

PHYSICS 210A : STATISTICAL PHYSICS
HW ASSIGNMENT #2 SOLUTIONS

(1) Consider a d -dimensional ideal gas with dispersion $\varepsilon(\mathbf{p}) = A|\mathbf{p}|^\alpha$, with $\alpha > 0$. Find the density of states $D(E)$, the statistical entropy $S(E)$, the equation of state $p = p(N, V, T)$, the heat capacity at constant volume $C_V(N, V, T)$, and the heat capacity at constant pressure $C_p(N, V, T)$.

Solution: The density of states is

$$D(E, V, N) = \frac{V^N}{N!} \int \frac{d^d p_1}{h^d} \cdots \int \frac{d^d p_N}{h^d} \delta(E - Ap_1^\alpha - \cdots - Ap_N^\alpha) .$$

The Laplace transform is

$$\begin{aligned} \widehat{D}(\beta, V, N) &= \frac{V^N}{N!} \left(\int \frac{d^d p}{h^d} e^{-\beta Ap^\alpha} \right)^N \\ &= \frac{V^N}{N!} \left(\frac{\Omega_d}{h^d} \int_0^\infty dp p^{d-1} e^{-\beta Ap^\alpha} \right)^N \\ &= \frac{V^N}{N!} \left(\frac{\Omega_d \Gamma(d/\alpha)}{\alpha h^d A^{d/\alpha}} \right)^N \beta^{-Nd/\alpha} . \end{aligned}$$

Now we inverse transform, recalling

$$K(E) = \frac{E^{t-1}}{\Gamma(t)} \iff \widehat{K}(\beta) = \beta^{-t} .$$

We then conclude

$$D(E, V, N) = \frac{V^N}{N!} \left(\frac{\Omega_d \Gamma(d/\alpha)}{\alpha h^d A^{d/\alpha}} \right)^N \frac{E^{\frac{Nd}{\alpha}-1}}{\Gamma(Nd/\alpha)}$$

and

$$\begin{aligned} S(E, V, N) &= k_B \ln D(E, V, N) \\ &= Nk_B \ln \left(\frac{V}{N} \right) + \frac{d}{\alpha} Nk_B \ln \left(\frac{E}{N} \right) + Na_0 , \end{aligned}$$

where a_0 is a constant, and we take the thermodynamic limit $N \rightarrow \infty$ with V/N and E/N fixed. From this we obtain the differential relation

$$\begin{aligned} dS &= \frac{Nk_B}{V} dV + \frac{d}{\alpha} \frac{Nk_B}{E} dE + s_0 dN \\ &= \frac{p}{T} dV + \frac{1}{T} dE - \frac{\mu}{T} dN , \end{aligned}$$

where s_0 is a constant. From the coefficients of dV and dE , we conclude

$$\begin{aligned} pV &= Nk_B T \\ E &= \frac{d}{\alpha} Nk_B T . \end{aligned}$$

Setting $dN = 0$, we have

$$\begin{aligned}\bar{d}Q &= dE + p dV \\ &= \frac{d}{\alpha} N k_B dT + p dV \\ &= \frac{d}{\alpha} N k_B dT + p d\left(\frac{N k_B T}{p}\right).\end{aligned}$$

Thus,

$$C_V = \left.\frac{\bar{d}Q}{dT}\right|_V = \frac{d}{\alpha} N k_B, \quad C_p = \left.\frac{\bar{d}Q}{dT}\right|_p = \left(1 + \frac{d}{\alpha}\right) N k_B.$$

(2) Find the velocity distribution $f(\mathbf{v})$ for the particles in problem (1). Compute the most probable speed, mean speed, and root-mean-square velocity.

