4 Statistical Ensembles : Worked Examples

(4.1) Consider a system of N identical but distinguishable particles, each of which has a nondegenerate ground state with energy zero, and a g-fold degenerate excited state with energy $\varepsilon > 0$.

- (a) Let the total energy of the system be fixed at $E = M\varepsilon$, where M is the number of particles in an excited state. What is the total number of states $\Omega(E, N)$?

- (b) What is the entropy $S(E, N)$? Assume the system is thermodynamically large. You may find it convenient to define $\nu \equiv M/N$, which is the fraction of particles in an excited state.

- (c) Find the temperature $T(\nu)$. Invert this relation to find $\nu(T)$.

- (d) Show that there is a region where the temperature is negative.

- (e) What happens when a system at negative temperature is placed in thermal contact with a heat bath at positive temperature?

Solution :

(a) Since each excited particle can be in any of g degenerate energy states, we have

$$\Omega(E, N) = \binom{N}{M} g^M = \frac{N! \, g^M}{M! \, (N - M)!} \quad .$$

(b) Using Stirling's approximation, we have

$$S(E, N) = k_{\mathrm{B}} \ln \Omega(E, N) = -N k_{\mathrm{B}} \Big\{ \nu \ln \nu + (1 - \nu) \ln(1 - \nu) - \nu \ln g \Big\} \quad ,$$

where $\nu = M/N = E/N\varepsilon$.

(c) The inverse temperature is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_N = \frac{1}{N\varepsilon} \left(\frac{\partial S}{\partial \nu} \right)_N = \frac{k_{\mathrm{B}}}{\varepsilon} \cdot \left\{ \ln \left(\frac{1 - \nu}{\nu} \right) + \ln g \right\} \quad ,$$

hence

$$k_{\mathrm{B}} T = \frac{\varepsilon}{\ln \left(\frac{1 - \nu}{\nu} \right) + \ln g} \quad .$$

Inverting,

$$\nu(T) = \frac{g \, e^{-\varepsilon / k_{\mathrm{B}} T}}{1 + g \, e^{-\varepsilon / k_{\mathrm{B}} T}} \quad .$$

(d) The temperature diverges when the denominator in the above expression for $T(\nu)$ vanishes. This occurs at $\nu = \nu^* \equiv g/(g + 1)$. For $\nu \in (\nu^*, 1)$, the temperature is negative! This is technically correct, and a consequence of the fact that the energy is bounded for this system: $E \in [0, N\varepsilon]$. The entropy as a function of ν therefore has a maximum at $\nu = \nu^*$. The model is unphysical though in that it neglects various excitations such as kinetic energy (*e.g.* lattice vibrations) for which the energy can be arbitrarily large.

(e) When a system at negative temperature is placed in contact with a heat bath at positive temperature, heat flows from the system to the bath. The energy of the system therefore decreases, and since $\frac{\partial S}{\partial E} < 0$, this results in a net
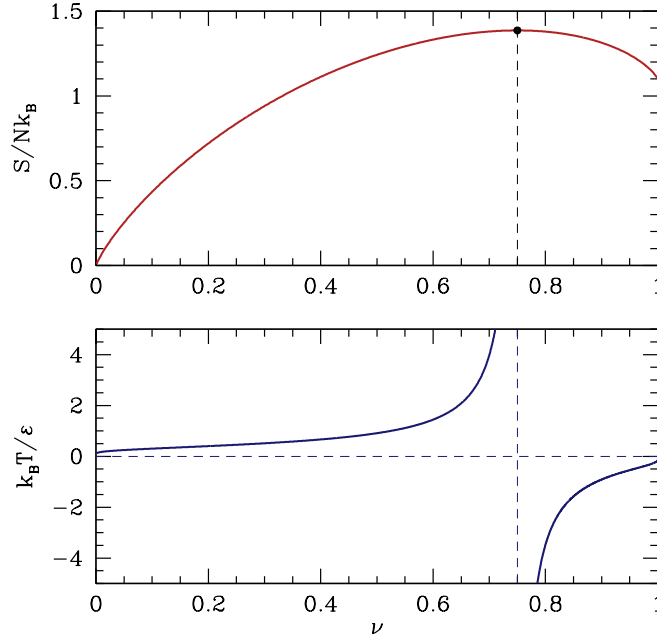
Figure 1: Bottom: dimensionless temperature $\theta(\nu) \equiv k_{\mathrm{B}}T/\varepsilon$ *versus* dimensionless energy density $\nu = E/N\varepsilon$ for problem 1, shown here for $g = 3$. Note that $T \to \mp\infty$ for $\nu \to \nu^* \pm 0^+$, where $\nu^* = g/(g+1)$ is the energy density at which the entropy is maximum. Top: dimensionless entropy $s(\nu) \equiv S/Nk_{\mathrm{B}}$ *versus* dimensionless energy density ν. Note the maximum at $\nu^* = g/(g+1)$, where g is the degeneracy of the excited level.

entropy increase, which is what is demanded by the Second Law of Thermodynamics. More precisely, let $đQ$ be the heat added *to* the system from the bath. The first law then says $dE = đQ$. The total entropy change due to such a differential heat transfer is

$$dS_{\mathrm{tot}} = dS + dS_{\mathrm{b}} = \left(\frac{1}{T} - \frac{1}{T_{\mathrm{b}}} \right) dE \quad ,$$

where $dS = dS_{\mathrm{sys}}$ is the entropy change of the system and T is the system temperature; $T_{\mathrm{b}} > 0$ is the temperature of the bath. We see that the Second Law, $dS_{\mathrm{tot}} \geq 0$, requires that $dE \leq 0$. For $đQ = dE < 0$, the total entropy increases. Note that the heat capacity of the system is

$$C = \frac{\partial E}{\partial T} = N\varepsilon \frac{\partial \nu}{\partial T} = \frac{N\varepsilon^2}{k_{\mathrm{B}}T^2} \frac{g\,e^{-\varepsilon/k_{\mathrm{B}}T}}{\left(1 + g\,e^{-\varepsilon/k_{\mathrm{B}}T}\right)^2}$$

and that $C \geq 0$. Even though the temperature T can be negative, we always have $C(T) \geq 0$; this is necessary for thermodynamic stability. We conclude that the system's temperature changes by $dT = dE/C$, so if $dE < 0$ we have $dT < 0$ and the system cools.

All should be clear upon examination of Fig. 1. When $\nu > \nu^*$, the system temperature is negative. Placing the system in contact with a bath at temperature $T_{\mathrm{b}} > 0$ will cause heat to flow from the system to the bath: $đQ = dE < 0$. This means $d\nu = dE/N\varepsilon < 0$, hence ν decreases and approaches ν^* from above, at which point $T = -\infty$. At this point, a further differential transfer $-đQ > 0$ from the system to the bath continues to result in an increase of total entropy, with $dS_{\mathrm{tot}} = -đQ/T_{\mathrm{b}}$ at $\nu = \nu^*$. Thus, ν crosses ν^*, and the temperature flips from $T = -\infty$ to $T = +\infty$. At this point, we can appeal to our normal intuition. The system is much hotter than the bath, and heat continues to flow to the bath. This has the (familiar) effect of lowering the system temperature,

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which will then approach T_b from above. Ultimately, both system and bath will be at temperature T_b, as required for thermodynamic equilibrium.

(4.2) Solve for the model in problem 1 using the ordinary canonical ensemble. The Hamiltonian is

$$\hat{H} = \varepsilon \sum_{i=1}^{N} \left(1 - \delta_{\sigma_i, 1}\right) \quad ,$$

where $\sigma_i \in \{1, \ldots, g+1\}$.

(a) Find the partition function $Z(T, N)$ and the Helmholtz free energy $F(T, N)$.

(b) Show that $\hat{M} = \frac{\partial \hat{H}}{\partial \varepsilon}$ counts the number of particles in an excited state. Evaluate the thermodynamic average $\nu(T) = \langle \hat{M} \rangle / N$.

(c) Show that the entropy $S = -\left(\frac{\partial F}{\partial T}\right)_N$ agrees with your result from problem 1.

Solution :

(a) We have

$$Z(T, N) = \text{Tr } e^{-\beta \hat{H}} = \left(1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}\right)^N \quad .$$

The free energy is

$$F(T, N) = -k_{\mathrm{B}} T \ln F(T, N) = -N k_{\mathrm{B}} T \ln \left(1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}\right) \quad .$$

(b) We have

$$\hat{M} = \frac{\partial \hat{H}}{\partial \varepsilon} = \sum_{i=1}^{N} \left(1 - \delta_{\sigma_i, 1}\right) \quad .$$

Clearly this counts all the excited particles, since the expression $1 - \delta_{\sigma_i, 1}$ vanishes if $i = 1$, which is the ground state, and yields 1 if $i \neq 1$, *i.e.* if particle i is in any of the g excited states. The thermodynamic average of $\hat{M}$ is $\langle \hat{M} \rangle = \left(\frac{\partial F}{\partial \varepsilon}\right)_{T,N}$, hence

$$\nu = \frac{\langle \hat{M} \rangle}{N} = \frac{g\, e^{-\varepsilon/k_{\mathrm{B}}T}}{1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}} \quad ,$$

which agrees with the result in problem 1c.

