

Non-interacting particles

1. Rotating gas: Consider a gas of N identical atoms confined to a spherical harmonic trap in three dimensions, i.e. the particles are subject to the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + \frac{K}{2} r_i^2 \right].$$

(a) Show that the angular momentum of each particle $\vec{L}_i = \vec{r}_i \times \vec{p}_i$ is a conserved quantity, i.e. $\{\vec{L}_i, \mathcal{H}\} = 0$. (Note that once interactions between particles are included, individual angular momenta are no longer conserved, while their sum $\vec{L} = \sum_{i=1}^N \vec{L}_i$ remains a conserved quantity.)

• Since different coordinates have zero Poisson bracket, we need to examine only a single coordinate i , and

$$\{\vec{L}_i, \mathcal{H}\} = \left\{ \vec{r}_i \times \vec{p}_i, \frac{p_i^2}{2m} + \frac{K}{2} r_i^2 \right\}.$$

A typical term in the above Poisson bracket is proportional to

$$\{(\vec{r} \times \vec{p})_\beta, p^2\} = \frac{\partial}{\partial x_\alpha} \epsilon_{\beta\gamma\delta} (x_\gamma p_\delta) \frac{\partial}{\partial p_\alpha} p_\beta p_\beta = 2\epsilon_{\beta\alpha\delta} p_\delta p_\alpha = 0.$$

The last summation leads to zero as it involves the product of an antisymmetric ($\epsilon_{\beta\alpha\delta}$) and a symmetric ($p_\delta p_\alpha$) tensor.

(b) Since angular momentum is conserved, a generalized canonical distribution can be defined with probability

$$p[\mu \equiv \{\vec{p}_i, \vec{r}_i\}] = \frac{1}{Z(\beta, \vec{\Omega})} \exp \left(-\beta \mathcal{H}(\mu) - \beta \vec{\Omega} \cdot \vec{L}(\mu) \right).$$

Compute the classical partition function for this gas of identical particles, assuming $\vec{\Omega} = \Omega \hat{z}$, with $\Omega < \sqrt{K/m}$.

• Since the Hamiltonian describes N identical non-interacting particles,

$$Z(N, \beta, \vec{\Omega}) = \frac{1}{N!} Z_1^N.$$

For $\vec{\Omega} = \Omega \hat{z}$, the terms acting on a single particle are

$$\mathcal{H}_1 + \vec{\Omega} \cdot \vec{L}_1 = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \frac{K(x^2 + y^2 + z^2)}{2} + \Omega(xp_y - yp_x).$$

The single particle partition function is thus given by

$$Z_1 = \int \frac{dz dp_z}{h} e^{-\frac{\beta p_z^2}{2m} - \frac{\beta K z^2}{2}} \int \frac{dx dp_y}{h} e^{-\frac{\beta p_y^2}{2m} - \frac{\beta K x^2}{2} - \beta \Omega x p_y} \int \frac{dy dp_x}{h} e^{-\frac{\beta p_x^2}{2m} - \frac{\beta K y^2}{2} + \beta \Omega y p_x}.$$

Performing the Gaussian integrals over the momenta yields

$$Z_1 = \frac{1}{\lambda^3} \int dz e^{-\frac{\beta K z^2}{2}} \int dx e^{-\frac{\beta(K-m\Omega^2)x^2}{2}} \int dy e^{-\frac{\beta(K-m\Omega^2)y^2}{2}} = \sqrt{\frac{2\pi}{\beta K}} \left(\frac{2\pi}{\beta(K-m\Omega^2)} \right),$$

where $\lambda_T = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength. (Note that the condition $K > m\Omega^2$ is required to keep the particles confined.) Thus the overall partition function is given by

$$Z(N, \beta, \vec{\omega}) = \frac{1}{N! \lambda_T^{3N}} \left[\sqrt{\frac{2\pi}{\beta K}} \left(\frac{2\pi}{\beta(K-m\Omega^2)} \right) \right]^N.$$

(c) Find the expectation value of angular momentum $\langle L_z \rangle$ in the above ensemble.

- From the form of the probability, it is easy to observe that

$$\langle L_z \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \Omega} = N k_B T \frac{2m\Omega}{K - m\Omega^2}.$$

(d) Write down the probability density of finding a particle at location (x, y, z) , and hence obtain the expectation values $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$.

- The PDF for coordinates is obtained from the joint probability $p[\vec{p}, \vec{r}]$ after integration over momenta as

$$p[\vec{r}] = \sqrt{\frac{\beta K}{2\pi}} e^{-\frac{\beta K z^2}{2}} \times \left(\frac{\beta(K-m\Omega^2)}{2\pi} \right) e^{-\frac{\beta(K-m\Omega^2)(x^2+y^2)}{2}}.$$

From the Gaussian form we can read off the variances

$$\langle z^2 \rangle = \frac{1}{\beta K}, \quad \langle x^2 \rangle = \langle y^2 \rangle = \frac{1}{\beta(K-m\Omega^2)}.$$

2. Polar rods: 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 given by

$$\mathcal{H}_{\text{rot.}} = \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - \mu E \cos \theta, \quad ,$$

where E is an external electric field. ($\phi \in [0, 2\pi]$, $\theta \in [0, \pi]$ are the azimuthal and polar angles, and p_ϕ , p_θ are their conjugate momenta.)

