \tag{1.P.7}$$

in the $n \to \infty$ 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?)

1.9 [Bertrand's paradox]

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.]

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 H the equation of motion may be written as

$$\frac{dq}{dt} = [q, H], \quad \frac{dp}{dt} = [p, H] - \alpha p, \tag{1.P.8}$$

where α is a small positive constant. That is, the system is not perfectly classical mechanical, but contains a certain effect of dissipation.[139]

(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 usual and K is quadratic in p.)

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

1.11 [Wrong logic in a popular textbook]

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

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

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.

1.12 [Another expression of microcanonical partition function]
Classically, the microcanonical distribution may be written as

$$\hat{w}(E) = \frac{1}{N!h^{3N}} \int \delta(H(q,p) - E)dqdp. \tag{1.P.9}$$

Show that this can be expressed as follows:

$$\hat{w}(E) = \frac{1}{N!h^{3N}|grad\,H|}d\sigma, \tag{1.P.10}$$

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

1.13 [Equipartition of energy with the aid of microcanonical ensemble]**r**
Within the microcanonical ensemble formalism[140] 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)

$$k_B T = \frac{2}{3N\langle K^{-1}\rangle}, \tag{1.P.11}$$

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

$$k_B T = \frac{2}{3}\langle \kappa \rangle, \tag{1.P.12}$$

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

1.14 [Generalized homogeneous function]

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[140]Use $\Omega(E)$, the phase volume of the states with the total energy not exceeding E.

As we will learn much later, various thermodynamic quantities diverge at 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 as[141]

$$f(\lambda^{y_1}\tau, \lambda^{y_2}p) = \lambda^d f(\tau, p), \qquad (1.P.13)$$

where λ (> 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.[142]

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

1.15. [Mixing entropy and Gibbs' paradox]$_\mathbf{r}$
We have two ideal gases with the same volume V, pressure P, and temperature T. These two gases consist of different chemical species. Assume that 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?

1.16 [To check that Boltzmann's formula does not contradict thermodynamics]$_\mathbf{r}$
Let us check that Boltzmann's principle (within classical physics) is indeed consistent with thermodynamics: that is, if $S = k_B \log \hat{w}(E, V)$,

$$dS = \frac{dE + PdV}{T}, \qquad (1.P.14)$$

where $\hat{w}(E, V)$ is the phase volume of microstates satisfying that the energy is in $(E - \delta E, E]$ and the volume is in $(V - \delta V, V]$. Here, we clearly know what E and V are in both mechanics and in thermodynamics. The pressure P can be computed mechanically, and T is related to the average kinetic energy K of the system.

Using the Boltzmann formula

$$dS = k_B \frac{1}{\hat{w}} \frac{\partial \hat{w}}{\partial E} dE + k_B \frac{1}{\hat{w}} \frac{\partial \hat{w}}{\partial V} dV. \qquad (1.P.15)$$

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

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[141]Precisely 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.
[142]B. 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.

1864. The demonstration is not very trivial, so we accept the following relation

$$k_B \frac{1}{\hat{w}} \frac{\partial \hat{w}(E,V)}{\partial V} \to \frac{P}{T} \qquad (1.\text{P}.16)$$

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

$$\hat{w}(E,V) = \int_{[E]} d\boldsymbol{q} d\boldsymbol{p} - \int_{[E-\delta E]} d\boldsymbol{q} d\boldsymbol{p} = \delta E \frac{\partial}{\partial E} \int_{[E]} d\boldsymbol{q} d\boldsymbol{p}, \qquad (1.\text{P}.17)$$

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

$$\int_{[E]} d\boldsymbol{q} d\boldsymbol{p} = \int d\boldsymbol{q} \int_{K(\boldsymbol{p}) \leq E - U(\boldsymbol{q})} d\boldsymbol{p}. \qquad (1.\text{P}.18)$$

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

$$\frac{\partial}{\partial E} \int_{[E]} d\boldsymbol{q} d\boldsymbol{p} = \int d\boldsymbol{q} \frac{S_{3N}}{3N} 2m \frac{3N}{2} [2m(E - U(\boldsymbol{q}))]^{3N/2-1}, \qquad (1.\text{P}.19)$$

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

$$\frac{1}{\hat{w}(E,V)} \frac{\partial \hat{w}(E,V)}{\partial E} = k_B \left(\frac{3N}{2} - 1 \right) \left\langle \frac{1}{K(\boldsymbol{p})} \right\rangle. \qquad (1.\text{P}.20)$$

(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 $\boldsymbol{p}^2/2m = 3k_B T/2$). Assuming that all the kinetic energies of the particles are statistically independent,[143] demonstrate that the formula in (2) is indeed equal to $1/T$.

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

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[143]This 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.

(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 dimensional analytically, 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).

1.17' [Generalization of 1.17]

There is an ideal gas consisting of N particles whose kinetic energy is given by $\varepsilon = c|\boldsymbol{p}|^{\alpha}$, where $\boldsymbol{p}$ is the momentum, and α and c are positive constants ($\alpha = 1$ is the superrelativistic case). Answer the following questions with dimensional analysis (+ perhaps a little of thermodynamic principles, if needed). [Explicit calculations will cost you significant points.]

(1) What is the equation of state?

(2) What is the pressure as a function of internal energy?

1.XX [Frenkel defect]

The atoms can be dislocated into interstitial sites upon heating a crystal. They are the *Frenkel defects*. Suppose each atom can occupy either a regular lattice site or an interstitial site. Let us assume that for each lattice site there are b interstitial sites. Assume that the crystal is made of N atoms. Here, we assume that the state of each atom does not depend on its environment.

