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 depends the properties of particular systems, but must be universal. That is, the probability $P(E_{\rm I})$ ($P(E_{\rm II})$) for the system I (resp., II) to have energy $E_{\rm I}$ (resp., $E_{\rm II}$) and the probabilty $P(E)$ for the compound system of I and II to have energy $E = E_{\rm I} + E_{\rm II}$ must have the same functional form. This must be so, as long as we expect statistical mechanics holds universally. Therefore,

$$P(E_{\rm I})P(E_{\rm II}) = P(E_{\rm I} + E_{\rm II}). \tag{0.P.1}$$

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

$$P(E) = Ce^{-\beta E}, \tag{0.P.2}$$

where C is a constant."
Needless to say, $\log P$ satisfies Cauchy's equation, and furthermore, we may assume that P is monotone$P$, it is correct that (0.P.2) is the general solution of (0.P.1). However, is this argument correct in any sense?
Solution
Everyone knows that (0.P.1) is incorrect. Although it is said that (0.P.2) is the correct solution, as is easily seen by substituting this into (0.P.1), $C^2 = C$ is requires. That is, $C = 1$. it is assumed that (0.P.1) is correct for any partition of E into two positive numbers, but it is obviously false. Then, why is an apparently plausible answer obtained? As can be seen from the correct answer $P = e^{-\beta(E-A)}$, this is because a similar equation as (0.P.1):

$$P_{\rm I}(E_{\rm I})P_{\rm II}(E_{\rm II}) = P_{\rm I+II}(E_{\rm I} + E_{\rm II}). \tag{0.P.3}$$

holds for the most probable partition of energy. Of course, the functional equation (0.P.3) does not give a meaningful solution without adding some conditions. For example, in terms of a commoon function ϕ and system specific constant C, we could require that $P_{\rm I}(E) = C_{\rm I}\phi(E)$. However, such an assumption does not have any compelling reason unless one know the correct answer.

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

$$H = D(S_z^2 - S(S+1)/2), \tag{0.P.4}$$

where $D > 0$ is a constant with $S = 3/2$ (the cation is in the term ${}^4\mathrm{F}_{3/2}$).
(0) Why can you apply statistical mechanics to this 'single' ion?
(1) Compute the occupation probability of each energy level at temperature T (you may use

the standard notation $\beta = 1/k_B T$).
(2) Calculate the entropy.
(3) At high temperatures approximately we have $C = k_B(T_0/T)^2$ with $T_0 = 0.18\text{K}$. Determine D in K.

Solution

(0) Statistical mechanics exploits the fact that any macroscopic system may be considered as a set of numerous statistically independent collection of subsystems. That is, if there is statistical independence and additivity, we may apply the statistical mechanics framework to the collection.
(1) There are 4 states but there are only two energy levels with $E = 3D/8$ and $-13D/8$. Therefore, $S_z = \pm 3/2$ is with $p = 1/2(1 + e^{2\beta D})$ and $S_z = \pm 1/2$ is with $p = 1/2(1 + e^{-2\beta D})$.
(2) The easiest method is to use the Shannon formula:[1]

$$S = -2k_B \left[\frac{1}{2(1+x)} \log \frac{1}{2(1+x)} + \frac{x}{2(1+x)} \log \frac{x}{2(1+x)} \right] = k_B \left\{ \log[2(1+x)] - \frac{x}{1+x} \log x \right\}, \tag{0.P.5}$$

where $x = e^{2\beta D}$.
(3) Setting x as above, we have

$$C = T\frac{dS}{dT} = -(2D\beta)\frac{dS}{d2D\beta} = -2D\beta \frac{dx}{d2D\beta}\frac{dS}{dx} = -2D\beta x \frac{dS}{dx} = k_B(2D\beta)^2 \frac{x}{(1+x)^2}. \tag{0.P.6}$$

Therefore,

$$C = k_B(D/k_B)^2/T^2. \tag{0.P.7}$$

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

2.3. [Vapor pressure of silicon]
The chemical potential μ_s of the atom in a solid is essentially given by the binding energy Δ of atom in the solid: $\mu_s = -\Delta$. Obtain the formula for the equilibrium vapor pressure of solid, and estimate the vapor pressure at room temperature of silicon for which $\Delta = 3\text{eV}$.

Solution

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

$$n = n_Q e^{-\beta\Delta} \Rightarrow p = k_B T n \tag{0.P.8}$$

We know $\hat{m} = 28$

$$n_Q = 28^{3/2} \times 10^{30} \simeq 1.5 \times 10^{32} \tag{0.P.9}$$

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

Therefore,

$$\begin{aligned} p &= k_BTn_Qe^{-\beta\Delta} = 1.38 \times 10^{-23} \times 300 \times 1.5 \times 10^{32} e^{-3/0.026}, && (0.P.10)\\ &= 4.8 \times 10^{-39}(Pa). && (0.P.11)\end{aligned}$$

2.4 [specific heat]
Suppose that a (3D) classical mechanical system has the following Hamiltonian

$$H = \sum_{i=1}^{N} a_k |\boldsymbol{p}_k + \boldsymbol{c}_k|^s \tag{0.P.12}$$

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

$$Z = \frac{V^N}{N!h^{3N}} \prod_k \int d^3pe^{-\beta a_k \boldsymbol{p}+[c_k|^s}. \tag{0.P.13}$$

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

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

$$[p] = [\beta a_k]^{-1/s}. \tag{0.P.14}$$

On the other hand,

$$[Zh^{3N}/V^N] = [p]^{3N} \propto [\beta^{-3N/s}] = (k_BT)^{3N/s}. \tag{0.P.15}$$

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

$$E = \frac{\partial \beta A}{\partial \beta} = -\frac{\partial \log \beta^{-3N/s}}{\partial \beta} \tag{0.P.16}$$

is independent of a_k, so is C.

From the fact that a_k is factored out, without any calculation you may conclude that C is independent of a_k.
Eq.(0.P.16) is correct, so you can proceed with this result, but let us proceed in a more conventional way (although I do not recommend this approach). (0.P.13) reads

$$Z = \frac{V^N}{N!h^{3N}} \prod_k (\beta a_k)^{-3/s} \int 4\pi\lambda^2 e^{-\lambda^s} d\lambda \propto \prod_k (\beta a_k)^{-3/s}. \tag{0.P.17}$$

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

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.