Solution: The momentum distribution is

$$g(\mathbf{p}) = C e^{-\beta A p^\alpha},$$

where C is a normalization constant, defined so that $\int d^d p g(\mathbf{p}) = 1$. Changing variables to $t \equiv \beta A p^\alpha$, we find

$$C = \frac{\alpha (\beta A)^{\frac{d}{\alpha}}}{\Omega_d \Gamma\left(\frac{d}{\alpha}\right)}.$$

The velocity \mathbf{v} is given by

$$\mathbf{v} = \frac{\partial \varepsilon}{\partial \mathbf{p}} = \alpha A p^{\alpha-1} \hat{\mathbf{p}}.$$

Thus, the speed distribution is given by

$$f(v) = C \int d^d p e^{-\beta A p^\alpha} \delta(v - \alpha A p^{\alpha-1}).$$

Thus,

$$\langle v^r \rangle = C \int d^d p e^{-\beta A p^\alpha} (\alpha A p^{\alpha-1})^r$$

Thus,

$$\|v\|_r = \langle v^r \rangle^{1/r} = \alpha A^{\alpha-1} (k_B T)^{1-\alpha^{-1}} \left(\frac{\Gamma\left(\frac{d-r}{\alpha} + r\right)}{\Gamma\left(\frac{d}{\alpha}\right)} \right)^{1/\alpha}.$$

To find the most probable speed, we extremize $f(v)$. We write

$$\delta(v - \alpha A p^{\alpha-1}) = \frac{\delta(p - (v/\alpha A)^{1/(\alpha-1)})}{\alpha(\alpha-1) A p^{\alpha-2}}.$$

We then find

$$f(v) = \frac{C}{\alpha(\alpha-1)A} p^{d-\alpha+1} e^{-\beta A p^\alpha} \Big|_{p=(v/\alpha A)^{1/(\alpha-1)}}.$$

Extremizing, we obtain

$$\beta A p^\alpha = \frac{d - \alpha + 1}{\alpha},$$

which means

$$v = \alpha A \left(\frac{d - \alpha + 1}{\alpha \beta A} \right)^{1 - \alpha^{-1}} = (\alpha A)^{\alpha^{-1}} (d - \alpha + 1)^{1 - \alpha^{-1}} (k_B T)^{1 - \alpha^{-1}}.$$

(3) A spin-1 Ising magnet is described by the noninteracting Hamiltonian

$$H = -\mu_0 H \sum_{i=1}^N \sigma_i,$$

where $\sigma_i = -1, 0, +1$.

(a) Find the entropy $S(H, T, N)$.

(b) Suppose the system starts off at a temperature $T = 10$ mK and a field $H = 20$ T. The field is then lowered adiabatically to $H = 1$ T. What is the final temperature of the system?

Solution: The partition function for a single spin is

$$\zeta = 1 + 2 \cosh(\beta \mu_0 H).$$

The free energy is therefore

$$F = -N k_B T \ln \left(1 + 2 \cosh(\mu_0 H / k_B T) \right).$$

The entropy is

$$S = - \left(\frac{\partial F}{\partial T} \right)_{VN} = N k_B \ln \left(1 + 2 \cosh(\mu_0 H / k_B T) \right) - N \frac{\mu_0 H}{T} \frac{2 \sinh(\mu_0 H / k_B T)}{1 + 2 \cosh(\mu_0 H / k_B T)}$$

Note that $S = N s(H/T)$. Thus, an adiabatic process is one which takes place at constant H/T . If H is lowered by a factor of 20, then T is lowered by a factor of 20. For this problem, then, the final temperature is 0.5 mK.

(4) Consider an adsorption model where each of N sites on a surface can accommodate either one or two adsorbate molecules. When one molecule is present the energy is $\varepsilon = -\Delta$, but when two are present the energy is $\varepsilon = -2\Delta + U$, where U models the local interaction of two adsorbate molecules at the same site. You should think of there being two possible binding locations within each adsorption site, so there are four possible states per site: unoccupied (1 possibility), singly occupied (2 possibilities), and doubly occupied (1 possibility). The surface is in equilibrium with a gas at temperature T and number density n .

(a) Find the surface partition function.

(b) Find the fraction f_j which contain j adsorbate molecules, where $j = 0, 1, 2$.