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

- The classical partition function is obtained by integrating over the angles θ and ϕ , and the corresponding momenta as

$$Z_{\text{rot}} = \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dp_\theta dp_\phi \exp \left[-\frac{\beta}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) + \beta\mu \cos \theta \right].$$

The Gaussian integrations over momenta are easily carried out, and after the change of variables to $x = \cos \theta$, we find

$$Z_{\text{rot}} = \left(\frac{2\pi I}{\beta h^2} \right) (2\pi) \int_{-1}^{+1} dx e^{\beta\mu E x} = \left(\frac{8\pi^2 I}{\beta h^2} \right) \frac{\sinh(\beta\mu E)}{\beta\mu E}.$$

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

- From the form of the partition function, we note that

$$P = \langle \mu \cos \theta \rangle = \frac{\partial \ln Z_{\text{rot}}}{\partial \beta E} = \mu \left[\coth(\beta\mu E) - \frac{1}{\beta\mu E} \right].$$

(c) Find the *zero-field* polarizability

$$\chi_T = \left. \frac{\partial P}{\partial E} \right|_{E=0}.$$

- The susceptibility is

$$\chi_T = \frac{\partial P}{\partial E} = \beta\mu^2 \left[-\frac{1}{\sinh^2(\beta\mu E)} + \frac{1}{(\beta\mu E)^2} \right] = \frac{1}{3} \frac{\mu^2}{k_B T} \quad \text{for } E = 0.$$

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

- The energy stored in this degree of freedom is

$$\langle E_{\text{rot}} \rangle = -\frac{\partial \ln Z_{\text{rot}}}{\partial \beta} = 2k_B T - \mu E \coth(\beta\mu E).$$

At high temperature $\langle E_{\text{rot}} \rangle \approx k_B T$ coming entirely from the kinetic energies. At temperatures $k_B T \ll \mu E$, the polarization is saturated, and $\langle E_{\text{rot}} \rangle \approx -\mu E + 2k_B T$.

(e) Sketch the rotational heat capacity per dipole.

- The classical heat capacity is $2k_B$ at low temperatures, and decreases to $1k_B$ at high temperatures, with a ‘knee’ at $k_B T \approx \mu E$.

3. Atomic/molecular hydrogen: A container of volume V at temperature T contains N atoms of hydrogen, some forming hydrogen molecules. The gas is sufficiently dilute that interactions and quantum degeneracies can be ignored.

(a) The Hamiltonian for N_1 hydrogen atoms is

$$H_a = \sum_{i=1}^{N_1} \frac{p_i^2}{2m}.$$

Calculate the partition function $Z_a(N_1, T, V)$.

- Using standard results for classical particles,

$$Z_a(N_1, T, V) = \frac{1}{N_1!} \left(\frac{V}{\lambda_a^3} \right)^{N_1}, \quad \text{with} \quad \lambda_a = \frac{h}{\sqrt{2\pi m k_B T}}.$$

(b) The Hamiltonian for $N_2 = (N - N_1)/2$ hydrogen molecules is

$$H_m = \sum_{i=1}^{N_2} \left[\frac{p_i^2}{4m} + \frac{L_i^2}{2I} - \epsilon \right],$$

where ϵ is the energy gained on forming a molecule, the mass of the molecule is twice the atomic mass, and I is its moment of inertia. It is assumed that the temperature is such that the vibrational levels of the molecule are frozen, while the rotational levels are fully excited and can be treated classically (as in previous problem). Calculate the partition function $Z_m(N_2, T, V)$.

- There is now an additional contribution to the single particle partition function due to the rotational degrees of freedom, given by

$$Z_{\text{rot.}} = \int \frac{d^2\Omega d^2L}{h^2} e^{-\beta L^2/2I} = \frac{4\pi}{h^2} \left(\sqrt{2\pi I k_B T} \right)^2.$$

Including the binding energy per molecule, the partition function of the N_2 molecules is given by

$$Z_m(N_2, T, V) = \frac{1}{N_2!} \left[\left(\frac{V}{\lambda_m^3} \right) \left(\frac{8\pi^2 I k_B T}{h^2} \right) e^{\beta\epsilon} \right]^{N_2}, \quad \text{with} \quad \lambda_a = \frac{h}{\sqrt{4\pi m k_B T}}.$$

(c) Find the ratio n_m/n_a^2 , where $n_a = N_a/V$ and $n_m = N_m/V$ are the densities of atomic and molecular hydrogen in equilibrium.