(c) The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_N = N k_{\mathrm{B}} \ln\left(1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}\right) + \frac{N\varepsilon}{T} \frac{g\, e^{-\varepsilon/k_{\mathrm{B}}T}}{1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}} \quad .$$

Working with our result for $\nu(T)$, we derive

$$1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T} = \frac{1}{1 - \nu}$$

$$\frac{\varepsilon}{k_{\mathrm{B}}T} = \ln\left(\frac{g(1 - \nu)}{\nu}\right) \quad .$$

Inserting these results into the above expression for S, we verify

$$S = -N k_{\mathrm{B}} \ln(1 - \nu) + N k_{\mathrm{B}} \nu \ln\left(\frac{g(1 - \nu)}{\nu}\right)$$

$$= -N k_{\mathrm{B}} \left\{\nu \ln \nu + (1 - \nu) \ln(1 - \nu) - \nu \ln g\right\} \quad ,$$

as we found in problem 1b.

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(4.3) Consider a system of noninteracting spin trimers, each of which is described by the Hamiltonian

$$\hat{H} = -J\left(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_1\right) - \mu_0 H\left(\sigma_1 + \sigma_2 + \sigma_3\right) \quad .$$

The individual spin polarizations σ_i are two-state Ising variables, with $\sigma_i = \pm 1$.

- (a) Find the single trimer partition function ζ.

- (b) Find the magnetization per trimer $m = \mu_0 \langle \sigma_1 + \sigma_2 + \sigma_3 \rangle$.

- (c) Suppose there are $N_\triangle$ trimers in a volume V. The magnetization density is $M = N_\triangle m/V$. Find the zero field susceptibility $\chi(T) = (\partial M/\partial H)_{H=0}$.

- (d) Find the entropy $S(T, H, N_\triangle)$.

- (e) Interpret your results for parts (b), (c), and (d) physically for the limits $J \to +\infty$, $J \to 0$, and $J \to -\infty$.

Solution :

The eight trimer configurations and their corresponding energies are listed in the table below.

$\lvert\sigma_1\sigma_2\sigma_3\rangle$	E	$\lvert\sigma_1\sigma_2\sigma_3\rangle$	E
$\lvert\uparrow\uparrow\uparrow\rangle$	$-3J - 3\mu_0 H$	$\lvert\downarrow\downarrow\downarrow\rangle$	$-3J + 3\mu_0 H$
$\lvert\uparrow\uparrow\downarrow\rangle$	$+J - \mu_0 H$	$\lvert\downarrow\downarrow\uparrow\rangle$	$+J + \mu_0 H$
$\lvert\uparrow\downarrow\uparrow\rangle$	$+J - \mu_0 H$	$\lvert\downarrow\uparrow\downarrow\rangle$	$+J + \mu_0 H$
$\lvert\downarrow\uparrow\uparrow\rangle$	$+J - \mu_0 H$	$\lvert\uparrow\downarrow\downarrow\rangle$	$+J + \mu_0 H$

Table 1: Spin configurations and their corresponding energies.

(a) The single trimer partition function is then

$$\zeta = \sum_\alpha e^{-\beta E_\alpha} = 2\,e^{3\beta J}\cosh(3\beta\mu_0 H) + 6\,e^{-\beta J}\cosh(\beta\mu_0 H) \quad .$$

(b) The magnetization is

$$m = \frac{1}{\beta\zeta}\frac{\partial\zeta}{\partial H} = 3\mu_0 \cdot \left(\frac{e^{3\beta J}\sinh(3\beta\mu_0 H) + e^{-\beta J}\sinh(\beta\mu_0 H)}{e^{3\beta J}\cosh(3\beta\mu_0 J) + 3\,e^{-\beta J}\cosh(\beta\mu_0 H)}\right)$$

(c) Expanding $m(T, H)$ to lowest order in H, we have

$$m = 3\beta\mu_0^2\,H \cdot \left(\frac{3\,e^{3\beta J} + e^{-\beta J}}{e^{3\beta J} + 3\,e^{-\beta J}}\right) + \mathcal{O}(H^3) \quad .$$

Thus,

$$\chi(T) = \frac{N_\triangle}{V} \cdot \frac{3\mu_0^2}{k_\mathrm{B} T} \cdot \left(\frac{3\,e^{3J/k_\mathrm{B} T} + e^{-J/k_\mathrm{B} T}}{e^{3J/k_\mathrm{B} T} + 3\,e^{-J/k_\mathrm{B} T}}\right) \quad .$$

(d) Note that

$$F = \frac{1}{\beta}\ln Z \quad , \quad E = \frac{\partial\ln Z}{\partial\beta} \quad .$$

Thus,

$$S = \frac{E - F}{T} = k_{\mathrm{B}} \left(\ln Z - \beta \, \frac{\partial \ln Z}{\partial \beta} \right) = N_{\triangle} k_{\mathrm{B}} \left(\ln \zeta - \beta \, \frac{\partial \ln \zeta}{\partial \beta} \right) \quad .$$

So the entropy is

$$S(T, H, N_{\triangle}) = N_{\triangle} k_{\mathrm{B}} \ln \left(2 \, e^{3\beta J} \cosh(3\beta \mu_0 H) + 6 \, e^{-\beta J} \cosh(\beta \mu_0 H) \right)$$

$$- 6 N_{\triangle} \beta J k_{\mathrm{B}} \cdot \left(\frac{e^{3\beta J} \cosh(3\beta \mu_0 H) - e^{-\beta J} \cosh(\beta \mu_0 H)}{2 \, e^{3\beta J} \cosh(3\beta \mu_0 H) + 6 \, e^{-\beta J} \cosh(\beta \mu_0 H)} \right)$$

$$- 6 N_{\triangle} \beta \mu_0 H k_{\mathrm{B}} \cdot \left(\frac{e^{3\beta J} \sinh(3\beta \mu_0 H) + e^{-\beta J} \sinh(\beta \mu_0 H)}{2 \, e^{3\beta J} \cosh(3\beta \mu_0 H) + 6 \, e^{-\beta J} \cosh(\beta \mu_0 H)} \right) \quad .$$

Setting $H = 0$ we have

$$S(T, H = 0, N_{\triangle}) = N_{\triangle} k_{\mathrm{B}} \ln 2 + N_{\triangle} k_{\mathrm{B}} \ln \left(1 + 3 \, e^{-4J/k_{\mathrm{B}}T} \right) + \frac{N_{\triangle} J}{T} \cdot \left(\frac{12 \, e^{-4J/k_{\mathrm{B}}T}}{1 + 3 \, e^{-4J/k_{\mathrm{B}}T}} \right)$$

$$= N_{\triangle} k_{\mathrm{B}} \ln 6 + N_{\triangle} k_{\mathrm{B}} \ln \left(1 + \tfrac{1}{3} \, e^{4J/k_{\mathrm{B}}T} \right) - \frac{N_{\triangle} J}{T} \cdot \left(\frac{4 \, e^{4J/k_{\mathrm{B}}T}}{3 + e^{4J/k_{\mathrm{B}}T}} \right) \quad .$$

(e) Note that for $J = 0$ we have $m = 3\mu_0^2 H / k_{\mathrm{B}} T$, corresponding to three independent Ising spins. The $H = 0$ entropy is then $N_{\triangle} k_{\mathrm{B}} \ln 8 = 3 N_{\triangle} k_{\mathrm{B}} \ln 2$, as expected. As $J \to +\infty$ we have $m = 9\mu_0^2 \, H / k_{\mathrm{B}} T = (3\mu_0)^2 H / k_{\mathrm{B}} T$, and each trimer acts as a single $\mathbb{Z}_2$ Ising spin, but with moment $3\mu_0$. The zero field entropy in this limit tends to $N_{\triangle} k_{\mathrm{B}} \ln 2$, again corresponding to a single $\mathbb{Z}_2$ Ising degree of freedom per trimer. For $J \to -\infty$, we have $m = \mu_0^2 \, H / k_{\mathrm{B}} T$ and $S = N_{\triangle} k_{\mathrm{B}} \ln 6$. This is because the only allowed (*i.e.* finite energy) states of each trimer are the three states with magnetization $+\mu_0$ and the three states with magnetization $-\mu_0$, all of which are degenerate at $H = 0$.

(4.4) In §4.9.4 of the lecture notes, we considered a simple model for the elasticity of wool in which each of N monomers was in one of two states A or B, with energies $\varepsilon_{\mathrm{A,B}}$ and lengths $\ell_{\mathrm{A,B}}$. Consider now the case where the A state is doubly degenerate due to a magnetic degree of freedom which does not affect the energy or the length of the $\mathrm{A}^{\pm}$ monomers.

(a) Generalize the results from this section of the lecture notes and show that you can write the Hamiltonian $\hat{H}$ and chain length $\hat{L}$ in terms of spin variables $S_j \in \{-1, 0, 1\}$, where $S_j = \pm 1$ if monomer j is in state $\mathrm{A}^{\pm}$, and $S_j = 0$ if it is in state B. Construct the appropriate generalization of $\hat{K} - \hat{H} - \tau \hat{L}$.

(b) Find the equilibrium length $L(T, \tau, N)$ as a function of the temperature, tension, and number of monomers.

(c) Now suppose an external magnetic field is present, so the energies of the $\mathrm{A}^{\pm}$ states are split, with $\varepsilon_{\mathrm{A}^{\pm}} = \varepsilon_{\mathrm{A}} \mp \mu_0 H$. Find an expression for $L(T, \tau, H, N)$.