Solution: The surface partition function is

$$\Xi = \left(1 + 2e^{\beta(\mu+\Delta)} + e^{2\beta(\mu+\Delta)} e^{-\beta U}\right)^N,$$

hence

$$\Omega = -Nk_B T \ln \left(1 + 2e^{(\mu+\Delta)/k_B T} + e^{2(\mu+\Delta)/k_B T} e^{-U/k_B T}\right).$$

In the gas, we have $e^{\mu/k_B T} = n\lambda_T^3$. Therefore

$$\begin{aligned} f_0 &= \frac{1}{1 + 2n\lambda_T^3 e^{\Delta/k_B T} + n^2\lambda_T^6 e^{2\Delta/k_B T} e^{-U/k_B T}} \\ f_1 &= \frac{2n\lambda_T^3 e^{\Delta/k_B T}}{1 + 2n\lambda_T^3 e^{\Delta/k_B T} + n^2\lambda_T^6 e^{2\Delta/k_B T} e^{-U/k_B T}} \\ f_2 &= \frac{(n\lambda_T^3)^2 e^{2\Delta/k_B T} e^{-U/k_B T}}{1 + 2n\lambda_T^3 e^{\Delta/k_B T} + n^2\lambda_T^6 e^{2\Delta/k_B T} e^{-U/k_B T}}. \end{aligned}$$

(5) Consider a system of dipoles with the Hamiltonian

$$H = \sum_{i<j} J_{ij}^{\alpha\beta} m_i^\alpha m_j^\beta - \mu_0 \sum_i \mathbf{H}_i^\alpha m_i^\alpha,$$

where

$$J_{ij}^{\alpha\beta} = \frac{J}{R_{ij}^3} (\delta^{\alpha\beta} - 3\hat{R}_{ij}^\alpha \hat{R}_{ij}^\beta).$$

Here \mathbf{R}_i is the spatial position of the dipole \mathbf{m}_i , and $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ with $\hat{R}_{ij}^\alpha \equiv R_{ij}^\alpha / R_{ij}$ the unit direction vector from j to i . The dipole vectors m_i^α are three-dimensional unit vectors. \mathbf{H}_i^α is the local magnetic field.

(a) Find an expression for the free energy $F(T, \{\vec{\mathbf{H}}_i\})$ valid to order β^2 , where $\beta = 1/k_B T$.

(b) Obtain an expression for the uniform field magnetic susceptibility tensor $\chi_{\alpha\beta}$.

(c) An experimentalist plots the quantity $T\chi_{\alpha\beta}$ versus T^{-1} for large temperatures. What should the data resemble if the dipoles are arranged in a cubic lattice structure? How about if they are arranged in a square lattice in the (x, y) plane? (You'll need to separately consider the various cases for the indices α and β . You will also need to numerically evaluate certain lattice sums.)

Solution: Since $Z = e^{-\beta F}$, we will need to expand Z to order β^3 in order to obtain F to order β^2 . We have

$$\begin{aligned} Z &= \text{Tr} e^{-\beta H} \\ &= \text{Tr} 1 - \beta \text{Tr} H + \frac{1}{2}\beta^2 \text{Tr} H^2 - \frac{1}{6}\beta^3 \text{Tr} H^3 + \mathcal{O}(\beta^4). \end{aligned}$$

Taking the logarithm, and recalling $\ln(1 + \varepsilon) = \sum_{k=1}^{\infty} (-1)^{k-1} \varepsilon^k / k$, we have

$$F = \text{Tr } H - \frac{1}{2} \beta \left[\text{Tr} (H^2) - (\text{Tr } H)^2 \right] + \frac{1}{6} \beta^2 \left[\text{Tr} (H^3) - 3 \text{Tr} (H^2) \text{Tr } H + 2 (\text{Tr } H)^3 \right] + \mathcal{O}(\beta^3) .$$