(1) What is the entropy of the state with n dislocated atoms? (You need not try to simplify the result.)

(2) Suppose it costs an energy ε for an atom to move into an interstitial site from a regular site. What happens to n, if we double the number of available interstitial sites? You may assume ε/k_BT is large enough.

(3) Instead of (2) what happens if $\varepsilon = 0$?

1.18 [Application of the Sackur-Tetrode equation[144]]

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 59.9J/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 630 K 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, estimate Planck's con-

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

stant. The reader may use the value of k_B.

1.19 [Negative temperature]
Let us consider the two state spin system containing 1 mole of spins as discussed in the text. Assume that under the magnetic field h, 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?

Exercises 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,

$$P(E_I)P(E_{II}) = P(E_I + E_{II}). \tag{2.P.1}$$

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

$$P(E) = Ce^{-\beta E}, \tag{2.P.2}$$

where C is a constant."
    Is this argument correct?

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

$$H = D(S_z^2 - S(S+1)/2), \tag{2.P.3}$$

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 $\beta = 1/k_BT$).
(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.

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 silicon for which $\Delta = 3$ eV.

2.4 [Specific heat]

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

$$H = \sum_{i=1}^{N} a_k |\boldsymbol{p}_k + \boldsymbol{c}_k|^s \qquad (2.\text{P}.4)$$

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

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

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

$$\frac{d\log \nu}{d\log V} = \gamma. \qquad (2.\text{P}.5)$$

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

2.7 [Application of equipartition of energy][95]
The internal motion of some ring puckering molecules (e.g., cyclobutanone) can be described by the following Hamiltonian:

$$H = \frac{p^2}{2m} + ax^4, \qquad (2.\text{P}.6)$$

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.

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

$$\left\langle \frac{1}{2} \frac{mv_x^2}{\sqrt{1 - v^2/c^2}} \right\rangle = \frac{1}{2} k_B T. \qquad (2.\text{P}.7)$$

2.9 [An equality about canonical ensemble]

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[95]original credit: B. Widom

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

$$\langle \Delta\Phi \rangle = \beta \left\langle (\nabla\Phi)^2 \right\rangle. \tag{2.P.8}$$

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

2.10 [Density operator for free particles: perhaps an elementary QM review]
The canonical density operator is given by

$$\rho = \frac{1}{Z} e^{-\beta H}, \tag{2.P.9}$$

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

$$\frac{\partial}{\partial\beta}\langle x|U(\beta)|x' \rangle = \frac{\hbar^2}{2m}\Delta_x \langle x|U(\beta)|x' \rangle, \tag{2.P.10}$$

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).

2.11 [Density operator for a spin system]

Let ρ be the density operator of a single $1/2$ quantum spin system whose Hamiltonian[96] is given by $H = -\gamma\boldsymbol{\sigma} \cdot \boldsymbol{B}$, where $\boldsymbol{\sigma}$ is $(\sigma_x, \sigma_y, \sigma_z)$ in terms of the Pauli spin operators.
(1) Obtain the matrix representation of ρ with respect to the base that diagonalizes σ_z.
(2) Find the average of σ_y.
(3) Obtain the matrix representation of ρ with respect to the base that diagonalizes σ_x.

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.

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:

$$H = DS_z^2. \tag{2.P.11}$$

(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.

2.14 [Absorption of mixed ideal gas, or convenient partition function][97]
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. [Hint: you must 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.

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[96]Precisely speaking, this is te interaction Hamiltonian of the system with the magnetic field.
[97]Original credit: UIUC Qual F95.

(3) Under 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.

2.15 [Adsorption on catalytic surface]
There are N adsorption centers on the catalyst surface exposed to a gas (ideal gas) of a certain chemical. Each adsorption center can accommodate at most two particles. The partition function for the single particle adsorption state is a_1 and the two particle adsorption state is a_2.
(1) Write down the single site (grand) partition function.
(2) Let $a_1 = 0$ (i.e., adsorption 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 adsorbed 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.

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).

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. As-

sume 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?

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

Starting from

$$Z = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}, \qquad (2.P.12)$$

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

2.19 [Equivalence of canonical and grand canonical ensembles]$_\mathbf{r}$

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

$$Z(T, N) \leq \left(\frac{aV}{N} \right)^N. \qquad (2.P.13)$$

Actually, show (classically)

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

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_BT obtained thermodynamically from the canonical partition function and that directly obtained from the grand partition function agree.

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.]

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) $(n, m \in \{1, 2, \cdots, 6\})$.

(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 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?

2.22 [Variational principle for free energy (classical case)[98]]
Let $H = H_0 + V$ be a system Hamiltonian.
(1) Show that

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

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 anharmonic oscillator with the Hamiltonian

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

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

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

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 the text.

2.23 [Gibbs-Bogoliubov's inequality (quantum case)][99]
Gibbs-Bogoliubov's inequality

$$A \leq A_0 + \langle H - H_0 \rangle_0 \tag{2.P.14}$$

holds in quantum statistical mechanics as well.
(1) Demonstrate Peierls' inequality:

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[98]This holds quantum mechanically as well, but the proof is not this simple.