Solution

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

$$z(\boldsymbol{E}) = \int d\boldsymbol{e}\, e^{\beta p \boldsymbol{e}\cdot\boldsymbol{E}} = \int d\boldsymbol{e}\, e^{\beta pE\cos\theta}, \tag{0.P.18}$$

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

$$z(\boldsymbol{E}) = 2\pi\int d\theta\,\sin\theta\, e^{\beta pE\cos\theta} = 2\pi\int_{-1}^{1} dx\, e^{\beta pEx} = \frac{4\pi}{\beta pE}\sinh\beta pE. \tag{0.P.19}$$

From the structure of z we can immediately see

$$\langle\boldsymbol{p}\rangle = k_BT\frac{\partial}{\partial\boldsymbol{E}}\log z(\boldsymbol{E}) = pL(\beta pE)\frac{\boldsymbol{E}}{E} \tag{0.P.20}$$

where $L(x)$ is the Langevin function

$$L(x) = \coth x - \frac{1}{x}. \tag{0.P.21}$$

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

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

$$dA = -SdT + \boldsymbol{E}\cdot d\boldsymbol{P},\quad d\Phi = -SdT - \boldsymbol{P}\cdot d\boldsymbol{E}. \tag{0.P.22}$$

Therefore,

$$\boldsymbol{P} = -\frac{\partial}{\partial\boldsymbol{E}}\Phi(\boldsymbol{E}) = k_BTN\frac{\partial}{\partial\boldsymbol{E}}\log z(\boldsymbol{E}), \tag{0.P.23}$$

which is equivalent to (including the correct sign) (0.P.20).

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

$$\epsilon = \beta p^2NL'(\beta pN)I. \tag{0.P.24}$$

2.6 [Internal degree of freedom]
There is a classical ideal gas of volume V consisting of N molecules whose internal degrees of freedom are expressed by a single harmonic oscillator with a frequency ν. The frequency depends on the volume of the system as

$$\frac{d\log\nu}{d\log V} = \gamma. \tag{0.P.25}$$

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

Solution
(1) The partition function is given by

$$Z = Z_0 Z_I, \tag{0.P.26}$$

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

$$Z_0 = \frac{V^N}{N!}\left(\frac{2mk_BT}{h^2}\right)^{3N/2} \tag{0.P.27}$$

and

$$Z_I = \left(\frac{1}{2\sinh\beta h\nu/2}\right)^N. \tag{0.P.28}$$

Therefore

$$P = -\left.\frac{\partial A}{\partial V}\right|_T = \frac{Nk_BT}{V} + P_I, \tag{0.P.29}$$

where

$$P_1 = \left.\frac{\partial k_BT\log Z_I}{\partial V}\right|_T = -Nk_BT\frac{\cosh\beta h\nu/2}{\sinh\beta h\nu/2}\frac{\beta h}{2}\frac{\partial\nu}{\partial V} = -\frac{Nh\nu}{2V}\gamma\coth\frac{\beta h\nu}{2}. \tag{0.P.30}$$

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

$$U = \frac{Nh\nu}{2}\coth\frac{\beta h\nu}{2} = \frac{h\nu}{2} + \frac{h\nu}{e^{\beta h\nu}-1} \tag{0.P.31}$$

then

$$P_I = -\gamma\frac{U}{V}. \tag{0.P.32}$$

That is,

$$P = \frac{Nk_BT}{V} - \gamma\frac{U}{V}. \tag{0.P.33}$$

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

$$C_P = \left.\frac{\partial H}{\partial T}\right|_P. \tag{0.P.34}$$

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

$$E = \frac{3}{2}Nk_BT + \frac{Nh\nu}{2}\coth\frac{\beta h\nu}{2}. \tag{0.P.35}$$

Therefore,

$$H = \frac{5}{2}Nk_BT + (1-\gamma)U. \tag{0.P.36}$$

Use (0.P.31).

$$C_P = \frac{5}{2}Nk_B + (1-\gamma)Nk_B\left(\frac{\beta h\nu}{e^{\beta h\nu}-1}\right)^2 e^{\beta h\nu}. \tag{0.P.37}$$

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

$$H = \frac{p^2}{2m} + \frac{a}{4}x^4, \tag{0.P.38}$$

where m is the effective mass of the oscillator and a is a positive constant. Obtain the constant volume specific heat of this gas around the room temperature.

Solution

We use the equipartition of energy:

$$2\left\langle \frac{p^2}{2m}\right\rangle = k_BT. \tag{0.P.39}$$

and

$$4\left\langle ax^4\right\rangle = k_BT. \tag{0.P.40}$$

Therefore,

$$\langle H\rangle = \frac{3}{4}k_BT. \tag{0.P.41}$$

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

$$C_V = \frac{15}{4}k_B \tag{0.P.42}$$

per molecule.

2.8. [Equipartition of energy for relativistic gas]
For a classical relativistic ideal gas show that the counterpart of the law of equipartition of kinetic energy reads

$$\left\langle \frac{1}{2}\frac{mv_x^2}{\sqrt{1-v^2/c^2}}\right\rangle = \frac{1}{2}k_BT. \tag{0.P.43}$$

Solution

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

$$\epsilon = c\sqrt{\boldsymbol{p}^2 + m^2c^2}. \tag{0.P.44}$$

We know the general relation to demonstrate the equipartition:

$$\left\langle p_x \frac{\partial \epsilon}{\partial p_x} \right\rangle = \langle p_x v_x \rangle = k_B T. \tag{0.P.45}$$

Note that

$$p_i = \frac{m v_i}{\sqrt{1 - (v/c)^2}}, \tag{0.P.46}$$

This concludes the demonstration.

2.9 [An equality about canonical ensemble]
Let Φ be the total potential energy of classical system. Show

$$\langle \Delta \Phi \rangle = \beta \left\langle (\nabla \Phi)^2 \right\rangle. \tag{0.P.47}$$

here the Laplacian is understood as an operator in the 3N-space.

Solution

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

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

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

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

$$\rho = \frac{1}{Z} e^{-\beta H}, \tag{0.P.48}$$

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

Let $U(\beta) = e^{-\beta H}$ and $H = p^2/2m$. There are two ways to compute $\langle x | U(\beta) | x' \rangle$ (x and x' are 3D position vectors), and bra and kets are normalized

A.

(1) Show that

$$\frac{\partial}{\partial \beta} \langle x | U(\beta) | x' \rangle = \frac{\hbar^2}{2m} \Delta_x \langle x | U(\beta) | x' \rangle, \tag{0.P.49}$$

where Δ_x is the Laplacian with respect to the coordinates x.
(2) What is the initial condition (i.e., $\langle x|U(0)|x\rangle$)?