Solution :

(a) Take

$$\hat{H} = \sum_{j=1}^{N} \left[\varepsilon_{\mathrm{B}} + (\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}}) S_j^2 \right] \quad , \qquad \hat{L} = \sum_{j=1}^{N} \left[\ell_{\mathrm{B}} + (\ell_{\mathrm{A}} - \ell_{\mathrm{B}}) S_j^2 \right] \quad ,$$

resulting in

$$\hat{K} = \hat{H} - \tau \hat{L} = N(\varepsilon_{\mathrm{B}} - \tau \ell_{\mathrm{B}}) + \Delta \sum_{j=1}^{N} S_j^2 \quad ,$$

where

$$\Delta = (\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}}) - \tau(\ell_{\mathrm{A}} - \ell_{\mathrm{B}}) \quad .$$

(b) The partition function is

$$Y(T, \tau, N) = e^{-G/k_{\mathrm{B}}T} = \mathsf{Tr}\, e^{-\hat{K}/k_{\mathrm{B}}T}$$
$$= e^{-N(\varepsilon_{\mathrm{B}} - \tau \ell_{\mathrm{B}})/k_{\mathrm{B}}T} \left(1 + 2\, e^{-\Delta/k_{\mathrm{B}}T}\right)^{N} \quad .$$

Thus, the Gibbs free energy is

$$G(T, \tau, N) = -k_{\mathrm{B}}T \ln Y(T, \tau, N) = N(\varepsilon_{\mathrm{B}} - \tau \ell_{\mathrm{B}}) - N k_{\mathrm{B}} T \ln\left(1 + 2\, e^{-\Delta/k_{\mathrm{B}}T}\right) \quad .$$

The equilibrium length is

$$L = -\frac{\partial G}{\partial \tau} = N\ell_{\mathrm{B}} + N(\ell_{\mathrm{A}} - \ell_{\mathrm{B}}) \cdot \frac{2\, e^{-\Delta/k_{\mathrm{B}}T}}{1 + 2\, e^{-\Delta/k_{\mathrm{B}}T}} \quad .$$

Note that $L = N\ell_{\mathrm{A}}$ for $\Delta \to -\infty$ and $L = N\ell_{\mathrm{B}}$ for $\Delta \to +\infty$.

(c) Accounting for the splitting of the two A states,

$$L = N\ell_{\mathrm{B}} + N(\ell_{\mathrm{A}} - \ell_{\mathrm{B}}) \cdot \frac{2\, e^{-\Delta/k_{\mathrm{B}}T} \cosh(\mu_0 H/k_{\mathrm{B}}T)}{1 + 2\, e^{-\Delta/k_{\mathrm{B}}T} \cosh(\mu_0 H/k_{\mathrm{B}}T)} \quad .$$

(4.5) Consider a generalization of the situation in §4.4 of the notes where now three reservoirs are in thermal contact, with any pair of systems able to exchange energy.

(a) Assuming interface energies are negligible, what is the total density of states $D(E)$? Your answer should be expressed in terms of the densities of states functions $D_{1,2,3}$ for the three individual systems.

(b) Find an expression for $P(E_1, E_2)$, which is the joint probability distribution for system 1 to have energy E_1 while system 2 has energy E_2 and the total energy of all three systems is $E_1 + E_2 + E_3 = E$.

(c) Extremize $P(E_1, E_2)$ with respect to $E_{1,2}$. Show that this requires the temperatures for all three systems must be equal: $T_1 = T_2 = T_3$. Writing $E_j = E_j^* + \delta E_j$, where E_j^* is the extremal solution ($j = 1, 2$), expand $\ln P(E_1^* + \delta E_1 , E_2^* + \delta E_2)$ to second order in the variations δE_j. Remember that

$$S = k_{\rm B} \ln D \quad , \quad \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T} \quad , \quad \left(\frac{\partial^2 S}{\partial E^2} \right)_{V,N} = -\frac{1}{T^2 C_V} \quad .$$

(d) Assuming a Gaussian form for $P(E_1, E_2)$ as derived in part (c), find the variance of the energy of system 1,

$$\mathsf{Var}(E_1) = \left\langle (E_1 - E_1^*)^2 \right\rangle \quad .$$

Solution :

(a) The total density of states is a convolution:

$$D(E) = \int\limits_{-\infty}^{\infty} \!\! dE_1 \int\limits_{-\infty}^{\infty} \!\! dE_2 \int\limits_{-\infty}^{\infty} \!\! dE_3 \, D_1(E_1) \, D_2(E_2) \, D_3(E_3) \, \delta(E - E_1 - E_2 - E_3) \quad .$$

(b) The joint probability density $P(E_1, E_2)$ is given by

$$P(E_1, E_2) = \frac{D_1(E_2) \, D_2(E_2) \, D_3(E - E_1 - E_2)}{D(E)} \quad .$$

(c) We set the derivatives $\partial \ln P/\partial E_{1,2} = 0$, which gives

$$\frac{\partial \ln P}{\partial E_1} = \frac{\partial \ln D_1}{\partial E_1} - \frac{\partial D_3}{\partial E_3} = 0 \quad , \quad \frac{\partial \ln P}{\partial E_2} = \frac{\partial \ln D_3}{\partial E_2} - \frac{\partial D_3}{\partial E_3} = 0 \quad ,$$

where $E_3 = E - E_1 - E_2$ in the argument of $D_3(E_3)$. Thus, we have

$$\frac{\partial \ln D_1}{\partial E_1} = \frac{\partial \ln D_2}{\partial E_2} = \frac{\partial \ln D_3}{\partial E_3} \equiv \frac{1}{T} \quad .$$

Expanding $\ln P(E_1^* + \delta E_1 , E_2^* + \delta E_2)$ to second order in the variations δE_j, we find the first order terms cancel, leaving

$$\ln P(E_1^* + \delta E_1 , E_2^* + \delta E_2) = \ln P(E_1^* , E_2^*) - \frac{(\delta E_1)^2}{2 k_{\rm B} T^2 C_1} - \frac{(\delta E_2)^2}{2 k_{\rm B} T^2 C_2} - \frac{(\delta E_1 + \delta E_2)^2}{2 k_{\rm B} T^2 C_3} + \cdots \quad ,$$

where $\partial^2 \ln D_j/\partial E_j^2 = -1/2 k_{\rm B} T^2 C_j$, with C_j the heat capacity at constant volume and particle number. Thus,

$$P(E_1, E_2) = \frac{\sqrt{\det(\mathcal{C}^{-1})}}{2\pi k_{\rm B} T^2} \exp \left(-\frac{1}{2 k_{\rm B} T^2} \, \mathcal{C}_{ij}^{-1} \, \delta E_i \, \delta E_j \right) \quad ,$$

where the matrix $\mathcal{C}^{-1}$ is defined as

$$\mathcal{C}^{-1} = \begin{pmatrix} C_1^{-1} + C_3^{-1} & C_3^{-1} \\ C_3^{-1} & C_2^{-1} + C_3^{-1} \end{pmatrix} \quad .$$

One finds

$$\det(\mathcal{C}^{-1}) = C_1^{-1} C_2^{-1} + C_1^{-1} C_3^{-1} + C_2^{-1} C_3^{-1} \quad .$$

The prefactor in the above expression for $P(E_1, E_2)$ has been fixed by the normalization condition $\int dE_1 \int dE_2 P(E_1, E_2) = 1$.

(d) Integrating over E_2, we obtain $P(E_1)$:

$$P(E_1) = \int_{-\infty}^{\infty} dE_2 \, P(E_1, E_2) = \frac{1}{\sqrt{2\pi k_\mathrm{B} \widetilde{C}_1 T^2}} e^{-(\delta E_1)^2 / 2 k_\mathrm{B} \widetilde{C}_1 T^2} \quad ,$$

where

$$\widetilde{C}_1 = \frac{C_2^{-1} + C_3^{-1}}{C_1^{-1} C_2^{-1} + C_1^{-1} C_3^{-1} + C_2^{-1} C_3^{-1}} \quad .$$

Thus,

$$\langle (\delta E_1)^2 \rangle = \int_{-\infty}^{\infty} dE_1 \, (\delta E_1)^2 = k_\mathrm{B} \widetilde{C}_1 T^2 \quad .$$

(4.6) Show that the Boltzmann entropy $S = -k_{\mathrm{B}} \sum_n P_n \ln P_n$ agrees with the statistical entropy $S(E) = k_{\mathrm{B}} \ln D(E, V, N)$ in the thermodynamic limit.