[99]M D Girardeau and R M Mazo, "Variational methods in statistical mechanics,"

$$Tre^{-\beta H} \geq \sum_i e^{-\langle i|H|i\rangle}, \qquad (2.\text{P}.15)$$

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

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

$$e^{-\beta A} \geq \sum_i e^{-\beta\langle i|H|i\rangle} = e^{-\beta A_0} \sum_i e^{\beta(A_0-\langle i|H_0|i\rangle)} e^{-\beta\langle i|(H-H_0)|i\rangle}. \qquad (2.\text{P}.16)$$

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

2.24 (1) For any density operator ρ

$$A \leq Tr[\rho(H + k_B T \log \rho)], \qquad (2.\text{P}.17)$$

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

(2) Suppose ρ is the canonical density operator $\rho = e^{\beta(A_0-H_0)}$ 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)

$$A[\sum \lambda_i H_i] \geq \sum A[\lambda_i H_i]. \qquad (2.\text{P}.18)$$

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:

$$A = A_0 + \varepsilon\langle H_1\rangle_0 - \frac{1}{2}\beta\varepsilon^2\langle(H_1 - \langle H_1\rangle_0)^2\rangle_0 + \cdots, \qquad (2.\text{P}.19)$$

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].[100]

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

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

DNA tension. The work W dissipated during the cycle is measured at 300 K and the experimental results were as follows:

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 $\langle W \rangle$?

2.28 [Fluctuation and spring constant][101]
Inside the F_1ATPase 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 290 K. 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, by adding 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.

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

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

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[101]If 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_1ATPase: how an ATP-driven molecular machine may work," Ann. Rev. Biophys. Biomol. Struct., **33**, 245 (2005).

(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.

2.30 [Equilibrium fluctuation]
(1) Obtain $\langle \delta S \delta V \rangle$.
(2) Obtain $\langle \delta P \delta T \rangle$.

2.31 [Fluctuation and Le Chatelier-Braun's principle]
(1) Show the following elementary algebraic inequality:

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

where x and X make a conjugate pair of thermodynamic variables (with respect to energy).
(2) What is the relation between this inequality and the Le Chatelier-Braun principle? (Thus, you understand how natural the Le Chatelier-Braun principle is.)

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

$$\langle (E - \langle E \rangle)^2 \rangle / \langle E \rangle^2 = 2/3N. \tag{2.P.20}$$

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.[102]

2.34 [Chemical equilibrium constant[103]]
The reaction

$$A \underset{k_-}{\overset{k_+}{\rightleftarrows}} B. \tag{2.P.21}$$

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

$$\frac{d[A]}{dt} = k_-[B] - k_+[A] = -\frac{d[B]}{dt}. \tag{2.P.22}$$

For all $t > 0$ show that

$$\frac{[B]_F(t)}{[A]_B(t)} = K, \tag{2.P.23}$$

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 (6.2.163) is time-independent and equal to the chemical equilibrium constant. [However, this cannot be a general relation, but holds only under ideal solution and reaction conditions.]

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[102] 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.

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

Exercises 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 (one-particle) ground state.
(3F) Compute the average occupation number N 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)

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.

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.

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 tempera-

ture 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.

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?

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 $T_f > T_i$?

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?

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]

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).

3.10 [Effective intereaction 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

$$H = \frac{\boldsymbol{p}_1^2}{2m} + \frac{\boldsymbol{p}_2^2}{2m}, \tag{3.P.1}$$

and the canonical partition function is

$$Z = Tre^{-\beta H}, \tag{3.P.2}$$

where the trace is with respect to the microstates specified by two momenta $|\boldsymbol{p}, \boldsymbol{p}'\rangle$. To compute this trace semi-classically, we introduce a single-particle momentum state $|\boldsymbol{p}\rangle$.

(1) Express $|\boldsymbol{p}, \boldsymbol{p}'\rangle$ both for the boson and fermion cases in terms of single particle kets $|\boldsymbol{p}\rangle$. 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 $\langle \boldsymbol{r}|\boldsymbol{p}\rangle$ (i.e., the wave function) of the momentum ket $|\boldsymbol{p}\rangle$.

(3) Let $\boldsymbol{r}_i$ be the position vector of the i-th particle. Find the position representation of $|\boldsymbol{p}, \boldsymbol{p}'\rangle$. [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:

$$Tr \quad \to \quad \frac{1}{N!} \int_{V^N} d\{\boldsymbol{r}_k\} \prod_{k=1}^{N} \langle \boldsymbol{r}_k| \cdots \prod_{k=1}^{N} |\boldsymbol{r}_k\rangle \tag{3.P.3}$$

$$= \quad \frac{1}{N!} \int_{V^N} d\{\boldsymbol{r}_k\} \prod_{k=1}^{N} \langle \boldsymbol{r}_k| \left[\left(\sum_{\{\boldsymbol{p}_i\}} |\{\boldsymbol{p}_i\}\rangle\langle\{\boldsymbol{p}_i\}| \right) \cdots \left(\sum_{\{\boldsymbol{p}_i\}} |\{\boldsymbol{p}_i\}\rangle\langle\{\boldsymbol{p}_i\}| \right) \right] \prod_{k=1}^{N} |\boldsymbol{r}_k\rangle \tag{3.P.4}$$

If the volume is big enough, we should be able to replace the summation over momenta by integration over them. The replacement rule is

$$\sum_{\{\boldsymbol{p}_i\}} \to \frac{V^N}{h^{3N}} \int d\{\boldsymbol{p}_i\}. \tag{3.P.5}$$

Justify this for $N = 1$ in 1-space.

(5) Write Z down using $h^{-3/2} e^{i\boldsymbol{r}\cdot\boldsymbol{p}/\hbar} = \langle \boldsymbol{r}_i|\boldsymbol{p}\rangle$. Beyond this point, let us simplify formulas by taking the $V \to \infty$ limit. You need not perform the integration.

(6) The outcome of (5) must have the following form:

$$\frac{1}{2h^6} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{p} d\boldsymbol{p}' e^{-\beta(\boldsymbol{p}^2 + \boldsymbol{p}'^2)/2m} [\cdots]. \tag{3.P.6}$$

Perform the integral in this expression and find F in the following formula:

$$Z = \frac{1}{2h^6} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{p} d\boldsymbol{p}' \, e^{-\beta(\boldsymbol{p}^2 + \boldsymbol{p}'^2)/2m} F \tag{3.P.7}$$

(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.