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

(4) Compute Z, using the result in (3). You may use (3) to study the finite volume system as long as the temperature is not too low.
B.
We can directly compute $\langle x|U(\beta)|x'\rangle$ with the aid of the momentum representation of $U(\beta)$:

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

(5) We use

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

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

(6) Perform the integral in (5).

Solution

A(1) We immediately obtain

$$-\frac{d}{d\beta}U = HU, \tag{0.P.50}$$

so its position representation is obtained as given. Notice that

$$\langle x|H|x'\rangle = -\frac{\hbar^2}{2m}\Delta_x\delta(x-x'). \tag{0.P.51}$$

(2) $U(0)=1$, so $\langle x|U(0)|x\rangle = \delta(x-x')$ (if you use the continuum approximation) or $=\delta_{x,x'}$ (if you honestly treat the finiteness of the system).
(3) This is a diffusion equation, so the solution may be obtained by looking up any standard textbook; it is the Green's function with the vanishing boundary condition at infinity

$$\langle x|U(\beta)|x'\rangle = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} e^{-mk_BT(x-x')^2/2\hbar^2}.$$

This clearly exhibit that quantum effect becomes important at low temperatures (as can easily be guessed from the thermal wave length proportional to $1/\sqrt{T}$).
(4) $Z = TrU(\beta)$, so

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

This is consistent with (1.7.3).

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

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

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

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

so

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

(6)

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

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

2.11 [Density matrix for a spin system]
Let ρ be the density operator of a single 1/2 quantum spin system whose Hamiltonian 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 that diagonalizes σ_z.
(2) Find the average of σ_y.
(3) Obtain the matrix representation of ρ that diagonalizes σ_x.
Solution
(1) We take the direction of $\boldsymbol{B}$ to be the z axis.

$$\rho = \frac{1}{C}\begin{pmatrix} e^{\beta\gamma B} & 0 \\ 0 & e^{-\beta\gamma B}\end{pmatrix}, \tag{0.P.52}$$

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

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

$$e^{\gamma\boldsymbol{B}\cdot\boldsymbol{\sigma}} = \sum_{n=0}^{\infty}\frac{1}{(2n)!}(\gamma B)^{2n} + \sum_{n=0}^{\infty}\frac{1}{(2n+1)!}(\gamma B)^{2n+1}\frac{\boldsymbol{B}}{B}\cdot\boldsymbol{\sigma} = \cosh\gamma B + \frac{\boldsymbol{B}}{B}\cdot\boldsymbol{\sigma}\sinh\gamma B. \tag{0.P.53}$$

(2)

$$\langle\sigma_y\rangle = Tr\sigma_y\rho = Tr\begin{pmatrix} 0 & ie^{\beta\gamma B} \\ -ie^{-\beta\gamma B} & 0\end{pmatrix} = 0. \tag{0.P.54}$$

This should be obvious without any calculation.

(3) With the basis that diagonalizes σ_z we have

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{0.P.55}$$

Therefore

$$\sigma_x \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}. \tag{0.P.56}$$

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

$$U = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \tag{0.P.57}$$

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

$$U^* \begin{pmatrix} 0 & ie^{\beta\gamma B} \\ -ie^{-\beta\gamma B} & 0 \end{pmatrix} U = \frac{1}{2} \begin{pmatrix} 1 & -\tanh\beta\gamma B \\ -\tanh\beta\gamma B & 1 \end{pmatrix}. \tag{0.P.58}$$

2.12 [Legendre vs Laplace]
Consider an ideal gas consisting of N atoms under constant pressure p and temperature T.
(1) What is the most convenient partition function and the thermodynamic potential? Compute the partition function. You may use the ideal gas canonical partition function.
(2) Obtain the enthalpy of the system.
Solution
(1) We should use the pressure ensemble:

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

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

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

This gives

$$G = -Nk_BT\log\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} + Nk_BT\log\frac{p}{k_BT},$$

which is

$$G = A - k_BT\log N! + Nk_BT\log\frac{pV}{k_BT} = A + Nk_BT = A + pV.$$

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

$$H = \frac{\partial G/T}{\partial 1/T} = -\frac{\partial \log Q}{\partial \beta} = \frac{5}{2}Nk_BT.$$

Thermodynamically, $H = E + pV = E + Nk_BT$. Consistent. This is of course consistent with the constant pressure specific heat.

2.13 [Constant magnetic field ensemble]
The following situation is the same as **1.18**: N lattice sites have spins of $S = 1$ (in the term ${}^3P$), and the spin Hamiltonian has the following form:

$$H = DS_z^2. \tag{0.P.59}$$

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

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{H}{T}dM + \cdots, \tag{0.P.60}$$

the generalized partition function reads

$$Z_H = (1 + e^{-\beta D + \beta\mu H} + e^{-\beta D - \beta\mu H})^N. \tag{0.P.61}$$

(2) The resulting generalized Massieu function

$$\psi = k_B \log Z_H \tag{0.P.62}$$

satisfies

$$d\psi = -Ed\left(\frac{1}{T}\right) + Md\left(\frac{H}{T}\right) + \cdots. \tag{0.P.63}$$

Therefore,

$$M = \frac{\partial \psi}{\partial (H/T)} = N\frac{\mu(e^{-\beta D + \beta\mu H} - e^{-\beta D - \beta\mu H})}{1 + e^{-\beta D + \beta\mu H} + e^{-\beta D - \beta\mu H}} = N\frac{\sinh \beta\mu H}{e^{-\beta D}/2 + \cosh \beta\mu H}. \tag{0.P.64}$$

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

(3) Under a given (partial) pressures of A and B $n_E : n_A : n_B = 1 : 1 : 18$ (here E means empty). Find the maximum concentration n_A obtainable with changing only the partial pressure of B. (UIUC Qual F95).

Solution

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

$$\Xi = 1 + e^{\beta(E_A+\mu_A)} + e^{\beta(E_B+\mu_B)}, \tag{0.P.65}$$

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

$$\mu_X = k_B T \log(\beta p_X / n_{QX}) = k_B T \log(p_X/p_{QX}) \tag{0.P.66}$$

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

$$\Xi = 1 + p_A e^{\beta E_A}/p_{QA} + p_B e^{\beta E_B}/p_{QB}. \tag{0.P.67}$$

I do not require you to compute n_Q that is a matter of simple calculation as in **1.4.5**.