Solution :

Let's first examine the canonical partition function, $Z = \int\limits_0^\infty dE\, D(E)\, e^{-\beta E}$. We compute this integral via the saddle point method, extremizing the exponent, $\ln D(E) - \beta E$, with respect to E. The resulting maximum lies at $\bar{E}$ such that $\frac{1}{T} = \frac{\partial S}{\partial E}\big|_{\bar{E}}$, where $S(E) = k_{\mathrm{B}} \ln D(E)$ is the statistical entropy computed in the microcanonical ensemble. The ordinary canonical partition function is then

$$
Z \approx D(\bar{E})\, e^{-\beta \bar{E}} \int\limits_{-\infty}^\infty d\,\delta E\; e^{-(\delta E)^2 / 2k_{\mathrm{B}} T^2 C_V}
$$

$$
= (2\pi k_{\mathrm{B}} T^2 C_V)^{1/2}\, D(\bar{E})\, e^{-\beta \bar{E}} \quad .
$$

Taking the logarithm, we obtain the Helmholtz free energy,

$$
F = -k_{\mathrm{B}} T \ln Z = -k_{\mathrm{B}} \ln D(\bar{E}) + \bar{E} - \tfrac{1}{2} k_{\mathrm{B}} T \ln\!\big(2\pi k_{\mathrm{B}} T^2 C_V\big) \quad .
$$

Now $S_{\mathrm{OCE}} = -k_{\mathrm{B}} \sum_n P_n \ln P_n$, with $P_n = \frac{1}{Z} e^{-\beta E_n}$. Therefore

$$
S_{\mathrm{OCE}}(T) = \frac{k_{\mathrm{B}}}{Z} \int\limits_0^\infty dE\, D(E)\, e^{-\beta E} \big(\ln Z + \beta E\big)
$$

$$
= k_{\mathrm{B}} \ln Z + \frac{1}{T} \cdot \frac{\int_0^\infty dE\, E\, D(E)\, e^{-\beta E}}{\int_0^\infty dE\, D(E)\, e^{-\beta E}} \quad .
$$

The denominator of the second term is Z, which we have already evaluated. We evaluate the numerator using the same expansion about $\bar{E}$. The only difference is the additional factor of $E = \bar{E} + \delta E$ in the integrand. The δE term integrates to zero, since the remaining factors in the integrand yield $D(\bar{E})\, e^{-\beta \bar{E}}\, e^{-(\delta E)^2 / 2k_{\mathrm{B}} T^2 C_V}$, which is even in δE. Thus, the second term in the above equation is simply $\bar{E}/T$, and we obtain

$$
S_{\mathrm{OCE}} = k_{\mathrm{B}} \ln D(\bar{E}) + \tfrac{1}{2} k_{\mathrm{B}} \ln\!\big(2\pi k_{\mathrm{B}} T^2 C_V\big) \quad .
$$

The RHS here is dominated by the first term, which is extensive, whereas the second term is of order $\ln V$. Thus, we conclude that $S_{\mathrm{OCE}}(T, V, N) = S_{\mu\mathrm{CE}}(\bar{E}, V, N)$, where $\bar{E}$ and T are related by $\frac{1}{T} = \frac{\partial S}{\partial E}\big|_{\bar{E}}$.

(4.7) Consider rod-shaped molecules with moment of inertia I, and a dipole moment μ. The contribution of the rotational degrees of freedom to the Hamiltonian is

$$\hat{H}_{\mathrm{rot}} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta} - \mu E\cos\theta \quad,$$

where E is the external electric field, and (θ, ϕ) are polar and azimuthal angles describing the molecular orientation[1].

- (a) Calculate the contribution of the rotational degrees of freedom of each dipole to the classical partition function.

- (b) Obtain the mean polarization $P = \langle \mu\cos\theta \rangle$ of each dipole.

- (c) Find the zero-field isothermal polarizability, $\chi(T) = \left(\frac{\partial P}{\partial E}\right)_{E=0}$.

- (d) Calculate the rotational energy per particle at finite field E, and comment on its high and low-temperature limits.

- (e) Sketch the rotational heat capacity per dipole as a function of temperature.

Solution :

(a) The rotational contribution to the single particle partition function is

$$\xi_{\mathrm{rot}} = \int_{-\infty}^{\infty}dp_\theta \int_{-\infty}^{\infty}dp_\phi \int_0^\pi d\theta \int_0^{2\pi}d\phi \; e^{-p_\theta^2/2Ik_{\mathrm{B}}T} \, e^{-p_\phi^2/2Ik_{\mathrm{B}}T\sin^2\theta} \, e^{\mu E\cos\theta/k_{\mathrm{B}}T}$$

$$= 2\pi \cdot (2\pi Ik_{\mathrm{B}}T)^{1/2} \int_0^\pi d\theta \; e^{\mu E\cos\theta/k_{\mathrm{B}}T} \int_{-\infty}^{\infty}dp_\theta \; e^{-p_\phi^2/2Ik_{\mathrm{B}}T\sin^2\theta}$$

$$= 4\pi^2 Ik_{\mathrm{B}}T \int_0^\pi d\theta \; \sin\theta \, e^{\mu E\cos\theta/k_{\mathrm{B}}T} = \frac{8\pi^2 I(k_{\mathrm{B}}T)^2}{\mu E} \sinh\left(\frac{\mu E}{k_{\mathrm{B}}T}\right) \quad.$$

The translational contribution is $\xi_{\mathrm{tr}} = V\lambda_T^{-3}$. The single particle free energy is then

$$f = -k_{\mathrm{B}}T\ln\left(8\pi^2 Ik_{\mathrm{B}}^2T^2\right) + k_{\mathrm{B}}T\ln(\mu E) - k_{\mathrm{B}}T\ln\sinh\left(\frac{\mu E}{k_{\mathrm{B}}T}\right) - k_{\mathrm{B}}T\ln\left(V/\lambda_T^3\right) \quad.$$

(b) The mean polarization of each dipole is

$$P = -\frac{\partial f}{\partial E} = -\frac{k_{\mathrm{B}}T}{E} + \mu\,\mathrm{ctnh}\left(\frac{\mu E}{k_{\mathrm{B}}T}\right) \quad.$$

(c) We expand $\mathrm{ctnh}\,(x) = \frac{1}{x} + \frac{x}{3} + \mathcal{O}(x^3)$ in a Laurent series, whence $P = \mu^2 E/3k_{\mathrm{B}}T + \mathcal{O}(E^3)$. Then $\chi(T) = \mu^2/3k_{\mathrm{B}}T$, which is of the Curie form familiar from magnetic systems.

(d) We have $\xi_{\mathrm{rot}} = \mathrm{Tr}\, e^{-\beta\hat{h}_{\mathrm{rot}}}$, hence

$$\varepsilon_{\mathrm{rot}} = \langle\hat{h}_{\mathrm{rot}}\rangle = -\frac{\partial\ln\xi_{\mathrm{rot}}}{\partial\beta} = -\frac{\partial}{\partial\beta}\left\{-2\ln\beta + \ln\sinh(\beta\mu E)\right\}$$

$$= 2k_{\mathrm{B}}T - \mu E\,\mathrm{ctnh}\left(\frac{\mu E}{k_{\mathrm{B}}T}\right) \quad.$$

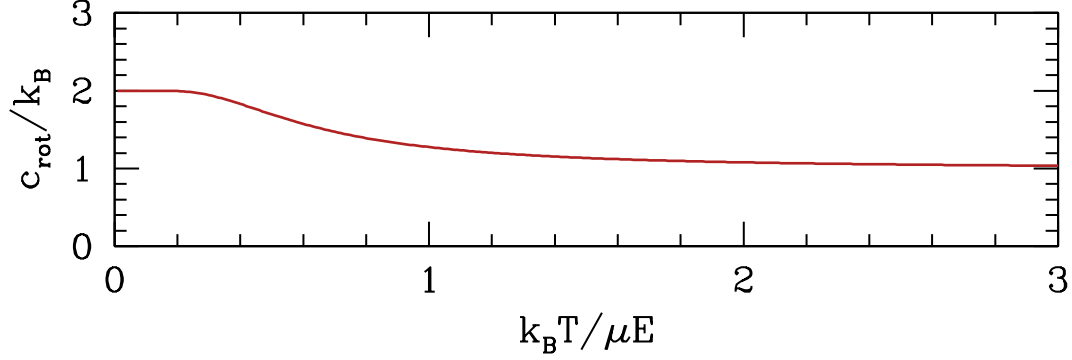[1]This is problem 4.12 from vol. 1 of M. Kardar.

Figure 2: Rotational heat capacity $c_{\rm rot}(T)$ for problem 7.

At high temperatures $T \gg \mu E/k_{\rm B}$, the argument of $\operatorname{ctnh} x$ is very small, and using the Laurent expansion we find $\varepsilon_{\rm rot} = k_{\rm B}T$. This comports with our understanding from equipartition, since there are only two quadratic degrees of freedom present (p_θ and p_ϕ). The orientational degree of freedom θ does not enter because $\mu E \cos\theta \ll k_{\rm B}T$ in this regime. Unlike the rotational kinetic energy, the rotational potential energy is bounded. In the limit $T \ll \mu E/k_{\rm B}$, we have that the argument of $\operatorname{ctnh} x$ is very large, hence $\varepsilon_{\rm rot} \approx 2k_{\rm B}T - \mu E$. This can be understood as follows. If we change variables to $\tilde{p}_\phi \equiv p_\phi/\sin\theta$, then we have

$$\xi_{\rm rot} = \int\limits_{-\infty}^{\infty} dp_\theta \int\limits_{-\infty}^{\infty} d\tilde{p}_\phi \int\limits_{0}^{\pi} d\theta \, \sin\theta \int\limits_{0}^{2\pi} d\phi \, e^{-p_\theta^2/2Ik_{\rm B}T} \, e^{-\tilde{p}_\phi^2/2Ik_{\rm B}T} \, e^{\mu E \cos\theta/k_{\rm B}T}$$

$$= \int\limits_{-\infty}^{\infty} dp_\theta \int\limits_{-\infty}^{\infty} d\tilde{p}_\phi \int\limits_{-1}^{1} dx \int\limits_{0}^{2\pi} d\phi \, e^{-p_\theta^2/2Ik_{\rm B}T} \, e^{-\tilde{p}_\phi^2/2Ik_{\rm B}T} \, e^{\mu E x/k_{\rm B}T} \quad ,$$

where $x = \cos\theta$. We see that x appears *linearly* in the energy, and simple dimensional analysis reveals that any degree of freedom ζ which appears homogeneously as $U(\zeta) \propto \zeta^r$ contributes $k_{\rm B}T/r$ to the average energy. In our case, we have quadratic contributions to the Hamiltonian from p_θ and $\tilde{p}_\phi$, a linear contribution from $x = \cos\theta$, and ϕ itself does not appear. Hence $\varepsilon = -\mu E + 2 \times \frac{1}{2}k_{\rm B}T + k_{\rm B}T = -\mu E + 2k_{\rm B}T$. The $-\mu E$ term is the minimum value of the potential energy.