We define the trace as

$$\text{Tr } F(\hat{m}_1, \dots, \hat{m}_N) = \int \prod_{j=1}^N \frac{d\hat{m}_j}{4\pi} F(\hat{m}_1, \dots, \hat{m}_N) ,$$

so that $\text{Tr } 1 = 1$. Thus,

$$\text{Tr} (m_i^\mu m_j^\nu) = \frac{1}{3} \delta_{ij} \delta^{\mu\nu} .$$

Clearly the trace of any product of an odd number of terms m_i^μ with the same i , no matter what the choices of the $\text{O}(3)$ indices (*e.g.* μ), must vanish, since the trace itself is invariant under $\hat{m}_i \rightarrow -\hat{m}_i$. It isn't so easy to compute traces of higher order even products, since the unit vector constraint on \hat{m}_i invalidates the application of Wick's theorem, which can be invoked when computing the averages of Gaussianly distributed variables. For example, one finds $\text{Tr} (\hat{m}^x \hat{m}^x \hat{m}^y \hat{m}^y) = \frac{2}{3}$ while $\text{Tr} (\hat{m}^x \hat{m}^x \hat{m}^x \hat{m}^x) = \frac{1}{5}$. No matter; we shall only need $\text{Tr} (m_i^\mu m_j^\nu)$, computed above.

We now write $H = H_0 + H_1$, where $H_0 = \sum_{i < j} J_{ij}^{\alpha\beta} m_i^\alpha m_j^\beta$ and $H_1 = -\mu_0 \sum_i H_i^\alpha m_i^\alpha$. Eliminating the odd terms whose traces vanish, we have

$$\begin{aligned} \text{Tr } H &= \text{Tr}(H_0 + H_1) = 0 \\ \text{Tr} (H^2) &= \text{Tr} (H_0^2 + 2 H_0 H_1 + H_1^2) = \text{Tr} (H_0^2) + \text{Tr} (H_1^2) \\ \text{Tr} (H^3) &= \text{Tr} (H_0^3 + 3 H_0^2 H_1 + 3 H_0 H_1^2 + H_1^3) = \text{Tr} (H_0^3) + \text{Tr} (H_0 H_1^2) . \end{aligned}$$

Note that $\text{Tr } H_0 = 0$ since i and j are distinct in the sum. We may now compute

$$\begin{aligned} \text{Tr} (H_0^2) &= \sum_{i < j} J_{ij}^{\mu\nu} J_{ij}^{\mu\nu} \\ \text{Tr} (H_1^2) &= \frac{1}{3} \mu_0^2 \sum_i H_i^\alpha H_i^\alpha \\ \text{Tr} (H_0^3) &= 3 \sum_{i < j < k} J_{ij}^{\mu\nu} J_{jk}^{\nu\lambda} J_{ki}^{\lambda\mu} \\ \text{Tr} (H_0 H_1^2) &= \frac{1}{3} \mu_0^2 \sum_{i < j} J_{ij}^{\mu\nu} H_i^\mu H_j^\nu . \end{aligned}$$

Next we must contract the $\text{O}(3)$ indices. We find

$$\begin{aligned} J_{ij}^{\mu\nu} J_{ij}^{\mu\nu} &= \frac{6J^2}{R_{ij}^6} \\ J_{ij}^{\mu\nu} J_{jk}^{\nu\lambda} J_{ki}^{\lambda\mu} &= \left[-6 + 9 (\hat{R}_{ij} \cdot \hat{R}_{jk})^2 + 9 (\hat{R}_{jk} \cdot \hat{R}_{ki})^2 + 9 (\hat{R}_{ki} \cdot \hat{R}_{ij})^2 \right. \\ &\quad \left. - 27 (\hat{R}_{ij} \cdot \hat{R}_{jk})(\hat{R}_{jk} \cdot \hat{R}_{ki})(\hat{R}_{ki} \cdot \hat{R}_{ij}) \right] \cdot \frac{J^3}{R_{ij}^3 R_{jk}^3 R_{ki}^3} . \end{aligned}$$