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

$$d(k_B T \log \Xi) = SdT + pdV + N_A d\mu_A + N_B d\mu_B + \cdots, \tag{0.P.68}$$

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

$$n_A = \frac{\partial(k_B T \log \Xi)}{\partial \mu_A} = \frac{p_A e^{\beta E_A}/p_{QA}}{1 + p_A e^{\beta E_A}/p_{QA} + p_B e^{\beta E_B}/p_{QB}}, \tag{0.P.69}$$

$$n_B = \frac{p_B e^{\beta E_B}/p_{QB}}{1 + p_A e^{\beta E_A}/p_{QA} + p_B e^{\beta E_B}/p_{QB}}, \tag{0.P.70}$$

$$n_E = \frac{1}{1 + p_A e^{\beta E_A}/p_{QA} + p_B e^{\beta E_B}/p_{QB}},. \tag{0.P.71}$$

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

2.15 [Absorption on catalytic surface]

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

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

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

(3) Now, the pressure of the chemical is doubled (with the temperature kept constant) and

the average number of particles absorbed on the catalytic surface is n_1. Find n_1 in terms of N and n_0. a_1 is still assumed to be zero.
(4) If $a_1 > 0$, does the number of absorbed molecules increase from n_0 in (2) (i.e., the $a_1 = 0$ case)? Demonstrate your answer and give a brief physical explanation.

Solution

(1)

$$\Xi_{single} = 1 + a_1 e^{\beta\mu} + a_2 e^{2\beta\mu}. \tag{0.P.72}$$

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

$$n_0 = N \frac{2a_2x^2}{1 + a_2x^2}, \tag{0.P.73}$$

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

$$x = \sqrt{\frac{n_0/N}{(2 - n_0/N)a_2}}. \tag{0.P.74}$$

Therefore,

$$\mu = k_BT \log \sqrt{\frac{n_0/N}{(2 - n_0/N)a_2}}. \tag{0.P.75}$$

(3) If the pressure is doubled, the fugacity doubles. Therefore, (0.P.74) tells us that

$$2\sqrt{\frac{n_0/N}{(2 - n_0/N)a_2}} = \sqrt{\frac{n_1/N}{(2 - n_1/N)a_2}}. \tag{0.P.76}$$

Solving this for n_1, we get

$$n_1 = \frac{8n_0}{2 + 3n_0/N}. \tag{0.P.77}$$

(4) Equation (0.P.73) now reads

$$n = N\frac{a_1x + 2a_2x^2}{1 + a_1x + a_2x^2}. \tag{0.P.78}$$

This may be written as

$$n = N\left(1 + \frac{a_2x^2 - 1}{1 + a_1x + a_2x^2}\right). \tag{0.P.79}$$

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

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

2.16 [Gas under a weight]
Suppose there is a vertical cylindrical container of cross section s whose top wall is a movable piston of cross section s with mass M. The piston is assumed to move only in the vertical direction (z-direction) and feels gravity. The container contains N ($\gg 1$) classical noninteracting particles with mass m.
(1) Write down the Hamiltonian of the gas + piston system (write the piston vertical momentum as p_M).
(2) Obtain the pressure P of the gas, and write the Hamiltonian in terms of P and the volume of the gas $V = sz$, where z is the position of the piston from the bottom of the container.
(3) Now, the mechanical variables are the phase variables of the gas system and the piston momentum p_M and $z = V/s$. Compute the canonical partition function of the whole system.
(4) You should have realized that the calculation in (3), apart from the unimportant contribution in the thermodynamic limit of the piston momentum, is the calculation of the pressure ensemble. [That is, the heavy piston acts as a constant pressure device.] Obtain the equation of state of the gas in the cylinder (a trivial question).
Solution
(1)

$$H = \sum_{i=1}^{N} \frac{{p_i}^2}{2m} + \frac{p_M^2}{2M} + Mgz. \tag{0.P.80}$$

(2) From the force balance, we have

$$Ps = Mg \;\Rightarrow\; PV = Mgz. \tag{0.P.81}$$

Therefore, (0.P.80) can be rewritten as

$$H = \sum_{i=1}^{N} \frac{{p_i}^2}{2m} + \frac{p_M^2}{2M} + PV. \tag{0.P.82}$$

(3)

$$\begin{aligned} Z &= \frac{1}{N!h^{3N+1}} \int d^N\boldsymbol{p} d^N\boldsymbol{q} dp_M dz\, e^{-\beta H}, && (0.P.83)\\ &= \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}\left(\frac{2\pi M k_B T}{h^2}\right)^{1/2}\int V^N e^{-\beta PV}\frac{dV}{s} && (0.P.84)\\ &= \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}\left(\frac{2\pi M k_B T}{h^2}\right)^{1/2}(\beta P)^{-N}. && (0.P.85)\end{aligned}$$

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

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

$$Z = Q\left(\frac{2\pi M k_B T}{h^2}\right)^{1/2}, \tag{0.P.86}$$

where

$$Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} (\beta P)^{-N}. \tag{0.P.87}$$

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

$$G = -N k_B T \log \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} + N k_B T \log \frac{P}{k_B T}, \tag{0.P.88}$$

$dG = -SdT + VdP$, so

$$V = \left.\frac{\partial G}{\partial P}\right|_T = \frac{N k_B T}{P}. \tag{0.P.89}$$

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

$$H = \left.\frac{\partial (G/T)}{\partial (1/T)}\right|_P = \frac{5}{2} N k_B T. \tag{0.P.90}$$

2.17 [Ideal gas with the aid of grand canonical ensemble]
Let us study the classical ideal gas with the aid of the grand canonical ensemble. Let μ be the chemical potential.
(1) Compute the grand canonical partition function for a monatomic ideal gas. Assume that the mass of the atom is m.
(2) Find the internal energy and the pressure as a function of chemical potential μ.
(3) Suppose the expectation value of the number of particles is N. How is the chemical potentialdetermined?
(4) Are the results obtained above (especially the results of (2)) consistent with what you already know?
Solution
(1) By definition

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} V^N e^{b\mu N} = \exp\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V e^{b\mu}\right] \tag{0.P.91}$$

(2) From this we get

$$P = \frac{k_B T}{V} \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V e^{\beta\mu}. \tag{0.P.92}$$