(e) The rotational heat capacity per molecule, sketched in Fig. 2, is given by

$$c_{\rm rot} = \frac{\partial \varepsilon_{\rm rot}}{\partial T} = 2k_{\rm B} - k_{\rm B}\left(\frac{\mu E/k_{\rm B}T}{\sinh(\mu E/k_{\rm B}T)}\right)^2 \quad .$$

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(4.8) Consider a surface containing N_s adsorption sites which is in equilibrium with a two-component nonrelativistic ideal gas containing atoms of types A and B . (Their respective masses are m_A and m_B). Each adsorption site can be in one of three possible states: (i) vacant, (ii) occupied by an A atom, with energy $-\Delta_A$, and (ii) occupied with a B atom, with energy $-\Delta_B$.

 (a) Find the grand partition function for the surface, $\Xi_{\text{surf}}(T, \mu_A, \mu_B, N_s)$.

 (b) Suppose the number densities of the gas atoms are n_A and n_B. Find the fraction $f_A(n_A, n_B, T)$ of adsorption sites with A atoms, and the fraction $f_0(n_A, n_B, T)$ of adsorption sites which are vacant.

Solution :

(a) The surface grand partition function is

$$\Xi_{\text{surf}}(T, \mu_A, \mu_B, N_s) = \left(1 + e^{(\Delta_A + \mu_A)/k_B T} + e^{(\Delta_B + \mu_B)/k_B T}\right)^{N_s} \quad .$$

(b) From the grand partition function of the gas, we have

$$n_A = \lambda_{T,A}^{-3}\, e^{\mu_A/k_B T} \quad , \qquad n_B = \lambda_{T,B}^{-3}\, e^{\mu_B/k_B T} \quad ,$$

with

$$\lambda_{T,A} = \sqrt{\frac{2\pi \hbar^2}{m_A k_B T}} \quad , \qquad \lambda_{T,B} = \sqrt{\frac{2\pi \hbar^2}{m_B k_B T}} \quad .$$

Thus,

$$f_0 = \frac{1}{1 + n_A\, \lambda_{T,A}^3\, e^{\Delta_A/k_B T} + n_B\, \lambda_{T,B}^3\, e^{\Delta_B/k_B T}}$$

$$f_A = \frac{n_A\, \lambda_{T,A}^3\, e^{\Delta_A/k_B T}}{1 + n_A\, \lambda_{T,A}^3\, e^{\Delta_A/k_B T} + n_B\, \lambda_{T,B}^3\, e^{\Delta_B/k_B T}}$$

$$f_B = \frac{n_B\, \lambda_{T,B}^3\, e^{\Delta_B/k_B T}}{1 + n_A\, \lambda_{T,A}^3\, e^{\Delta_A/k_B T} + n_B\, \lambda_{T,B}^3\, e^{\Delta_B/k_B T}} \quad .$$

Note that $f_0 + f_A + f_B = 1$.

(4.9) Consider a two-dimensional gas of identical classical, noninteracting, massive relativistic particles with dispersion $\varepsilon(\boldsymbol{p}) = \sqrt{\boldsymbol{p}^2 c^2 + m^2 c^4}$.

(a) Compute the free energy $F(T, V, N)$.

(b) Find the entropy $S(T, V, N)$.

(c) Find an equation of state relating the fugacity $z = e^{\mu/k_{\mathrm{B}}T}$ to the temperature T and the pressure p.

Solution :

(a) We have $Z = (\zeta A)^N / N!$ where A is the area and

$$\zeta(T) = \int \frac{d^2p}{h^2} e^{-\beta\sqrt{p^2c^2 + m^2c^4}} = \frac{2\pi}{(\beta hc)^2} \left(1 + \beta mc^2\right) e^{-\beta mc^2} \quad .$$

To obtain this result it is convenient to change variables to $u = \beta\sqrt{p^2 c^2 + m^2 c^4}$, in which case $p\,dp = u\,du/\beta^2 c^2$, and the lower limit on u is mc^2. The free energy is then

$$F = -k_{\mathrm{B}}T \ln Z = Nk_{\mathrm{B}}T \ln\left(\frac{2\pi \hbar^2 c^2 N}{(k_{\mathrm{B}}T)^2 A}\right) - Nk_{\mathrm{B}}T \ln\left(1 + \frac{mc^2}{k_{\mathrm{B}}T}\right) + Nmc^2 \quad .$$

where we are taking the thermodynamic limit with $N \to \infty$.

(b) We have

$$S = -\frac{\partial F}{\partial T} = -Nk_{\mathrm{B}} \ln\left(\frac{2\pi \hbar^2 c^2 N}{(k_{\mathrm{B}}T)^2 A}\right) + Nk_{\mathrm{B}} \ln\left(1 + \frac{mc^2}{k_{\mathrm{B}}T}\right) + Nk_{\mathrm{B}}\left(\frac{mc^2 + 2k_{\mathrm{B}}T}{mc^2 + k_{\mathrm{B}}T}\right) \quad .$$

(c) The grand partition function is

$$\Xi(T, V, \mu) = e^{-\beta\Omega} = e^{\beta pV} = \sum_{N=0}^{\infty} Z_N(T, V, N) \, e^{\beta\mu N} \quad .$$

We then find $\Xi = \exp\left(\zeta A \, e^{\beta\mu}\right)$, and

$$p = \frac{(k_{\mathrm{B}}T)^3}{2\pi(\hbar c)^2}\left(1 + \frac{mc^2}{k_{\mathrm{B}}T}\right) e^{(\mu - mc^2)/k_{\mathrm{B}}T} \quad .$$

Note that

$$n = \frac{\partial(\beta p)}{\partial\mu} = \frac{p}{k_{\mathrm{B}}T} \quad \Longrightarrow \quad p = nk_{\mathrm{B}}T \quad .$$

(4.10) A nonrelativistic gas of spin-$\frac{1}{2}$ particles of mass m at temperature T and pressure p is in equilibrium with a surface. There is no magnetic field in the bulk, but the surface itself is magnetic, so the energy of an adsorbed particle is $-\Delta - \mu_0 H \sigma$, where $\sigma = \pm 1$ is the spin polarization and H is the surface magnetic field. The surface has N_S adsorption sites.

  (a) Compute the Landau free energy of the gas $\Omega_{\text{gas}}(T, V, \mu)$. Remember that each particle has two spin polarization states.

  (b) Compute the Landau free energy of the surface $\Omega_{\text{surf}}(T, H, N_S)$. Remember that each adsorption site can be in one of three possible states: empty, occupied with $\sigma = +1$, and occupied with $\sigma = -1$.

  (c) Find an expression for the fraction $f(p, T, \Delta, H)$ of occupied adsorption sites.

  (d) Find the surface magnetization, $M = \mu_0 \big(N_{\text{surf},\uparrow} - N_{\text{surf},\downarrow} \big)$.

Solution :

(a) We have

$$\Xi_{\text{gas}}(T, V, \mu) = \sum_{N=0}^{\infty} e^{N\mu/k_B T} \, Z(T, V, N) = \sum_{N=0}^{\infty} \frac{V^N}{N!} \, e^{N\mu/k_B T} \, 2^N \, \lambda_T^{-3N}$$

$$= \exp\left(2 V k_B T \lambda_T^{-3} \, e^{\mu/k_B T} \right) \quad,$$

where $\lambda_T = \sqrt{2\pi \hbar^2 / m k_B T}$ is the thermal wavelength. Thus,

$$\Omega_{\text{gas}} = -k_B T \ln \Xi_{\text{gas}} = -2 V k_B T \lambda_T^{-3} \, e^{\mu/k_B T} \quad.$$

(b) Each site on the surface is independent, with three possible energy states: $E = 0$ (vacant), $E = -\Delta - \mu_0 H$ (occupied with $\sigma = +1$), and $E = -\Delta + \mu_0 H$ (occupied with $\sigma = -1$). Thus,

$$\Xi_{\text{surf}}(T, H, N_S) = \left(1 + e^{(\mu + \Delta + \mu_0 H)/k_B T} + e^{(\mu + \Delta - \mu_0 H)/k_B T} \right)^{N_S} \quad.$$

The surface free energy is

$$\Omega_{\text{surf}}(T, H, N_S) = -k_B T \ln \Xi_{\text{surf}} = -N_S k_B T \ln \left(1 + 2 \, e^{(\mu + \Delta)/k_B T} \cosh(\mu_0 H / k_B T) \right) \quad.$$

(c) The fraction of occupied surface sites is $f = \langle N_{\text{surf}} / N_S \rangle$. Thus,

$$f = -\frac{1}{N_S} \frac{\partial \Omega_{\text{surf}}}{\partial \mu} = \frac{2 \, e^{(\mu + \Delta)/k_B T} \cosh(\mu_0 H / k_B T)}{1 + 2 \, e^{(\mu + \Delta)/k_B T} \cosh(\mu_0 H / k_B T)} = \frac{2}{2 + e^{-(\mu + \Delta)/k_B T} \operatorname{sech}(\mu_0 H / k_B T)} \quad.$$

To find $f(p, T, \Delta, H)$, we must eliminate μ in favor of p, the pressure in the gas. This is easy! From $\Omega_{\text{gas}} = -pV$, we have $p = 2 k_B T \lambda_T^{-3} \, e^{\mu/k_B T}$, hence

$$e^{-\mu/k_B T} = \frac{2 k_B T}{p \lambda_T^3} \quad.$$

Thus,

$$f(p, T, \Delta, H) = \frac{p \lambda_T^3}{p \lambda_T^3 + k_B T \, e^{-\Delta/k_B T} \operatorname{sech}(\mu_0 H / k_B T)} \quad.$$

Note that $f \to 1$ when $\Delta \to \infty$, when $T \to 0$, when $p \to \infty$, or when $H \to \infty$.