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)$_\mathbf{r}$ Obtain the chemical potential (the Fermi level) to order T^2 around $T = 0$D
(2) Obtain the pressure P to order T^2 around $T = 0$.

3.12 [Derivation of Maxwell's distribution]
Maxwell derived in his *Illustrations of the Dynamical Theory of Gases* (1860) the density distribution function $f(\boldsymbol{v})$ of the gas particle velocity.

Maxwell assumed that orthogonal components of the velocity are statistically independent. This implies that we may write

$$f(\boldsymbol{v}) = \phi_x(v_x)\phi_y(v_y)\phi_z(v_z), \tag{3.P.8}$$

where ϕ_x, etc., are density distribution function for each component. Maxwell also assumed isotropy. Hence, f is a function of $v^2 \equiv |\boldsymbol{v}|^2$, so we may regard $f(\boldsymbol{v}) \equiv F(v^2)$, 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

$$F(x + y + z) = \psi(x)\psi(y)\psi(z). \tag{3.P.9}$$

If F and ψ are both once differentiable, we obtain

$$F'(x + y + z) = \psi(x)\psi(y)\psi'(z). \tag{3.P.10}$$

Setting $y = z = 0$, we have

$$F(x) = \psi(x)\psi(0)\psi(0), \quad F'(x) = \psi(x)\psi(0)\psi'(0), \tag{3.P.11}$$

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?[39]
(2) Since we know the result of equilibrium statistical mechanics, if the particle 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

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[39]If we do not assume the continuity of F, there would be uncountably many solutions.

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 $K \propto \boldsymbol{v}^2$ 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,[40] 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.

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 a classical system.[41]

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?

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.

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.

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[40]However, 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.

[41]cf ProblWS p176.

(2) Find the magnetization when the outer shell has one electron for each ion. Compare the result with the result of (1) for $\mu = E_0$.[42]D

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)D
(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 $\log D_t(\varepsilon)$.

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:

$$\langle N \rangle = \sum_{i=0}^{\infty} \langle \hat{n}_i \rangle = \int_0^{\infty} d\varepsilon \, D_t(\varepsilon). \tag{3.P.12}$$

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, ther 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 $\cdots$:

$$\frac{\langle N \rangle}{V} = \frac{1}{V} \langle \hat{n}_0 \rangle + \frac{1}{V} \langle \hat{n}_1 \rangle + \frac{1}{V} \int_0^{\infty} d\varepsilon \, D_t(\varepsilon). \tag{3.P.13}$$

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 $\langle \langle \hat{n}_0 \rangle / (\langle \hat{n}_1 \rangle + \langle \hat{n}_2 \rangle + \langle \hat{n}_3 \rangle) = \langle \hat{n}_0 \rangle / 3 \langle \hat{n}_1 \rangle$ for a very small negative chemical potential μ[43] required by the Bose-Einstein condensation. How big is it as a function of V?

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[42]UIUC QualFall 95
[43]which is not zero, because the system is finite.

(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).

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

$$\frac{\partial E_0}{\partial \mu} \simeq \frac{3}{2} N_0(T), \tag{3.P.14}$$

where

$$N_0(T) \equiv N(T, 0) = \frac{V}{h^3} \int_0^\infty \frac{1}{e^{\beta p^2/2m} - 1} 4\pi p^2 dp. \tag{3.P.15}$$

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

$$N = N_0(T) + \frac{V}{h^3} \int_0^\infty \left\{ \frac{1}{e^{\beta(p^2/2m-\mu)} - 1} - \frac{1}{e^{\beta p^2/2m} - 1} \right\} 4\pi p^2 dp. \tag{3.P.16}$$

(3) Show that we may approximate the second term of (6.3.123) as

$$\int_0^\infty \left\{ \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} - \frac{1}{e^{\beta\varepsilon} - 1} \right\} \sqrt{\varepsilon} d\varepsilon \simeq k_B T \mu \int_0^\infty d\varepsilon \frac{1}{\sqrt{\varepsilon}(\varepsilon + |\mu|)} = -\pi k_B T \sqrt{|\mu|}. \tag{3.P.17}$$

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.]

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.[44] It is hard to treat this in terms of the canonical ensemble, so we discuss

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[44]Actually, BEC is observed in a collection of Rb atoms confined in a (not spherically symmetric) 3D harmonic potential.

this with the aid of the grand canonical theory; if N is larger than 10^3, then $\log N/N$[45] 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

$$N_0(T) = N \left(1 - \left(\frac{T}{T_c} \right)^\gamma \right), \tag{3.P.18}$$

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 $\zeta(3) = 1.2020569031595\cdots$.)

(5) If a 2D harmonic potential can trap 2D Bose gas,[46] can we observe Bose-Einstein condensation?

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?

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.

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

$$\phi(r) = \varepsilon \left[e^{-2(r-d)/a} - 2e^{-(r-d)/a} \right], \tag{3.P.19}$$

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.

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[45]It is emphasized again that the error is not of order $\sqrt{N}/N = 1/\sqrt{N}$, but $\log N/N$.

[46]This is virtually realized on graphene.

(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.

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.]