Since

$$d(PV/T) = -Ed(1/T) + (P/T)dV + Nd(\mu/T), \tag{0.P.93}$$

$$E = T^2 \left.\frac{\partial k_B \log \Xi}{\partial T}\right|_{\mu/T, V} = \frac{3}{2} k_B T \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V e^{\beta\mu}. \tag{0.P.94}$$

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

$$N = \frac{1}{k_B}\frac{\partial}{\partial \beta\mu}\frac{PV}{T} = \frac{\partial}{\partial \beta\mu}\log \Xi = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V e^{\beta\mu}, \tag{0.P.95}$$

we obtain

$$\mu = k_B T \log \frac{N}{V}\left(\frac{2\pi m k_B T}{h^2}\right)^{-3/2}. \tag{0.P.96}$$

The result agrees with the result obtained in the text. If $n \ll n_Q$ (i.e., the classical case without overlapping of de Broglie wave packets), μ deviates verymuch to the negative side ($\mu \ll 0$).
(4) Thus, as has already been stated at various places, the results of the grand canonical ensemble completely reproduces the properties of the callsic ideal gas..

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

$$Z = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}, \tag{0.P.97}$$

obtain the microcanonical partition fucntion $W(E)$ (with the aid of Laplace inverse transformation).
Solution

$$W(E) = \frac{1}{2\pi i}\int_{\beta^*-9\infty}^{\beta^*+i\infty} Z(\beta)e^{\beta E}d\beta. \tag{0.P.98}$$

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

$$\frac{1}{2\pi i}\int_{s'-i\infty}^{s'+i\infty}\frac{e^{sx}}{x^{k+1}}ds = \frac{x^k}{\Gamma(k+1)}. \tag{0.P.99}$$

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

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

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

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

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

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

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

$$Z(T,N) \leq \left(\frac{aV}{N}\right)^N . \tag{0.P.100}$$

Actually, show (classically)

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

where Z_0 is the canonical partition function for the ideal gas (e.g., (1.7.3)). This is just eq.(0.P.100) above

(2) Show that the infinite sum defining the grand partition function actually converges. The reader may use eq.(0.P.100) 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.

Solution

(1) The canonical partition function reads

$$Z(T,N) = \frac{1}{N!}\int d\Gamma e^{-\beta(K+\Phi)} \leq \frac{1}{N!}\int d\Gamma e^{-\beta K}e^{\beta BN} = Z_0(T,N)e^{\beta NB}, \tag{0.P.101}$$

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

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

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

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

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

$$\Xi(T,\mu) \le \sum_{N=0}^{\infty} \frac{1}{N!}(aVe^{\beta\mu-1})^N = \exp\left(aVe^{\beta\mu-1}\right).$$

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

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

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

$$\sum_{N=N_0}^{\infty} Z(T,N)e^{\beta\mu N} \le \sum_{N=N_0}^{\infty} \frac{1}{N!}(aVe^{\beta\mu-1})^N \simeq \sum_{N=N_0}^{\infty} \left(\frac{aVe^{\beta\mu}}{N}\right)^N \tag{0.P.102}$$

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

$$\frac{aVe^{\beta\mu}}{N_0} < 0.1, \tag{0.P.103}$$

then

$$\sum_{N=N_0}^{\infty} Z(T,N)e^{\beta\mu N} < \sum_{N=N_0}^{\infty} 0.1^N. \tag{0.P.104}$$

The sum on the RHS is obviously bounded by 0.2 (by 1/9, at worst $N_0 = 1$). Thus, the choice (0.P.103) is enough. Such N_0 can clearly be chosen proportional to V.

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

$$\max_N Z(T,N)e^{\beta\mu N} \le \Xi(T,\mu). \tag{0.P.105}$$

Notice that the largest term cannot be less than 1, because the $N = 0$ term is never smaller than 1.[2] To obtain the upper bound Ξ is divided into the sum up to $N_0 - 1$ and that beyond $N_0 - 1$:

$$\Xi(T,\mu) = \sum_{N=0}^{N_0-1} Z(T,N)e^{\beta\mu N} + \sum_{N=N_0}^{\infty} Z(T,N)e^{\beta\mu N}. \tag{0.P.106}$$

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

$$\Xi(T,\mu) \le \sum_{N=0}^{N_0-1} Z(T,N)e^{\beta\mu N} + \max_N Z(T,N)e^{\beta\mu N}. \tag{0.P.107}$$

---

[2] Notice that $Z(T,0) \ge 1$: recall

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

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

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

$$\sum_{N=0}^{N_0-1} Z(T,N)e^{\beta\mu N} \le N_0 \max_N Z(T,N)e^{\beta\mu N}. \tag{0.P.108}$$

Therefore, we have

$$\Xi(T,\mu) \le (N_0+1) \max_N Z(T,N)e^{\beta\mu N}. \tag{0.P.109}$$

Combining this with (0.P.105) we get the desired result.

(5) The grand canonical ensemble asserts

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

From the above inequality

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

Notice that

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

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

$$\left(\frac{PV}{Nk_BT}\right)_{th} \le \frac{PV}{Nk_BT} \le \left(\frac{PV}{Nk_BT}\right)_{th} + \frac{1}{N}\log(N_0+1).$$

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

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

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

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

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

Solution

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

$$-\frac{A}{T} = \sup_T[-E/T - (-S)]. \tag{0.P.110}$$

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

$$\frac{d(-A/T)}{d1/T} = -A - \frac{1}{T}\frac{dA}{d1/T} = -A + T\frac{dA}{dT}. \tag{0.P.111}$$

Therefore,

$$\frac{d^2(-A/T)}{d(1/T)^2} = -T^2\frac{d}{dT}\left(-A - T\frac{dA}{dT}\right) = -T^3\frac{d^2A}{dT^2} > 0 \tag{0.P.112}$$

Therefore, A is a concave function of T.

(2) We consider the Legendre transformation

$$f^*(\alpha) = \sup_x[\alpha x - f(x)] \tag{0.P.113}$$

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

Remember that convex functions are continuous.

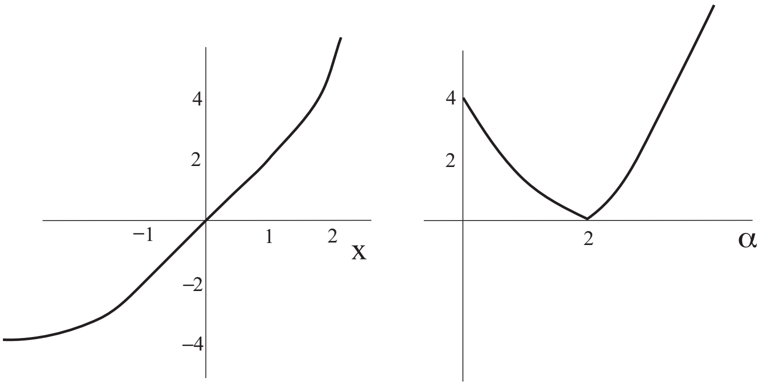
2.21 [Information]

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

(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



Left: f, **Right**: f^*.