(d) The surface magnetization is

$$M = -\frac{\partial \Omega_{\text{surf}}}{\partial H} = N_{\text{S}}\,\mu_0 \cdot \frac{2\,e^{(\mu+\Delta)/k_{\text{B}}T}\,\sinh(\mu_0 H/k_{\text{B}}T)}{1 + 2\,e^{(\mu+\Delta)/k_{\text{B}}T}\,\cosh(\mu_0 H/k_{\text{B}}T)}$$

$$= \frac{N_{\text{S}}\,\mu_0\,p\,\lambda_T^3\,\tanh(\mu_0 H/k_{\text{B}}T)}{p\,\lambda_T^3 + k_{\text{B}}T\,e^{-\Delta/k_{\text{B}}T}\text{sech}(\mu_0 H/k_{\text{B}}T)} \quad .$$

(4.11) A classical gas consists of particles of two species: A and B. The dispersions for these species are

$$\varepsilon_{\mathrm{A}}(\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} \quad , \quad \varepsilon_{\mathrm{B}}(\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{4m} - \Delta \quad .$$

In other words, $m_{\mathrm{A}} = m$ and $m_{\mathrm{B}} = 2m$, and there is an additional energy offset $-\Delta$ associated with the B species.

(a) Find the grand potential $\Omega(T, V, \mu_{\mathrm{A}}, \mu_{\mathrm{B}})$.

(b) Find the number densities $n_{\mathrm{A}}(T, \mu_{\mathrm{A}}, \mu_{\mathrm{B}})$ and $n_{\mathrm{B}}(T, \mu_{\mathrm{A}}, \mu_{\mathrm{B}})$.

(c) If $2\mathrm{A} \rightleftharpoons \mathrm{B}$ is an allowed reaction, what is the relation between n_{A} and n_{B}?
(*Hint : What is the relation between μ_{A} and μ_{B}?*)

(d) Suppose initially that $n_{\mathrm{A}} = n$ and $n_{\mathrm{B}} = 0$. Find n_{A} in equilibrium, as a function of T and n and constants.

Solution :

(a) The grand partition function Ξ is a product of contributions from the A and B species, and the grand potential is a sum:

$$\Omega = -Vk_{\mathrm{B}}T \lambda_T^{-3} e^{\mu_{\mathrm{A}}/k_{\mathrm{B}}T} - 2^{3/2} Vk_{\mathrm{B}}T \lambda_T^{-3} e^{(\mu_{\mathrm{B}}+\Delta)/k_{\mathrm{B}}T}$$

Here, we have defined the thermal wavelength for the A species as $\lambda_T \equiv \lambda_{T,\mathrm{A}} = \sqrt{2\pi\hbar^2/mk_{\mathrm{B}}T}$. For the B species, since the mass is twice as great, we have $\lambda_{T,\mathrm{B}} = 2^{-1/2}\lambda_{T,\mathrm{A}}$.

(b) The number densities are

$$n_{\mathrm{A}} = -\frac{1}{V} \cdot \frac{\partial \Omega}{\partial \mu_{\mathrm{A}}} = V\lambda_T^{-3} e^{\mu_{\mathrm{A}}/k_{\mathrm{B}}T}$$

$$n_{\mathrm{B}} = -\frac{1}{V} \cdot \frac{\partial \Omega}{\partial \mu_{\mathrm{B}}} = 2^{3/2} V\lambda_T^{-3} e^{(\mu_{\mathrm{B}}+\Delta)/k_{\mathrm{B}}T} \quad .$$

If the reaction $2\mathrm{A} \rightleftharpoons \mathrm{B}$ is allowed, then the chemical potentials of the A and B species are related by $\mu_{\mathrm{B}} = 2\mu_{\mathrm{A}} \equiv 2\mu$. We then have

$$n_{\mathrm{A}}\lambda_T^3 = e^{\mu/k_{\mathrm{B}}T} \quad , \quad n_{\mathrm{B}}\lambda_T^3 = 2^{3/2} e^{(2\mu+\Delta)/k_{\mathrm{B}}T} \quad .$$

(c) The relation we seek is therefore

$$n_{\mathrm{B}} = 2^{3/2} n_{\mathrm{A}}^2 \lambda_T^3 e^{\Delta/k_{\mathrm{B}}T} \quad .$$

(d) If we initially have $n_{\mathrm{A}} = n$ and $n_{\mathrm{B}} = 0$, then in general we must have

$$n_{\mathrm{A}} + 2n_{\mathrm{B}} = n \qquad \Longrightarrow \qquad n_{\mathrm{B}} = \tfrac{1}{2}(n - n_{\mathrm{A}}) \quad .$$

Thus, eliminating n_{B}, we have a quadratic equation,

$$2^{3/2} \lambda_T^3 e^{\Delta/k_{\mathrm{B}}T} n_{\mathrm{A}}^2 = \tfrac{1}{2}(n - n_{\mathrm{A}}) \quad ,$$

the solution of which is

$$n_{\mathrm{A}} = \frac{-1 + \sqrt{1 + 16\sqrt{2}\, n\lambda_T^3\, e^{\Delta/k_{\mathrm{B}}T}}}{8\sqrt{2}\, \lambda_T^3\, e^{\Delta/k_{\mathrm{B}}T}} \quad .$$

(4.12) The potential energy density for an isotropic elastic solid is given by

$$\mathcal{U}(\boldsymbol{x}) = \mu \operatorname{Tr} \varepsilon^2 + \tfrac{1}{2}\lambda \left(\operatorname{Tr} \varepsilon\right)^2$$

$$= \mu \sum_{\alpha,\beta} \varepsilon_{\alpha\beta}^2(\boldsymbol{x}) + \tfrac{1}{2}\lambda \left(\sum_{\alpha} \varepsilon_{\alpha\alpha}(\boldsymbol{x})\right)^2 \quad,$$

where μ and λ are the Lamé parameters and

$$\varepsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u^\alpha}{\partial x^\beta} + \frac{\partial u^\beta}{\partial x^\alpha}\right) \quad,$$

with $\boldsymbol{u}(\boldsymbol{x})$ the local displacement field, is the *strain tensor*. The Cartesian indices α and β run over x, y, z. The kinetic energy density is

$$\mathcal{T}(\boldsymbol{x}) = \tfrac{1}{2}\rho \, \dot{\boldsymbol{u}}^2(\boldsymbol{x}) \quad.$$

(a) Assume periodic boundary conditions, and Fourier transform to wavevector space,

$$u^\alpha(\boldsymbol{x}, t) = \tfrac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \hat{u}_{\boldsymbol{k}}^\alpha(t) \, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

$$\hat{u}_{\boldsymbol{k}}^\alpha(t) = \tfrac{1}{\sqrt{V}} \int d^3x \, u^\alpha(\boldsymbol{x}, t) \, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}} \quad.$$

Write the Lagrangian $L = \int d^3x \, (\mathcal{T} - \mathcal{U})$ in terms of the generalized coordinates $\hat{u}_{\boldsymbol{k}}^\alpha(t)$ and generalized velocities $\dot{\hat{u}}_{\boldsymbol{k}}^\alpha(t)$.

(b) Find the Hamiltonian H in terms of the generalized coordinates $\hat{u}_{\boldsymbol{k}}^\alpha(t)$ and generalized momenta $\hat{\pi}_{\boldsymbol{k}}^\alpha(t)$.

(c) Find the thermodynamic average $\langle \boldsymbol{u}(0) \cdot \boldsymbol{u}(\boldsymbol{x})\rangle$.

(d) Suppose we add in a nonlocal interaction of the strain field of the form

$$\Delta U = \tfrac{1}{2}\int d^3x \int d^3x' \, \operatorname{Tr} \varepsilon(\boldsymbol{x}) \, \operatorname{Tr} \varepsilon(\boldsymbol{x}') \, v(\boldsymbol{x} - \boldsymbol{x}') \quad.$$

Repeat parts (b) and (c).