(a) Thus, the free energy is

$$F = -\frac{3J^2}{k_B T} \sum_{i < j} \frac{1}{R_{ij}^6} - \frac{\mu_0^2}{6 k_B T} \sum_i H_i^\alpha H_i^\alpha + \frac{\mu_0^2 J}{18 (k_B T)^2} \sum_{i < j} \left(\frac{\delta^{\mu\nu} - 3\hat{R}_{ij}^\mu \hat{R}_{ij}^\nu}{R_{ij}^3} \right) H_i^\mu H_j^\nu$$

$$+ \frac{J^3}{(k_B T)^2} \sum_{i < j < k} \frac{-2 + 3\hat{R}_{ij} \cdot \hat{R}_{jk} + 3\hat{R}_{jk} \cdot \hat{R}_{ki} + 3\hat{R}_{ki} \cdot \hat{R}_{ij} - 9(\hat{R}_{ij} \cdot \hat{R}_{jk})(\hat{R}_{jk} \cdot \hat{R}_{ki})(\hat{R}_{ki} \cdot \hat{R}_{ij})}{R_{ij}^3 R_{jk}^3 R_{ki}^3}$$

to order β^2 .

(b) We have

$$\chi_{ij}^{\mu\nu} = \frac{\partial \langle \mu_0 m_i^\mu \rangle}{\partial H_j^\nu} = -\frac{\partial^2 F}{\partial H_i^\mu \partial H_j^\nu}$$

$$= \frac{\mu_0^2}{3k_B T} \delta^{\mu\nu} \delta_{ij} - \frac{\mu_0^2 J}{9 (k_B T)^2} \left(\frac{\delta^{\mu\nu} - 3\hat{R}_{ij}^\mu \hat{R}_{ij}^\nu}{R_{ij}^3} \right) (1 - \delta_{ij}) + \mathcal{O}(T^{-3}) .$$

The second term is here multiplied by $(1 - \delta_{ij})$ since i and j must be distinct in the corresponding term from the free energy. $\chi_{ij}^{\mu\nu}$ tells us how the moment at site i changes in response to a change in the magnetic field at site j . To get the uniform magnetic susceptibility, we differentiate the total moment $M^\mu = \mu_0 \sum_i \langle m_i^\mu \rangle$ with respect to a uniform field H^ν , and we then divide by the system volume. Thus,

$$\chi^{\mu\nu} = \frac{1}{V} \sum_{i,j} \chi_{ij}^{\mu\nu} = \frac{N}{V} \cdot \frac{\mu_0^2}{3k_B T} \delta^{\mu\nu} - \frac{\mu_0^2 J}{9 (k_B T)^2} \cdot \frac{1}{V} \sum_{i \neq j} \left(\frac{\delta^{\mu\nu} - 3\hat{R}_{ij}^\mu \hat{R}_{ij}^\nu}{R_{ij}^3} \right) + \mathcal{O}(T^{-3}) .$$

The above expression is valid for any spatial arrangement of the dipoles. They don't have to be in a regular lattice, for example.

(c) If the dipoles are located at the sites of a Bravais lattice, then we may write

$$\chi^{\mu\nu} = \frac{1}{V} \sum_{i,j} \chi_{ij}^{\mu\nu} = \frac{N}{V} \cdot \frac{\mu_0^2}{3k_B T} \delta^{\mu\nu} - \frac{N}{V} \cdot \frac{\mu_0^2 J}{9 (k_B T)^2} \sum_{\mathbf{R} \neq 0} \left(\frac{\delta^{\mu\nu} - 3\hat{R}^\mu \hat{R}^\nu}{R^3} \right) + \mathcal{O}(T^{-3}) ,$$

where the sum is over all Bravais lattice vectors (*i.e.* all lattice points) other than $\mathbf{R} = 0$. Now let's do the lattice sum in the second term for the case of a cubic lattice. We write $\mathbf{R} = (l \hat{x} + m \hat{y} + n \hat{z})a$, where a is the lattice constant and (l, m, n) are integers. We sum over all triples of integers (l, m, n) other than $(0, 0, 0)$. We then have

$$R = (l^2 + m^2 + n^2)^{1/2} a \quad , \quad \hat{R} = \frac{\mathbf{R}}{R} = \frac{l \hat{x} + m \hat{y} + n \hat{z}}{(l^2 + m^2 + n^2)^{1/2}} .$$