Exercises for Chapter 4 (rto Maxwell, rto Tonks, rto Debye-Hückel)

4.1. [Kac potential]

There is an imperfect classical gas with a binary potential ϕ given by

$$\phi(|\boldsymbol{r}|) = \begin{cases} \infty & \text{if } |\boldsymbol{r}| < a, \\ -\varepsilon/l^3 & \text{if } a \le |\boldsymbol{r}| < l, \\ 0 & \text{otherwise.} \end{cases} \tag{4.P.1}$$

Here, $\varepsilon > 0$, a is a length scale of atom size, and the $l \to \infty$ limit is taken. (This is an example of the Kac potential.)

(1) Compute the second virial coefficient (in the $l \to \infty$ 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,

4.2 [van der Waals equation of state]r

(1) Show that the critical point is defined by

$$\left.\frac{\partial P}{\partial V}\right|_T = \left.\frac{\partial^2 P}{\partial V^2}\right|_T = 0. \tag{4.P.2}$$

(2)r 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).

$$P_r - 1 = A(T_r - 1) + B(T_r - 1)(n_r - 1) + C(n_r - 1)^3 + \cdots. \tag{4.P.3}$$

(5) For hydrogen gas H_2, $b = 26.61$ cm^3/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 $4\pi\varepsilon_0$).

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

$$A = -Nk_B T \left\{ \log\left[\frac{n_Q}{N}(V - Nb)\right] + 1 \right\} - \frac{aN^2}{V}. \tag{4.P.4}$$

(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.

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

$$\frac{\partial P}{\partial V} = -\frac{Nk_BT}{(V-N\sigma)^2} + a\frac{N^2}{V^3} > 0. \tag{4.P.5}$$

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).
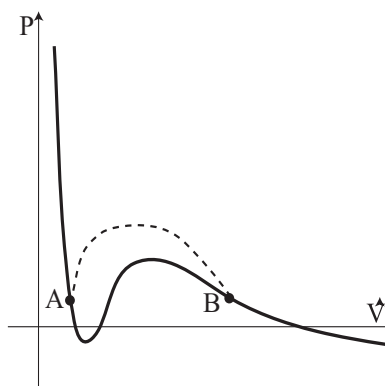
Since

$$G = E - ST + PV, \tag{4.P.6}$$

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:

$$\int_A^B PdV \tag{4.P.7}$$

agree.

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

$$Z_N(V) = \int_{(N-1)\sigma}^{V-\sigma} dx_N \cdots \int_\sigma^{x_3-\sigma} dx_2 \int_0^{x_2-\sigma} dx_1 \int dp_1 \cdots dp_n e^{-\sum_{i=1}^N p_i^2/2mk_BT + aN^2/k_BTV}. \tag{4.P.8}$$

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:

$$\Xi = \sum_{N=0}^M e^{VA(N/V)}, \tag{4.P.9}$$

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:

$$\Xi = e^{\beta PV} + e^{\beta P'V}. \tag{4.P.10}$$

Here, we have assumed that $A(n)$ have two maxima, and the two terms correspond respectively to the two maxima. Is this correct?

4.6 [Hard sphere fluid]
The virial equation of state for a fluid interacting with 2-body potential reads

$$\frac{P}{nk_BT} = 1 - \frac{2\pi}{3}\beta n \int_0^\infty \phi'(r)g(r)r^3 dr. \tag{4.P.11}$$

Using this formula, derive the equation of state for the hard sphere fluid:

$$\frac{P_H}{nk_BT} = 1 + \frac{2\pi}{3}ng(\sigma)\sigma^3, \tag{4.P.12}$$

where σ is the diameter of the sphere. Strictly speaking, $g(\sigma)$ is $\lim_{r\searrow\sigma} g(r)$.

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 $\phi(\boldsymbol{r}) = \phi(r)$. 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

$$P/nk_BT = 1 - \frac{2\pi}{3}n\beta \int_0^\infty \phi'(r)g(r)r^3 dr, \tag{4.P.13}$$

obtain the augmented van der Waals equation of state for a Kac fluid:

$$\beta P = \beta P_H + \frac{n^2}{2}\beta \int d^3\boldsymbol{r} \, \phi(\boldsymbol{r}). \tag{4.P.14}$$

Notice that the radial distribution function of the Kac fluid is the same as the had sphere fluid with the same number density.[54]

4.8 [Functional differentiation]
Compute the following functional derivative.

$$\frac{\delta}{\delta\psi(\boldsymbol{x})} \int d^3\boldsymbol{r} \left[\frac{1}{2}(\nabla\psi(\boldsymbol{r}))^2 - \frac{1}{2}\tau\psi^2(\boldsymbol{r}) + \frac{1}{4}\psi^4(\boldsymbol{r})\right], \tag{4.P.15}$$

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.[55] 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,

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[54]However, we cannot derive the Maxwell's rule requirement.
[55]If $(Lf)(x)$ 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.

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

$$\frac{\delta S}{\delta \phi(\boldsymbol{r})} \tag{4.P.16}$$

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.

4.9 [Functional derivatives of canonical partition function]
Redo the calculations (4.4.25)-(4.4.27) 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 in direct 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 $h(r)$?

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 $n^{(1)}(\boldsymbol{x}|U)$ in terms of the Boltzmann factor $\exp[-\beta U(\boldsymbol{x})]$.
(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.

4.12. [*Scaled particle theory* of hard core fluid][56]
As we know well by now, for a spherical hard core fluid

$$P/nk_BT = 1 + \frac{2\pi}{3}n\sigma^3 g(\sigma), \tag{4.P.17}$$

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[56]R. 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.