Solution :

To do the mode counting we are placing the system in a box of dimensions $L_x \times L_y \times L_z$ and imposing periodic boundary conditions. The allowed wavevectors $\boldsymbol{k}$ are of the form

$$\boldsymbol{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z}\right) \quad.$$

We shall repeatedly invoke the orthogonality of the plane waves:

$$\int\limits_0^{L_x} dx \int\limits_0^{L_y} dy \int\limits_0^{L_z} dz \, e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}} = V\delta_{\boldsymbol{k},\boldsymbol{k}'} \quad,$$

where $V = L_x L_y L_z$ is the volume. When we Fourier decompose the displacement field, we must take care to note that $\hat{u}_{\boldsymbol{k}}^\alpha$ is complex, and furthermore that $\hat{u}_{-\boldsymbol{k}}^\alpha = \left(\hat{u}_{\boldsymbol{k}}^\alpha\right)^*$, since $u^\alpha(\boldsymbol{x})$ is a real function.

(a) We then have

$$T = \int\limits_{-\infty}^{\infty} dx \, \tfrac{1}{2}\rho \, \dot{\boldsymbol{u}}^2(\boldsymbol{x}, t) = \tfrac{1}{2}\rho \sum_{\boldsymbol{k}} \left|\dot{\hat{u}}_{\boldsymbol{k}}^\alpha(t)\right|^2$$

and

$$U = \int\limits_{-\infty}^{\infty} dx \left[\tfrac{1}{2}\mu \, \frac{\partial u^\alpha}{\partial x^\beta} \frac{\partial u^\alpha}{\partial x^\beta} + \tfrac{1}{2}(\lambda + \mu)\left(\boldsymbol{\nabla}\cdot\boldsymbol{u}\right)^2 \right]$$

$$= \tfrac{1}{2}\sum_{\boldsymbol{k}} \left(\mu\,\delta^{\alpha\beta} + (\lambda+\mu)\,\hat{k}^\alpha\,\hat{k}^\beta \right) \boldsymbol{k}^2\,\hat{u}^\alpha_{\boldsymbol{k}}(t)\,\hat{u}^\beta_{-\boldsymbol{k}}(t) \quad .$$

The Lagrangian is of course $L = T - U$.

(b) The momentum $\hat{\pi}^\alpha_{\boldsymbol{k}}$ conjugate to the generalized coordinate $\hat{u}^\alpha_{\boldsymbol{k}}$ is

$$\hat{\pi}^\alpha_{\boldsymbol{k}} = \frac{\partial L}{\partial \dot{\hat{u}}^\alpha_{\boldsymbol{k}}} = \rho\,\dot{\hat{u}}^\alpha_{-\boldsymbol{k}} \quad ,$$

and the Hamiltonian is

$$H = \sum_{\boldsymbol{k}} \hat{\pi}^\alpha_{\boldsymbol{k}}\,\dot{\hat{u}}^\alpha_{\boldsymbol{k}} - L$$

$$= \sum_{\boldsymbol{k}} \left\{ \frac{\left|\hat{\pi}^\alpha_{\boldsymbol{k}}\right|^2}{2\rho} + \tfrac{1}{2}\left[\mu\left(\delta^{\alpha\beta} - \hat{k}^\alpha\,\hat{k}^\beta\right) + (\lambda + 2\mu)\,\hat{k}^\alpha\,\hat{k}^\beta \right]\boldsymbol{k}^2\,\hat{u}^\alpha_{\boldsymbol{k}}\,\hat{u}^\beta_{-\boldsymbol{k}} \right\} \quad .$$

Note that we have added and subtracted a term $\mu\,\hat{k}^\alpha\,\hat{k}^\beta$ within the expression for the potential energy. This is because $\mathbb{P}_{\alpha\beta} = \hat{k}^\alpha\,\hat{k}^\beta$ and $\mathbb{Q}_{\alpha\beta} = \delta^{\alpha\beta} - \hat{k}^\alpha\,\hat{k}^\beta$ are *projection operators* satisfying $\mathbb{P}^2 = \mathbb{P}$ and $\mathbb{Q}^2 = \mathbb{Q}$, with $\mathbb{P} + \mathbb{Q} = \mathbb{I}$, the identity. $\mathbb{P}$ projects any vector onto the direction $\hat{\boldsymbol{k}}$, and $\mathbb{Q}$ is the projector onto the (two-dimensional) subspace orthogonal to $\hat{\boldsymbol{k}}$.

(c) We can decompose $\hat{\boldsymbol{u}}_{\boldsymbol{k}}$ into a *longitudinal* component parallel to $\hat{\boldsymbol{k}}$ and a *transverse* component perpendicular to $\hat{\boldsymbol{k}}$, writing

$$\hat{\boldsymbol{u}}_{\boldsymbol{k}} = i\hat{\boldsymbol{k}}\,\hat{u}^\parallel_{\boldsymbol{k}} + i\hat{\mathbf{e}}_{\boldsymbol{k},1}\,\hat{u}^{\perp,1}_{\boldsymbol{k}} + i\hat{\mathbf{e}}_{\boldsymbol{k},2}\,\hat{u}^{\perp,2}_{\boldsymbol{k}} \quad ,$$

where $\{\hat{\mathbf{e}}_{\boldsymbol{k},1}\,,\,\hat{\mathbf{e}}_{\boldsymbol{k},2}\,,\,\hat{\boldsymbol{k}}\}$ is a right-handed orthonormal triad for each direction $\hat{\boldsymbol{k}}$. A factor of i is included so that $\hat{u}^\parallel_{-\boldsymbol{k}} = \left(\hat{u}^\parallel_{\boldsymbol{k}}\right)^*$, *etc.* With this decomposition, the potential energy takes the form

$$U = \tfrac{1}{2}\sum_{\boldsymbol{k}} \left[\mu\,\boldsymbol{k}^2 \left(\left|\hat{u}^{\perp,1}_{\boldsymbol{k}}\right|^2 + \left|\hat{u}^{\perp,2}_{\boldsymbol{k}}\right|^2 \right) + (\lambda + 2\mu)\,\boldsymbol{k}^2\left|\hat{u}^\parallel_{\boldsymbol{k}}\right|^2 \right] \quad .$$

Equipartition then means each independent degree of freedom which is quadratic in the potential contributes an average of $\tfrac{1}{2}k_{\mathrm{B}}T$ to the total energy. Recalling that $u^\parallel_{\boldsymbol{k}}$ and $u^{\perp,j}_{\boldsymbol{k}}$ ($j = 1,2$) are complex functions, and that they are each the Fourier transform of a real function (so that $\boldsymbol{k}$ and $-\boldsymbol{k}$ terms in the sum for U are equal), we have

$$\left\langle \mu\,\boldsymbol{k}^2\left|\hat{u}^{\perp,1}_{\boldsymbol{k}}\right|^2 \right\rangle = \left\langle \mu\,\boldsymbol{k}^2\left|\hat{u}^{\perp,2}_{\boldsymbol{k}}\right|^2 \right\rangle = 2 \times \tfrac{1}{2}k_{\mathrm{B}}T$$

$$\left\langle (\lambda + 2\mu)\,\boldsymbol{k}^2\left|\hat{u}^\parallel_{\boldsymbol{k}}\right|^2 \right\rangle = 2 \times \tfrac{1}{2}k_{\mathrm{B}}T \quad .$$

Thus,

$$\left\langle \left|\hat{\boldsymbol{u}}_{\boldsymbol{k}}\right|^2 \right\rangle = 4 \times \tfrac{1}{2}k_{\mathrm{B}}T \times \frac{1}{\mu\boldsymbol{k}^2} + 2 \times \tfrac{1}{2}k_{\mathrm{B}}T \times \frac{1}{(\lambda + 2\mu)\,\boldsymbol{k}^2}$$

$$= \left(\frac{2}{\mu} + \frac{1}{\lambda + 2\mu} \right) \frac{k_{\mathrm{B}}T}{\boldsymbol{k}^2} \quad .$$

Then

$$\langle \boldsymbol{u}(0) \cdot \boldsymbol{u}(\boldsymbol{x}) \rangle = \frac{1}{V} \sum_{\boldsymbol{k}} \langle |\hat{\boldsymbol{u}}_{\boldsymbol{k}}|^2 \rangle \, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

$$= \int \frac{d^3k}{(2\pi)^3} \left(\frac{2}{\mu} + \frac{1}{\lambda + 2\mu} \right) \frac{k_{\mathrm{B}}T}{\boldsymbol{k}^2} \, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

$$= \left(\frac{2}{\mu} + \frac{1}{\lambda + 2\mu} \right) \frac{k_{\mathrm{B}}T}{4\pi|\boldsymbol{x}|} \quad .$$

Recall that in three space dimensions the Fourier transform of $4\pi/\boldsymbol{k}^2$ is $1/|\boldsymbol{x}|$.

(d) The $\boldsymbol{k}$-space representation of ΔU is

$$\Delta U = \tfrac{1}{2} \sum_{\boldsymbol{k}} \boldsymbol{k}^2 \, \hat{v}(\boldsymbol{k}) \, \hat{k}^\alpha \, \hat{k}^\beta \, \hat{u}^\alpha_{\boldsymbol{k}} \, \hat{u}^\beta_{-\boldsymbol{k}} \quad ,$$

where $\hat{v}(\boldsymbol{k})$ is the Fourier transform of the interaction $v(\boldsymbol{x} - \boldsymbol{x}')$:

$$\hat{v}(\boldsymbol{k}) = \int d^3r \, v(\boldsymbol{r}) \, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \quad .$$

We see then that the effect of ΔU is to replace the Lamé parameter λ with the $\boldsymbol{k}$-dependent quantity,

$$\lambda \to \lambda(\boldsymbol{k}) \equiv \lambda + \hat{v}(\boldsymbol{k}) \quad .$$

With this simple replacement, the results of parts (b) and (c) retain their original forms, *mutatis mutandis*.