It is clear that the off-diagonal terms in $\chi^{\mu\nu}$ must vanish due to the cubic symmetry. For example, when $\mu = x$ and $\nu = y$ we have to compute

$$\sum'_{l,m,n} \frac{lm}{(l^2 + m^2 + n^2)^{5/2}} = 0 ,$$

since the summand is odd separately in both l and m . The prime on the sum indicates that the term $(0, 0, 0)$ is to be excluded.

Next, consider the diagonal elements. For a cubic lattice, we must have $\chi^{xx} = \chi^{yy} = \chi^{zz}$, so we need only compute the xx term:

$$\sum_{\mathbf{R} \neq 0} \left(\frac{1 - 3\hat{R}^x \hat{R}^x}{R^3} \right) = \frac{1}{a^3} \sum'_{l,m,n} \frac{m^2 + n^2 - 2l^2}{(l^2 + m^2 + n^2)^{5/2}} = 0 .$$

To see why this term vanishes, note that any permutation of the triple (l, m, n) is also a Bravais lattice site. Summing over all permutations, we see that the above sum must vanish. We therefore conclude that all components of the $\mathcal{O}(T^{-2})$ term in the susceptibility vanish for a cubic lattice. In fact, it is clear from the outset that

$$\text{Tr}(\delta^{\mu\nu} - 3\hat{R}^\mu \hat{R}^\nu) = 0 ,$$

so this result coupled with the cubic symmetry immediately tells us that the $\mathcal{O}(T^{-2})$ must vanish for all components.

For a square lattice, we set $n = 0$. The off-diagonal component χ^{xy} still vanishes due to the square symmetry, but now we have $\chi^{xx} = \chi^{yy} = -\frac{1}{2}\chi^{zz}$. The lattice sum for the xx term is

$$-\sum'_{l,m} \frac{m^2 - 2l^2}{(l^2 + m^2)^{5/2}} = \sum'_{l,m} \frac{l^2}{(l^2 + m^2)^{5/2}} = 1.7302 ,$$

where the numerical value is obtained by numerical summation. Thus,

$$\begin{aligned} \chi^{\mu\nu}(\text{SC}) &= \frac{N}{V} \cdot \frac{\mu_0^2}{3k_B T} \delta^{\mu\nu} + \mathcal{O}(T^{-3}) \\ \chi^{\mu\nu}(\text{SQ}) &= \frac{N}{V} \cdot \frac{\mu_0^2}{3k_B T} \delta^{\mu\nu} + \frac{N}{V} \cdot \frac{\mu_0^2 J}{9(k_B T)^2} \cdot \frac{1.7302}{a^3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} + \mathcal{O}(T^{-3}) \end{aligned}$$

for simple cubic and square lattices, respectively. Thus, if we plot $T\chi^{\mu\nu}$ versus T^{-1} at high temperatures, we should observe a straight line with intercept $n\mu_0^2/3k_B$, with $n = N/V$. The slope of the line is zero for the case of a cubic lattice, but for a square lattice, we should observe a positive slope of $1.7302 n\mu_0^2 J/9k_B^2$ for χ^{xx} and χ^{yy} and a negative slope of twice this magnitude for χ^{zz} .

(6) The general form of the kinetic energy for a rotating body is

$$T = \frac{1}{2}I_1(\dot{\phi} \sin \theta \sin \psi + \dot{\theta} \cos \psi)^2 + \frac{1}{2}I_2(\dot{\phi} \sin \theta \cos \psi - \dot{\theta} \sin \psi)^2 + \frac{1}{2}I_3(\dot{\phi} \cos \theta + \dot{\psi})^2 ,$$

where (ϕ, θ, ψ) are the Euler angles.