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 information of this message?
(5) Finally, you are told that face pair is actually $(2,5)$. What is the information in this final statement?
As you guess, in what order the information is given, if the total information you gain does not depend on the actual 'path,' because the extent of your ignorance is a 'state function.'
Solution
(1) There are 36 distinguishable states and they are all equally probable. Therefore, the total uncertainty is $\log_2 36 = 5.16$ bits, or the surprisal you have when you are told, say, $(1,1)$ actually happens is 5.16 bits. That is, you need 5.16 bits of information to pinpoint a particular elementary event.

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

(3) Red = 1: Green = 4, 5 or 6
Red = 2: Green = 3, 4, 5 or 6.
Therefore, there are $7 \times 2 = 14$ states remaining. This uncertainty is $\log_2 14 = 3.81$. We had 4.91 bits of uncertainty, so this message must have conveyed 1.1 bits.
(4) Obviously, 1 bit.
(5) There is no uncertainty remaining, so 2.81 bits (this is, needless to say, the surprisal of an event of probability 1/7)

2.22 [Variational principle for free energy (classical case)[3]]
Let $H = H_0 + V$ be a system Hamiltonian.

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

(1) Show that

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

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 unharmonic oscillator with the Hamiltonian

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

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

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

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

Solution

(1)

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

Therefore, with the aid of Jensen's inequality

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

That is, we are done.

(2) We know

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

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

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

That is,

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

Minimizing the right hand side wrt K, we obtain

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

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

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

2.23 [Gibbs-Bogoliubov's inequality (quantum case)][4]
Gibbs-Bogoliubov's inequality

$$A \leq A_0 + \langle H - H_0 \rangle_0 \tag{0.P.114}$$

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

$$Tre^{-\beta H} \geq \sum_i e^{-\langle i|H|i\rangle}, \tag{0.P.115}$$

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

$$e^{-\beta A} \geq \sum_i e^{-\beta\langle i|H|i\rangle} = e^{-\beta A_0}\sum_i e^{\beta(A_0 - \langle i|H_0|i\rangle)} e^{-\beta\langle i|(H-H_0)|i\rangle}. \tag{0.P.116}$$

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

2.24 (1) For any density operator P

$$A \leq TrP(H + k_B T \log P), \tag{0.P.117}$$

where A is the free energy for the system whose hamiltonian is H.
(2) Suppose P is the canonical density operator $P = e^{\beta(A_0 - H_0)}$ for a system with the Hamiltonian H_0. The, show that the above inequality is jsut Gibbs-Bogoliubov's inequality.

2.25 [Convexity of free energy] (Ruellle)

$$A[\sum \lambda_i H_i] \geq \sum A[\lambda_i H_i]. \tag{0.P.118}$$

Soluton
Hölder + Peierls proves this.

2.26 [Thermodynamic perturbation theory]
Suppose the system Hamiltonian is given as $H = H_0 + \epsilon H_1$, where ϵ は is a (small) constant. Demnonstratet the following expansion formula:

$$A = A_0 + \epsilon\langle H_1\rangle_0 - \frac{1}{2}\beta\epsilon^2\langle (H_1 - \langle H_1\rangle_0)^2\rangle_0 + \cdots, \tag{0.P.119}$$

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

wgere 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]
When Jarzynski's equality is actually used to obtain ΔA from, e.g., computer experiments, the moments of work are computed instead of obtaining the distribution of the work. To this end, it is convenient to use *cumulants*.[5]
(1) Suppose the average of a stochastic variable x is zero. Let us define the second cumulant $\langle x^2\rangle_C$ and the fourth cumulant $\langle x^4\rangle_C$ as

$$\log\langle\exp(\lambda x)\rangle = \frac{\lambda^2}{2}\langle x^2\rangle_C + \frac{\lambda^4}{4!}\langle x^4\rangle_C + \cdots$$

On the other hand, the second moment $\langle x^2\rangle$ and the fourth moment $\langle x^4\rangle$ are defined as

$$\langle\exp(\lambda x)\rangle = 1 + \frac{\lambda^2}{2}\langle x^2\rangle + \frac{\lambda^4}{4!}\langle x^4\rangle + \cdots.$$

Demonstrate that

$$\langle x^2\rangle_C = \langle x^2\rangle,$$
$$\langle x^4\rangle_C = \langle x^4\rangle - 3\langle x^2\rangle^2.$$

(2) With a certain protocol, starting from a canonical distribution at a temperature 300K (i.e., $k_BT = 4$pNnm; you may use this number), work has been added to an isolated system to modify the initial Hamiltonian H_0 into the final one H_1 by tweaking the control parameter. The work needed to change the parameter in the Hamiltonian was observed again and again under isolation starting with an equilibrium state at $T = 300$K. The average work was 78 pNnm, the standard deviation was 15 pNnm, and the fourth order moment around the average was 157,000 (pNnm)^4.
What is the ΔA between the equilibrium states defined by $H(0)$ and $H(1)$ at 300K (up to the fourth order cumulant approximtion)?
Solution
(1) We expand

$$\log\langle\exp(\lambda x)\rangle = \log\left[1 + \frac{\lambda^2}{2}\langle x^2\rangle + \frac{\lambda^4}{4!}\langle x^4\rangle + \cdots\right]$$

with the aid of $\log(1+f) = f - f^2/2 + \cdots$. We obtain

$$\begin{aligned}\log\langle\exp(\lambda x)\rangle &= \left[\frac{\lambda^2}{2}\langle x^2\rangle + \frac{\lambda^4}{4!}\langle x^4\rangle + \cdots\right] - \frac{1}{2}\left[\frac{\lambda^2}{2}\langle x^2\rangle + \frac{\lambda^4}{4!}\langle x^4\rangle + \cdots\right]^2, \\ &= \frac{\lambda^2}{2}\langle x^2\rangle + \frac{\lambda^4}{4!}\langle x^4\rangle - \frac{\lambda^4}{8}\langle x^2\rangle^2 + \text{higher order in } \lambda.\end{aligned}$$

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[5] We will discuss this concept in more detail in conjunction to imperfect gas.