(4.13) For polyatomic molecules, the full internal partition function is written as the product

$$\xi(T) = \frac{g_{\rm el} \cdot g_{\rm nuc}}{g_{\rm sym}} \cdot \xi_{\rm vib}(T) \cdot \xi_{\rm rot}(T) \quad ,$$

where $g_{\rm el}$ is the degeneracy of the lowest electronic state[2], $g_{\rm nuc} = \prod_j (2I_j + 1)$ is the total nuclear spin degeneracy, $\xi_{\rm vib}(T)$ is the vibrational partition function, and $\xi_{\rm rot}(T)$ is the rotational partition function[3]. The integer $g_{\rm sym}$ is the *symmetry factor* of the molecule, which is defined to be the number of identical configurations of a given molecule which are realized by rotations when the molecule contains identical nuclei. Evaluate $g_{\rm nuc}$ and $g_{\rm sym}$ for the molecules CH_4 (methane), CH_3D, CH_2D_2, CHD_3, and CD_4. Discuss how the successive deuteration of methane will affect the vibrational and rotational partition functions. For the vibrations your discussion can be qualitative, but for the rotations note that all one needs, as we derived in problem (6), is the product $I_1 I_2 I_3$ of the moments of inertia, which is the determinant of the inertia tensor $I_{\alpha\beta}$ *in a body-fixed center-of-mass frame*. Using the parallel axis theorem, one has

$$I_{\alpha\beta} = \sum_j m_j \left(r_j^2 \, \delta_{\alpha\beta} - r_j^\alpha \, r_j^\beta \right) + M \left(R^2 \, \delta_{\alpha\beta} - R^\alpha R^\beta \right)$$

where $M = \sum_j m_j$ and $R = M^{-1} \sum_j m_j r_j$. Recall that methane is structurally a tetrahedron of hydrogen atoms with a carbon atom at the center, so we can take $r_1 = (0,0,0)$ to be the location of the carbon atom and $r_{2,3,4,5} = (1,1,1), (1,-1,-1), (-1,1,-1), (-1,-1,1)$ to be the location of the hydrogen atoms, with all distances in units of $\frac{1}{\sqrt{3}}$ times the $C - H$ separation.

Solution :

The total partition function is given by

$$Z(T,V,N) = \frac{V^N}{N!} \left(\frac{2\pi\hbar^2}{Mk_{\rm B}T} \right)^{3N/2} \xi_{\rm int}^N(T) \quad ,$$

The Gibbs free energy per particle is

$$\mu(T,p) = \frac{G(T,p,N)}{N} = k_{\rm B}T \ln \left(\frac{p\,\lambda_T^d}{k_{\rm B}T} \right) - k_{\rm B}T \ln \xi(T)$$

$$= k_{\rm B}T \ln \left(\frac{p\,\lambda_T^d}{k_{\rm B}T} \right) - k_{\rm B}T \ln \left(\frac{g_{\rm el} \cdot g_{\rm nuc}}{g_{\rm sym}} \right)$$

$$+ k_{\rm B}T \sum_a \ln \left(2\sinh(\Theta_a/2T) \right) - k_{\rm B}T \ln \left[\left(\frac{2k_{\rm B}T}{\hbar^2} \right)^{3/2} \sqrt{\pi I_1 I_2 I_3} \right] \quad .$$

The electronic degeneracy is $g_{\rm el} = 1$ for all stages of deuteration. The nuclear spin of the proton is $I = \frac{1}{2}$ and that of the deuteron is $I = 1$. Thus there is a nuclear degeneracy of $2I_{\rm p} + 1 = 2$ for each hydrogen nucleus and $2I_{\rm d} + 1 = 3$ for each deuterium nucleus. The symmetry factor is analyzed as follows. For methane CH_4, there are four threefold symmetry axes, resulting in $g_{\rm sym} = 12$. The same result holds for CD_4. For CH_3D or CHD_3, there is a single threefold axis, hence $g_{\rm sym} = 3$. For CH_2D_2, the two hydrogen nuclei lie in a plane together with the carbon, and the two deuterium nuclei lie in a second plane together with the carbon. The intersection of these two planes provides a twofold symmetry axis, about which a $180°$ rotation will rotate one hydrogen into the other and one deuterium into the other. Thus $g_{\rm sym} = 2$.

To analyze the rotational partition function, we need the product $I_1 I_2 I_3$ of the principal moments of inertia, which is to say the determinant of the inertia tensor $\det I$. We work here in units of amu for mass and $\frac{1}{\sqrt{3}}$ times the $C - H$

separation for distance. The inertia tensor is

$$I_{\alpha\beta} = \sum_j m_j \left(r_j^2\, \delta_{\alpha\beta} - r_j^\alpha\, r_j^\beta \right) + M \left(\boldsymbol{R}^2\, \delta_{\alpha\beta} - R^\alpha R^\beta \right)$$

where

$$M = \sum_j m_j$$

$$\boldsymbol{R} = M^{-1} \sum_j m_j \boldsymbol{r}_j \quad .$$

The locations of the four hydrogen/deuterium ions are:

$$L1 : (+1, +1, +1)$$
$$L2 : (+1, -1, -1)$$
$$L3 : (-1, +1, -1)$$
$$L4 : (-1, -1, +1) \quad .$$

For CH_4 we have $M = 16$ and $\boldsymbol{R} = 0$. The inertia tensor is

$$I_{CH_4} = \begin{pmatrix} 8 & 0 & 0 \\ 0 & 8 & 0 \\ 0 & 0 & 8 \end{pmatrix} \quad .$$

Similarly, for CD_4 we have

$$I_{CD_4} = \begin{pmatrix} 16 & 0 & 0 \\ 0 & 16 & 0 \\ 0 & 0 & 16 \end{pmatrix} \quad .$$

For CH_3D, there is an extra mass unit located at L1 relative to methane, so $M = 17$. The CM is at $\boldsymbol{R} = \frac{1}{17}(+1, +1, +1)$. According to the general formula above for $I_{\alpha\beta}$, thie results in two changes to the inertia tensor, relative to I_{CH_4}. We find

$$\Delta I = \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} + \frac{1}{17} \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} \quad ,$$

where the first term accounts for changes in I in the frame centered at the carbon atom, and the second term shifts to the center-of-mass frame. Thus,

$$I_{CH_3D} = \begin{pmatrix} 10 + \frac{2}{17} & -\frac{18}{17} & -\frac{18}{17} \\ -\frac{18}{17} & 10 + \frac{2}{17} & -\frac{18}{17} \\ -\frac{18}{17} & -\frac{18}{17} & 10 + \frac{2}{17} \end{pmatrix} \quad .$$

For CHD_3, we regard the system as CD_4 with a missing mass unit at L1, hence $M = 19$. The CM is now at $\boldsymbol{R} = \frac{1}{17}(-1, -1, -1)$. The change in the inertia tensor relative to I_{CD_4} is then

$$\Delta I = -\begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} + \frac{1}{19} \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} \quad .$$

Thus,

molecule	mass M (amu)	degeneracy factor g_{nuc}	symmetry factor g_{sym}	det I (amu) $\cdot a^2/3$
CH_4	16	$2^4 = 16$	$4 \times 3 = 12$	8^3
CH_3D	17	$2^3 \cdot 3 = 24$	$1 \times 3 = 3$	$8 \cdot \left(11 + \frac{3}{17}\right)^2$
CH_2D_2	18	$2^2 \cdot 3^2 = 36$	$1 \times 2 = 2$	$12 \cdot \left(8 + \frac{2}{9}\right) \cdot \left(16 + \frac{2}{9}\right)$
CHD_3	19	$2 \cdot 3^3 = 54$	$1 \times 3 = 3$	$16 \cdot \left(13 + \frac{3}{19}\right)^2$
CD_4	20	$3^4 = 81$	$4 \times 3 = 12$	16^3

Table 2: Nuclear degeneracy, symmetry factor, and $I_1 I_2 I_3$ product for successively deuterated methane.

$$I_{\text{CHD}_3} = \begin{pmatrix} 14 + \frac{2}{19} & \frac{18}{19} & \frac{18}{19} \\ \frac{18}{19} & 14 + \frac{2}{19} & \frac{18}{19} \\ \frac{18}{19} & \frac{18}{19} & 14 + \frac{2}{19} \end{pmatrix} \ .$$

Finally, for CH_2D_2. we start with methane and put extra masses at L1 and L2, so $M = 18$ and $\boldsymbol{R} = \frac{1}{9}(+1,0,0)$. Then

$$\Delta I = - \begin{pmatrix} 4 & 0 & 0 \\ 0 & 4 & -2 \\ 0 & -2 & 4 \end{pmatrix} + \frac{2}{9} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and

$$I_{\text{CH}_2\text{D}_2} = \begin{pmatrix} 12 & 0 & 0 \\ 0 & 12 + \frac{2}{9} & -2 \\ 0 & -2 & 12 + \frac{2}{9} \end{pmatrix} \ .$$

For the vibrations, absent a specific model for the small oscillations problem the best we can do is to say that adding mass tends to lower the normal mode frequencies since $\omega \sim \sqrt{k/M}$.