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 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,

$$g(\sigma) = G(\sigma). \tag{4.P.18}$$

We have only to determine G to know the hard-core fluid pressure.
(1) Derive

$$p_0(r + dr) = p_0(r)[1 - 4\pi n r^2 G(r)dr]. \tag{4.P.19}$$

That is,

$$\frac{d}{dr} \log p_0(r) = -4\pi n r^2 G(r). \tag{4.P.20}$$

(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,

$$p_0(r) = e^{-\beta W(r)}. \tag{4.P.21}$$

Using this and the thermodynamic result for large r (i.e., for the usual macroscopic bubble!)

$$dW(r) = PdV + f[1 - (2\delta/r)]dA, \tag{4.P.22}$$

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,

$$\frac{P}{nk_BT} = \frac{1 + \eta + \eta^3}{(1 - \eta)^3}, \tag{4.P.23}$$

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.]

4.13 [Quantum effect on the second virial coefficient][57]
The second virial coefficient for a spherical symmetrical particle is, classically,

$$B = 2\pi \int_0^\infty (1 - e^{-\beta\phi(r)})r^2 dr. \tag{4.P.24}$$

Its quantum version should be obtained by replacing the Boltzmann factor $e^{-\beta\phi}$ with the diagonal element of the 2-body density operator $\rho(r)$:

$$B = 2\pi \int_0^\infty (1 - \mathcal{N}\rho(r))r^2 dr, \tag{4.P.25}$$

where $\mathcal{N}$ is the normalization constant to make $\mathcal{N}\rho(r) \to 1$ in the $r \to \infty$ limit.[58]

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}He, below 50 K the quantum correction increases the classical value by about 50%, but 10 % around 100 K, so the quantum correction is not very small.
(1) Let us assume that two-body Hamiltonian to be

$$H = -\frac{\hbar^2}{2m}(\Delta_1 + \Delta_2) + \phi(|\boldsymbol{r}_1 - \boldsymbol{r}_2|), \tag{4.P.26}$$

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 $\langle \boldsymbol{r}_1, \boldsymbol{r}_2 | \rho | \boldsymbol{r}_1', \boldsymbol{r}_2' \rangle$ of the 2-body density operator satisfies the following equation:

$$\frac{\partial}{\partial \beta} \langle \boldsymbol{r}_1, \boldsymbol{r}_2 | \rho | \boldsymbol{r}_1', \boldsymbol{r}_2' \rangle = -H \langle \boldsymbol{r}_1, \boldsymbol{r}_2 | \rho | \boldsymbol{r}_1', \boldsymbol{r}_2' \rangle. \tag{4.P.27}$$

If we use the normalized eigenket $|i\rangle$ $(H|i\rangle = E_i|i\rangle)$ of H, we can write

$$\langle \boldsymbol{r}_1, \boldsymbol{r}_2 | \rho | \boldsymbol{r}_1', \boldsymbol{r}_2' \rangle = \sum_i \langle \boldsymbol{r}_1, \boldsymbol{r}_2 | i \rangle e^{-\beta E_i} \langle i | \boldsymbol{r}_1', \boldsymbol{r}_2' \rangle. \tag{4.P.28}$$

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[57]This is based on T. Kihara, *Molecular forces.*

[58]As 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 semiclassically. Therefore, normalizing the density operator appropriately, we can interpret it as a quantum statistical extension of the spatial Boltzmann factor.

Here, the summation may include integration.

(2) For the case with $\phi = 0$ (i.e., for the ideal gas case) obtain $\langle \boldsymbol{r}_1, \boldsymbol{r}_2 | \rho | \boldsymbol{r}'_1, \boldsymbol{r}'_2 \rangle$. 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

$$\langle \boldsymbol{r}_1, \boldsymbol{r}_2 | \rho | \boldsymbol{r}'_1, \boldsymbol{r}'_2 \rangle = \left(\frac{2\pi \hbar^2 \beta}{m} \right)^{-3} \exp \left[-\frac{m}{2\hbar^2 \beta} [(\boldsymbol{r}_1 - \boldsymbol{r}'_1)^2 + [(\boldsymbol{r}_2 - \boldsymbol{r}'_2)^2] + \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}'_1, \boldsymbol{r}'_2) \right] .$$
(4.P.29)

Note that $-k_B T \Psi$ corresponds to the 'quantum-corrected two-body interaction. Ψ satisfies the following equation:

$$\phi + \frac{\partial \Psi}{\partial \beta} + k_B T [(\boldsymbol{r}_1 - \boldsymbol{r}'_1) \cdot \nabla_1 + (\boldsymbol{r}_2 - \boldsymbol{r}'_2) \cdot \nabla_2] \Psi = \frac{\hbar^2}{2m} [(\nabla_1 \Psi)^2 + \Delta_1 \Psi + (\nabla_2 \Psi)^2 + \Delta_2 \Psi].$$
(4.P.30)

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

$$\Psi = \Psi_0 + \frac{\hbar^2}{2m} \Psi_1 + \cdots$$
(4.P.31)

and then introduce this into (6.4.146). Requiring the order by order agreement of the substituted result, we get

$$\phi + \frac{\partial}{\partial \beta} \Psi_0 + k_B T [(\boldsymbol{r}_1 - \boldsymbol{r}'_1) \cdot \nabla_1 + (\boldsymbol{r}_2 - \boldsymbol{r}'_2) \cdot \nabla_2] \Psi_0 = 0,$$
(4.P.32)

$$\frac{\partial}{\partial \beta} \Psi_1 + k_B T [(\boldsymbol{r}_1 - \boldsymbol{r}'_1) \cdot \nabla_1 + (\boldsymbol{r}_2 - \boldsymbol{r}'_2) \cdot \nabla_2] \Psi_1 = (\nabla_1 \Psi_0)^2 + \Delta_1 \Psi_0 + (\nabla_2 \Psi_0)^2 + \Delta_2 \Psi_0,$$
(4.P.33)

etc. First, we must solve the zeroth order equation. Show that the diagonal element of the only meaningful solution is $\Psi_0(\beta, \boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1, \boldsymbol{r}_2) = -\beta \phi(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)$.