Comparing this with the definition of cumulants, we get the desired results.

(2) According to Jarzynski's equality

$$\Delta A = -k_BT\log\langle e^{-\beta W}\rangle = -k_BT\log\langle e^{-\beta(\langle W\rangle+\delta W)}\rangle = \langle W\rangle - k_BT\log\langle e^{-\beta\delta W}\rangle$$

where $\langle W\rangle = 78$ pNnm is the average and δW is the deviation from it. Since its mean is zero, we may use the cumulant formula above around the average:

$$-k_BT\log\langle e^{-\beta\delta W}\rangle = -\frac{1}{2}\beta\langle\delta W^2\rangle_C - \frac{1}{24}\beta^3\langle\delta W^4\rangle_C = -\frac{1}{2}\frac{15^2}{4} - \frac{1}{24}\frac{1}{4^3}(157,000-3\times 15^4) = -28.1-3.3 = -3$$

Therefore, $\Delta A = 78 - 31 = 47$ pNnm.
Remark. Although I pretended that Jarzynski's equality facilitated computation of ΔA, computational experts recommend straightforward slow simulations, so the equality may remain as a theoretical curiosity.

2.28 [Jarzynski].[6]
A single stranded DNA with a certain binding protein is stretched slowly until the protein dissociates from the DNA. Then, the length of the DNA is returned slowly to the rather relaxed state where the binding of the molecule does not affect the DNA tension. The work W dissipated during the cycle is measured at 300K and the experimental results were as follows:

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

What is the best estimate of the (Gibbs) free energy change due to binding of the protein in the relaxed state of the single stranded DNA? How is your estimate different from the simple average $\langle W\rangle$?
Solution
Notice that $k_BT = 4.14$pNnm. $e^{-\beta W}$ is written in the above table. Thus,

$$\sum e^{-\beta W} = 373.1\times 10^{-10} \;\Rightarrow\; \left\langle e^{-\beta W}\right\rangle = 1.2\times 10^{-9} \qquad (0.P.120)$$

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

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

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

2.29 [Fluctuation and spring constant][7]
Inside the F_1ATPase is a rotator 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 [I forgot to put this word] mean square angle fluctuation of the stiff filament was 30 degrees at 290K. If the temperature is raised by 10%, by what percentage will the angular fluctuation change? Assume that the molecular structure is not affected by this temperature change.
(2) What is the torsional spring constant of this rotator captured by the surrounding ring?
(3) Now, adding an appropriate polymers to the ambient solution, the effective viscosity of the solution is doubled. What is the mean square angle fluctuation of the filament? You may assume that the polymers do not affect the ATPase itself.
Solution
(1) Suppose θ is the angular deviation around the equilibrium direction. Then, the torsional spring constant k reads

$$\tau = k\theta, \tag{0.P.121}$$

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

$$k^{-1} = \left.\frac{\partial \theta}{\partial \tau}\right|_T = \beta \langle (\delta\theta)^2 \rangle. \tag{0.P.122}$$

That is,

$$\langle (\delta\theta)^2 \rangle = k_B T/k. \tag{0.P.123}$$

Since we may assume k does not depend on T, the fluctuation should change by about 5%.
(2) You must measure the angle in radians.

$$k = 1.382 \times 10^{-23} \times 290/(\pi/6)^2 = 1.46 \times 10^{-20} \tag{0.P.124}$$

The unit is J/rad. Is it reasonable? It is about 15 pNnm/rad, a reasonable value.
(3) No change. The formula does not depend on the viscosity, so the amplitude of the fluctuation never changes. This is true however gooey the solution is. It is true that the oscillation becomes slow, but then small fluctuations can be accumulated to a size as large as when the viscosity is very low.

2.30 [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

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[7] If you wish to see the shape or 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).

be described in terms of S, V, N (or their conjugate variables).
(4) Show with the aid of grand partition function that

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

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

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

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

In more detail for those who are skeptic:

$$dx = \sum_j\left.\frac{\partial x}{\partial X_j}\right|_{X_1\cdots\check{X}_j\cdots X_n} dX_j, \tag{0.P.125}$$

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

$$\left.\frac{\partial x_i}{\partial x_k}\right|_{x_1\cdots\check{x}_k\cdots x_n} = \sum_j\left.\frac{\partial x_i}{\partial X_j}\right|_{X_1\cdots\check{X}_j\cdots X_n}\left.\frac{\partial X_j}{\partial x_k}\right|_{x_1\cdots\check{x}_k\cdots x_n}. \tag{0.P.126}$$

We put (0.P.125) into $\langle\delta X\delta y\rangle$ (regarding X is a representative of $\{X_j\}$ and y that of $\{x_k\}$ (the derivatives are mere constants, so you can take them out of the average symbol). Now, (0.P.126) tells you what you want.

(2)

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

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

$$\delta^2S = -\frac{1}{2T}(\delta N\delta\mu + \cdots) = -\frac{1}{2T}\left.\frac{\partial N}{\partial\mu}\right|_{S,V}\delta\mu^2 + \cdots.$$

Therefore,

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

That is,

$$\langle\delta\mu^2\rangle = k_BT\left.\frac{\partial\mu}{\partial N}\right|_{S,V}.$$

(4) Since

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

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

Therefore,

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

(5)

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

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

2.31 [Equilibrium fluctuation]
(1) Obtain $\langle \delta S \delta V \rangle$.
(2) Obtain $\langle \delta p \delta T \rangle$.
Solution
(1) Perhaps, the cleverest way is to us the fluctuation-response relation. We immediately obtain

$$\langle \delta S \delta V \rangle = k_B T \left. \frac{\partial V}{\partial T} \right|_p . \tag{0.P.127}$$

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

$$\frac{1}{2k_BT}[\delta S \delta T - \delta p \delta V] = \frac{1}{2k_BT} \left[\left. \frac{\partial T}{\partial S} \right|_V + 2 \left. \frac{\partial T}{\partial V} \right|_S \delta V \delta S - \left. \frac{\partial p}{\partial V} \right|_S \delta V^2 \right]. \tag{0.P.128}$$

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

$$\langle \delta S \delta V \rangle = k_B T \frac{1}{\frac{\partial(T,p)}{\partial(S,V)}} \left. \frac{\partial T}{\partial V} \right|_S = -k_B T \left. \frac{\partial S}{\partial p} \right|_T = k_B T \left. \frac{\partial V}{\partial T} \right|_p . \tag{0.P.129}$$