(a) Find the Hamiltonian $H(p_\phi, p_\theta, p_\psi)$ for a free asymmetric rigid body.

(b) Compute the rotational partition function,

$$\xi_{\text{rot}}(T) = \frac{1}{h^3} \int_{-\infty}^{\infty} dp_{\phi} \int_{-\infty}^{\infty} dp_{\theta} \int_{-\infty}^{\infty} dp_{\psi} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{2\pi} d\psi e^{-H(p_{\phi}, p_{\theta}, p_{\psi})/k_{\text{B}}T}$$

and show that you recover the result in §3.13.3 of the notes.

Solution: We define generalized coordinates (ϕ, θ, ψ) , in which case we may write $T = \frac{1}{2} \mathbb{T}_{ij} \dot{q}_i \dot{q}_j$, with

$$\mathbb{T}_{ij} = \begin{pmatrix} (I_1 \sin^2 \psi + I_2 \cos^2 \psi) \sin^2 \theta + I_3 \cos^2 \theta & (I_1 - I_2) \sin \theta \sin \psi \cos \psi & I_3 \cos \theta \\ (I_1 - I_2) \sin \theta \sin \psi \cos \psi & I_1 \cos^2 \psi + I_2 \sin^2 \psi & 0 \\ I_3 \cos \theta & 0 & I_3 \end{pmatrix}$$

The generalized momenta are $p_i = \partial T / \partial \dot{q}_i = \mathbb{T}_{ij} \dot{q}_j$, and the Hamiltonian is

$$H = \frac{1}{2} \mathbb{T}_{ij}^{-1} p_i p_j .$$

Recall the general formula for a matrix inverse: $M_{ij}^{-1} = (-1)^{i+j} \Delta_{ji} / \det M$, where the *minor* Δ_{ij} is the determinant of the square matrix formed from M by eliminating the i^{th} row and the j^{th} column. The matrix \mathbb{T} is of the form

$$\mathbb{T} = \begin{pmatrix} a & d & e \\ d & b & 0 \\ e & 0 & c \end{pmatrix} ,$$

hence the determinant is $\det \mathbb{T} = abc - cd^2 - be^2$ and the inverse is

$$\mathbb{T}^{-1} = \frac{1}{abc - cd^2 - be^2} \begin{pmatrix} bc & -cd & -be \\ -cd & ac - e^2 & de \\ -be & de & ab - d^2 \end{pmatrix} .$$

Taking the determinant of \mathbb{T} is straightforward, and one finds $\det \mathbb{T} = I_1 I_2 I_3 \sin^2 \theta$. The rotational partition function is then given by the multidimensional integral

$$\begin{aligned} \xi_{\text{rot}}(T) &= \frac{1}{h^3} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{2\pi} d\psi \int_{-\infty}^{\infty} dp_{\phi} \int_{-\infty}^{\infty} dp_{\theta} \int_{-\infty}^{\infty} dp_{\psi} e^{-\mathbb{T}_{ij}^{-1} p_i p_j / 2k_{\text{B}}T} \\ &= \frac{1}{h^3} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{2\pi} d\psi (2\pi k_{\text{B}}T)^{3/2} \sqrt{\det \mathbb{T}} \\ &= \left(\frac{2k_{\text{B}}T}{h^2} \right)^{3/2} \sqrt{\pi I_1 I_2 I_3} , \end{aligned}$$

as in §3.13.3 of the notes.