(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):

$$\frac{\partial}{\partial \beta} \Psi_1 = \lim_{\{\boldsymbol{r}'_i\} \to \{\boldsymbol{r}_i\}} \left[(\nabla_1 \Psi_0)^2 + \Delta_1 \Psi_0 + (\nabla_2 \Psi_0)^2 + \Delta_2 \Psi_0 \right] .$$
(4.P.34)

As can immediately be seen, to compute the RHS of this equation, we cannot use $\Psi_0(\beta, \boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1, \boldsymbol{r}_2) = -\beta \phi(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)$ that is already in the diagonal limit. The derivative must be computed from the original expression of Ψ_0. Find $\lim_{\{\boldsymbol{r}'_i\} \to \{\boldsymbol{r}_i\}} \nabla_1 \Psi_0$

and $\lim_{\{r'_i\} \to \{r_i\}} \nabla_2 \Psi_0$.

(5) To botain $\Delta_1 \Psi_0$ 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:

$$\Delta_i \Psi_0 = -\frac{1}{3}\beta \Delta_i \phi, \tag{4.P.35}$$

where $i = 1, 2$.

Obtain the diagonal element $\langle r_1, r_2 | \Psi_1 | r_1, r_2 \rangle$. 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 is't there any correction of odd order in h?

Exercises 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

$$\frac{P}{k_B T} = \sum_{\ell=1}^{\infty} b_\ell z^\ell, \tag{5.P.1}$$

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 demonstrated[115] 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 $T_c = T_a$.[116]**r**

5.2 [Crude version of rigorous Peierls' argument]**r**
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):

$$P_V(\gamma) \leq e^{-2\beta J |\gamma|},$$

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 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

$$P_V^0 \leq \sum_\gamma e^{-2\beta J |\gamma|}, \tag{5.P.2}$$

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[115]T. Kihara and J. Okutani, Chem. Phys. Lett., **8**, 63 (1971).
[116]This problem asks a mathematically trivial question, but the main point is the fact stated here.

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.

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.

5.4 [Griffiths' inequality]
Empirically, it is known that there is the following relation among critical exponents:

$$\alpha + \beta(1 + \delta) = 2. \tag{5.P.3}$$

(1) Thermodynamically, demonstrate the following inequality (*Griffiths' inequality*)

$$\alpha + \beta(1 + \delta) \geq 2. \tag{5.P.4}$$

[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.]

5.5 [A toy illustration of Lee-Yang theory][117]
Suppose the grand partition function of a fluid in a volume V is given by

$$\Xi_V = (1 + z)^V \frac{1 - z^V}{1 - z}, \tag{5.P.5}$$

where z is the fugacity.
(1) Find the zeros of Ξ_V. How does the distribution of the zeros change as $V \to \infty$?
(2) Obtain P for real positive z and locate the phase transition.
(3) Find the volume v per particle as a function of z.

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[117]S similar question can be found in Reichl

(4) Find the P-v relation, and demonstrate that phase coexistence does happen.

5.6 [The Lee-Yang circle theorem illustrated
The 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.

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:

$$A = \langle H \rangle + k_B T \int d\Gamma f(\Gamma) \log f(\Gamma). \tag{5.P.6}$$

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

$$H = -J \sum_{\langle i,j \rangle} S_i S_j. \tag{5.P.7}$$

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:

$$f = \phi(S_1)\phi(S_2)\cdots\phi(S_N), \tag{5.P.8}$$

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:

$$A = X_1 \left[\sum_S \phi(S)S \right]^2 + X_2 \sum_S \phi(S) \log \phi(S), \tag{5.P.9}$$

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.

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 Chapter2, but is reproduced here]:

$$A \leq A_0 + \langle H - H_0 \rangle_0. \tag{5.P.10}$$

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, $\langle \ \rangle_0$ 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.[118] 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 tehn 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

$$H_0 = \sum_i h s_i. \tag{5.P.11}$$

Derive the equation for h that minimizes the RHS of (6.5.43).

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:

$$\langle s_0 \rangle = \langle \tanh \beta J (s_{-1} + s_1) \rangle, \tag{5.P.12}$$

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.

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).

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[118]See, 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.

(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?

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

$$H = \sum_j \left[\frac{1}{2} q_j^2 - K q_j q_{j+1} \right]. \tag{5.P.13}$$

The partition function reads

$$Z = \left(\prod_j \int_{-\infty}^{\infty} dq_j \right) \prod_{j=1}^{N-1} \exp[w(q_j, q_{j+1})], \tag{5.P.14}$$

where

$$w(x, y) = -\frac{1}{4}(x^2 + y^2) + Kxy. \tag{5.P.15}$$

The partition function should be evaluated just as the 1-Ising model with the aid of the eigenvalue problem:

$$\lambda f(x) = \int_{-\infty}^{\infty} dy \, f(y) \exp\left[-\frac{1}{4}(x^2 + y^2) + Kxy \right]. \tag{5.P.16}$$

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 thee any phase transition?

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:

$$H = -\sum_{\langle i,j \rangle} J_{ij} s_i s_j - \sum_i h_i s_i. \tag{5.P.17}$$

Derive the basic equation for the mean-field theory for a square lattice:

$$\langle s_i \rangle = \left\langle \tanh(\beta \sum_j J_{ij} s_j + \beta h_i) \right\rangle. \tag{5.P.18}$$

If we introduce the crude approximation like (5.8.6), we obtain

$$\langle s_i \rangle = \tanh(\beta \sum_j J_{ij} \langle s_j \rangle + \beta h_i). \tag{5.P.19}$$

(2) We wish to compute the spatial correlation $\langle s_i s_j \rangle$. First, demonstrate that

$$\frac{\partial \langle s_i \rangle}{\partial h_k} = k_B T \langle s_i s_k \rangle \tag{5.P.20}$$

without any approximation.