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

$$\frac{1}{2k_BT}[\delta S \delta T - \delta p \delta V] = \frac{1}{2k_BT} \left[\left. \frac{\partial S}{\partial T} \right|_p \delta T^2 + 2 \left. \frac{\partial S}{\partial p} \right|_T \delta T \delta p - \left. \frac{\partial V}{\partial p} \right|_T \delta p^2 \right]. \tag{0.P.130}$$

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

$$\langle \delta T \delta p\rangle = k_B T \frac{1}{\left.\frac{\partial V}{\partial p}\right|_T \left.\frac{\partial S}{\partial T}\right|_p + \left.\frac{\partial S}{\partial p}\right|_T^2} \left.\frac{\partial S}{\partial p}\right|_T . \tag{0.P.131}$$

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

$$\langle \delta T \delta p\rangle = k_B T \frac{1}{\frac{\partial(V,S)}{\partial(p,T)}} \left.\frac{\partial S}{\partial p}\right|_T = k_B T \frac{\frac{\partial(S,T)}{\partial(p,T)}}{\frac{\partial(V,S)}{\partial(p,T)}} = k_B T \frac{\partial(S,T)}{\partial(V,S)} = -k_B T \left.\frac{\partial T}{\partial V}\right|_S . \tag{0.P.132}$$

2.32 [Fluctuation and Le Chatelier-Braun's principle]
(1) Show that

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

where x and X are conjugate pair of thermodynamic variables (wrt energy).
(2) What is the relation between this inequality and the Le Chatelier-Braun principle?

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

$$0 \le \langle (\delta X + t\delta x)^2\rangle = \langle \delta X^2\rangle + 2t\langle \delta x \delta X\rangle + t^2\langle \delta x^2\rangle \tag{0.P.133}$$

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

$$\langle \delta x \delta X\rangle^2 - \langle \delta X^2\rangle\langle \delta x^2\rangle \le 0. \tag{0.P.134}$$

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

$$\langle \delta X^2\rangle = k_B T \left.\frac{\partial x}{\partial X}\right|_y^{-1}, \ \langle \delta x^2\rangle = k_B T \left.\frac{\partial X}{\partial x}\right|_Y^{-1} . \tag{0.P.135}$$

Therefore,

$$\left.\frac{\partial x}{\partial X}\right|_y \le \left.\frac{\partial x}{\partial X}\right|_Y . \tag{0.P.136}$$

2.33 [Fluctuation of internal energy]
For a classical monatomic ideal gas consisting of N atoms, compute the fluctuation of its internal energy. Or show

$$\langle (E - \langle E\rangle)^2\rangle / \langle E\rangle^2 = 2/3N. \tag{0.P.137}$$

Solution
The situation must be under constant temperature and volume.

$$\langle \delta E^2\rangle = T^2\langle \delta S^2\rangle - 2Tp\langle \delta S \delta V\rangle + p^2\langle \delta V^2\rangle . \tag{0.P.138}$$

The volume fluctuation can be found as

$$\langle \delta V^2 \rangle = -k_B T \left.\frac{\partial V}{\partial p}\right|_T = k_B \frac{V}{p}. \tag{0.P.139}$$

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

$$\delta T = \left.\frac{\partial T}{\partial S}\right|_p \delta S + \cdots, \tag{0.P.140}$$

so

$$\langle \delta S^2 \rangle = T \left.\frac{\partial S}{\partial T}\right|_p = k_B C_p = \frac{5}{2} k_B^2 N. \tag{0.P.141}$$

Therefore, we need the answer to **1.29** (2).

$$\langle \delta S \delta V \rangle = k_B T \left.\frac{\partial V}{\partial T}\right|_p = k_B V. \tag{0.P.142}$$

Combining all the results, we obtain

$$\begin{aligned} \langle \delta E^2 \rangle &= k_B T^2 C_p - 2p k_B T^2 \left.\frac{\partial V}{\partial T}\right|_p - p^2 k_B T \left.\frac{\partial V}{\partial p}\right|_T, & \text{(0.P.143)} \\ &= k_B^2 T^2 \left(\frac{5}{2}N - 2N + N\right) = \frac{3}{2}(k_B T)^2 N. & \text{(0.P.144)} \end{aligned}$$

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

2.34 [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 → 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.[8].

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[8] 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.

Solution

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

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

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

$$\left.\frac{\partial x}{\partial X}\right|_y < \left.\frac{\partial x}{\partial X}\right|_Y . \tag{0.P.145}$$

Thus,

$$\left.\frac{\partial T}{\partial S}\right|_B = \frac{T}{C_B} < \left.\frac{\partial T}{\partial S}\right|_M = \frac{T}{C_M}. \tag{0.P.146}$$

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

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

$$\left.\frac{\partial S}{\partial T}\right|_E = \left.\frac{\partial S}{\partial T}\right|_D + \left.\frac{\partial S}{\partial D}\right|_T \left.\frac{\partial D}{\partial T}\right|_E . \tag{0.P.147}$$

With the aid of a Maxwell's relation we obtain

$$\left.\frac{\partial S}{\partial D}\right|_T = -\left.\frac{\partial E}{\partial T}\right|_D = \frac{D}{\epsilon^2 V}\frac{d\epsilon}{dT}. \tag{0.P.148}$$

Also

$$\left.\frac{\partial D}{\partial T}\right|_E = \frac{D}{\epsilon}\frac{d\epsilon}{dT}. \tag{0.P.149}$$

Therefore,

$$C_E = C_D + T\frac{ED}{\epsilon^2}\left(\frac{d\epsilon}{dT}\right)^2 . \tag{0.P.150}$$

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

(5) The original paper contains the answer.

2.35 [Chemical equilibrium constant[9]]
The reaction

$$A \underset{k_-}{\overset{k_+}{\rightleftarrows}} B. \tag{0.P.151}$$

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

$$\frac{d[A]}{dt} = k_-[B] - k_+[A] = -\frac{d[B]}{dt}. \tag{0.P.152}$$

For all $t > 0$ show that

$$\frac{[B]_F(t)}{[A]_B(t)} = K, \tag{0.P.153}$$

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 (0.P.153) 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.] **Solution**
Since $[A] + [B] = C$ (constant), $[B]_F(t)$ obeys

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

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

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

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

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

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

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

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