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

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

where g_{el} is the degeneracy of the lowest electronic state¹, $g_{\text{nuc}} = \prod_j (2I_j + 1)$ is the total nuclear spin degeneracy, $\xi_{\text{vib}}(T)$ is the vibrational partition function, and $\xi_{\text{rot}}(T)$ is the rotational partition function². The integer g_{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_{nuc} and g_{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

$$I_{\alpha\beta} = \sum_j m_j (\mathbf{r}_j^2 \delta_{\alpha\beta} - r_j^\alpha r_j^\beta) + M (\mathbf{R}^2 \delta_{\alpha\beta} - R^\alpha R^\beta)$$

where $M = \sum_j m_j$ and $\mathbf{R} = M^{-1} \sum_j m_j \mathbf{r}_j$. Recall that methane is structurally a tetrahedron of hydrogen atoms with a carbon atom at the center, so we can take $\mathbf{r}_1 = (0, 0, 0)$ to be the location of the carbon atom and $\mathbf{r}_{2,3,4,5} = (1, 1, 1)$, $(1, -1, -1)$, $(-1, 1, -1)$, $(-1, -1, 1)$ 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

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

The Gibbs free energy per particle is

$$\begin{aligned} \mu(T, p) &= \frac{G(T, p, N)}{N} = k_{\text{B}}T \ln \left(\frac{p \lambda_T^d}{k_{\text{B}}T} \right) - k_{\text{B}}T \ln \xi(T) \\ &= k_{\text{B}}T \ln \left(\frac{p \lambda_T^d}{k_{\text{B}}T} \right) - k_{\text{B}}T \ln \left(\frac{g_{\text{el}} \cdot g_{\text{nuc}}}{g_{\text{sym}}} \right) \\ &\quad + k_{\text{B}}T \sum_a \ln \left(2 \sinh(\Theta_a/2T) \right) - k_{\text{B}}T \ln \left[\left(\frac{2k_{\text{B}}T}{\hbar^2} \right)^{3/2} \sqrt{\pi I_1 I_2 I_3} \right] . \end{aligned}$$

The electronic degeneracy is $g_{\text{el}} = 1$ 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

¹We assume the temperature is low enough that we can ignore electronic excitations.

²Note that for linear polyatomic molecules such as CO_2 and HCN , we must treat the molecule as a rotor, *i.e.* we use eqn. 3.278 of the notes.

of $2I_p + 1 = 2$ for each hydrogen nucleus and $2I_d + 1 = 3$ for each deuterium nucleus. The symmetry factor is analyzed as follows. For methane CH_4 , there are four threefold symmetry axes, resulting in $g_{\text{sym}} = 12$. The same result holds for CD_4 . For CH_3D or CHD_3 , there is a single threefold axis, hence $g_{\text{sym}} = 3$. 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 $g_{\text{sym}} = 2$.

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

$$I_{\alpha\beta} = \sum_j m_j (\mathbf{r}_j^2 \delta_{\alpha\beta} - r_j^\alpha r_j^\beta) + M (\mathbf{R}^2 \delta_{\alpha\beta} - R^\alpha R^\beta)$$

where

$$M = \sum_j m_j$$

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

The locations of the four hydrogen/deuterium ions are:

$$\begin{aligned} \text{L1} &: (+1, +1, +1) \\ \text{L2} &: (+1, -1, -1) \\ \text{L3} &: (-1, +1, -1) \\ \text{L4} &: (-1, -1, +1) . \end{aligned}$$

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

$$I_{\text{CH}_4} = \begin{pmatrix} 8 & 0 & 0 \\ 0 & 8 & 0 \\ 0 & 0 & 8 \end{pmatrix} .$$

Similarly, for CD_4 we have

$$I_{\text{CD}_4} = \begin{pmatrix} 16 & 0 & 0 \\ 0 & 16 & 0 \\ 0 & 0 & 16 \end{pmatrix} .$$

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

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

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,

$$I_{\text{CH}_3\text{D}} = \begin{pmatrix} 10 + \frac{2}{17} & -\frac{18}{17} & -\frac{18}{17} \\ -\frac{18}{17} & 10 + \frac{2}{17} & -\frac{18}{17} \\ -\frac{18}{17} & -\frac{18}{17} & 10 + \frac{2}{17} \end{pmatrix}.$$

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 $\mathbf{R} = \frac{1}{17}(-1, -1, -1)$. The change in the inertia tensor relative to I_{CD_4} is then

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

Thus,

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

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

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