(3) Applying this to the following form of (6.5.79), obtain the equation for $\{\langle s_i s_k \rangle\}$:

$$\text{Arctanh}\langle s_i \rangle = \beta \sum_j J_{ij} \langle s_j \rangle + \beta h_i. \tag{5.P.21}$$

(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

$$\int dy \left(\frac{\delta(x-y)}{1-m^2} - \beta J(x-y) \right) g(y-z) = \delta(x-z). \tag{5.P.22}$$

We have already assumed the spatial translational symmetry and set $m(x) = m$. The Fourier transform of the coupling constant reads

$$J(k) = \sum_j e^{ik \cdot r_j} J(r_j) = 2^d J \cos k_x \cos k_y \cdots . \tag{5.P.23}$$

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 $T > T_c$):

$$G(k) \simeq \frac{1}{A + Bk^2}. \tag{5.P.24}$$

(6) Determine the critical exponent ν.

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:

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i, \tag{5.P.25}$$

$$H_L = -J' \sum_{\langle i,j \rangle} n_i n_j. \tag{5.P.26}$$

Let V ($\gg 1$) be the total number of lattice points and down spins are regarded particles.

(1) Following the procedure around p276, rewrite the canonical partition function of the Ising model in therms 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 $Vf = -k_BT \log Z$[119] 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.

5.14 [RG by Migdal approximation[120]]
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

$$K' = \frac{1}{4} \log \cosh 4K, \tag{5.P.27}$$

where the Hamiltonian is written in the following form:

$$H = -\sum K s_i s_j \tag{5.P.28}$$

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

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[119]Notice that this free energy is G rather than A, since h is on.

[120]

y-bond move   x-decimation   x-bond move   y-decimation
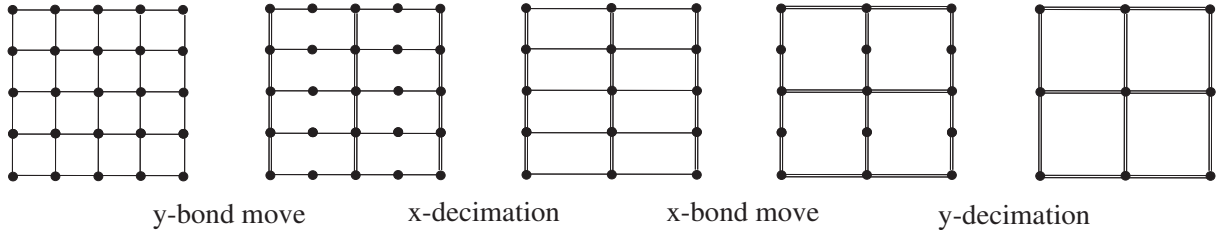
coupling constant due to the new bonds made by combining two vertical couplings is $2K_y$.

(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

$$
\begin{aligned}
K_x' &= \log \cosh(2K_x), &\text{(5.P.29)}\\
K_y' &= \frac{1}{2} \log \cosh(4K_y). &\text{(5.P.30)}
\end{aligned}
$$

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 *): $K_x^* = 2K_y^*$.

(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 can not say the result is impressive, but still there is an improvement from the mean-field approach. **5.8** ['Democracy']^{121}

Assume that there is a hierarchical organization whose decision at the level k is determined by s units at the level $k - 1$. Let us assume that level 0 corresponds

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^{121}cf. S. Galam and S. Wonczk, "Dictatorship from majority rule voting," Eur. Phys. J. B **18**, 183 (2000).

to individual persons, and level F is the decision of the organization; we assume there are sufficiently many levels (in practice, 5 is enough). This is sort of a coarse-graining system of people's opinions; any political system is a coarse-graining system of opinions, so no subtle voice of conscience can go through to the top.

(1) Suppose $s = 3$ and the strict majority rule is used. Find all the fixed points of this system, and tell which is stable and which is not.

(2) If $s = 4$ under the majority rule but when opinion A ties with B, always A is chosen. What is the minimum fraction of the people with opinion B to dominate the organization? How about the $s = 2$ case?

(3) Suppose $s = 5$ with strict majority rule, but there is an organizational propaganda for one opinion. Because of this, there is definitely one member in s at each level that its opinion is fixed. What is the minimum percentage of the anti-organizational opinion to prevail?

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.

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 lattice1-Ising model. We start with (5.10.12). The figure corresponding to Fig. 5.10.2 os as shown below:
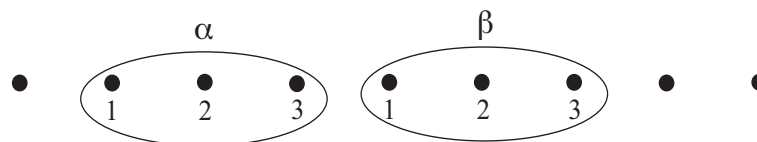
The equation corresponding to (5.10.13) is

$$K' s'_\alpha s'_\beta = K s_{\alpha 3} s_{\beta 1}, \tag{5.P.31}$$

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?

5.17 ['Democracy'][122]
Let us consider a hierarchical organization in which the decision at the kth 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 A.
(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?

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[122]cf. S. Galam and S. Wonczk, "Dictatorship from majority rule voting," Eur. Phys. J. B **18**, 183 (2000). The paper contains some trivial calculation errors, so trust your own result.

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