- The partition function for the mixture of atomic and molecular gases is obtained as

$$Z(N, T, V) = \sum_{N_2=1}^{N/2} Z_a(N - 2N_2, T, V) Z_m(N_2, T, V).$$

The largest term in the sum is obtained from the condition

$$\frac{\partial \ln Z_m}{\partial N_2} = 2 \frac{\partial \ln Z_a}{\partial N_1}.$$

With the standard simplifications for large N , the above equality yields

$$\ln \left[\left(\frac{V}{N_2 \lambda_m^3} \right) \left(\frac{8\pi^2 I k_B T}{h^2} \right) e^{\beta\epsilon} \right] = 2 \ln \left[\left(\frac{V}{N_1 \lambda_a^3} \right) \right].$$

Rearranging the above expression yields

$$\frac{n_m}{n_a^2} = \left(\frac{N_2}{V} \right) \left(\frac{V}{N_1} \right)^2 = \left(\frac{\lambda_m^3}{\lambda_a^6} \right) \left(\frac{h^2}{8\pi^2 I k_B T} \right) e^{-\beta\epsilon}.$$

4. Fluctuation-induced dipole interactions: The interaction between two dipole moments \vec{D}_1 and \vec{D}_2 , at a separation $\vec{r} = r \hat{r}$ is given by

$$V(\vec{r}) = \frac{3 \left(\vec{D}_1 \cdot \hat{r} \right) \left(\vec{D}_2 \cdot \hat{r} \right) - \left(\vec{D}_1 \cdot \vec{D}_2 \right)}{r^3}.$$

(a) Consider *permanent dipoles* of fixed magnitude $|\vec{D}_1| = D_1$ and $|\vec{D}_2| = D_2$ which can point in any direction in three dimensions. Find the expression for the partition function

$Z(r)$, obtained by integrating over all possible dipole orientations, at the lowest non-trivial order in βV . (**Hint:** Angular averages of vector components satisfy $\langle D_\alpha D_\beta \rangle_0 = D^2 \delta_{\alpha\beta}/3$.)

- The partition function is given by

$$Z(r) = \int d^2\Omega_1 d^2\Omega_2 e^{-\beta V} = Z_0 \left[1 - \beta \langle V \rangle_0 + \frac{\beta^2}{2} \langle V^2 \rangle_0 + \dots \right],$$

where $Z_0 = (4\pi)^2$ is the contribution of rotations at infinite temperature, while $\langle X \rangle_0$ indicates an average with respect to freely rotating dipoles. The first order averages are zero because of rotational symmetry, while in terms of their components, the second order averages take the form

$$\langle V^2 \rangle_0 = \frac{1}{r^6} [9 \langle D_{1,r} D_{1,r} D_{2,r} D_{2,r} \rangle_0 - 6 \langle D_{1,r} D_{1,\alpha} D_{2,r} D_{2,\alpha} \rangle_0 + \langle D_{1,\beta} D_{1,\alpha} D_{2,\beta} D_{2,\alpha} \rangle_0],$$

where the subscript r denotes the component along \hat{r} , while the indices α and β are summed over. The averages over orientations of the two dipoles are naturally independent, and using $\langle D_\alpha D_\beta \rangle_0 = D^2 \delta_{\alpha\beta}/3$ to compute the paired averages, gives

$$\langle V^2 \rangle_0 = \frac{D_1^2 D_2^2}{r^6} \left[9 \cdot \frac{1}{3} \cdot \frac{1}{3} - 6 \frac{\delta_{\alpha r}}{3} \frac{\delta_{\alpha r}}{3} + \frac{\delta_{\alpha\beta}}{3} \frac{\delta_{\alpha\beta}}{3} \right] = \frac{2D_1^2 D_2^2}{3r^6},$$

leading to

$$Z(r) = Z_0 \left(1 + \frac{\beta^2 D_1^2 D_2^2}{3r^6} + \dots \right) \approx Z_0 \exp \left[\frac{\beta^2 D_1^2 D_2^2}{3r^6} \right].$$

(b) The partition function $Z(r)$ can be interpreted as resulting from an effective fluctuation-induced potential $U(r)$. Find $U(r)$ at the lowest non-trivial order, and comment on its temperature dependence.

- Equating the Boltzmann weight for a potential $U(r)$ to $Z(r)$, we find

$$U(r) = -k_B T \ln \frac{Z(r)}{Z_0} = -\beta \frac{D_1^2 D_2^2}{3r^6}.$$

This potential diverges at zero temperature, as the permanent dipoles become aligned and want to come as close as possible to minimize energy. At high temperatures, entropy opposes this tendency and the interaction weakens.

(c) Most atoms and molecules do not have a permanent dipole moment, but are *polarizable*, i.e. there is an energy cost of $D^2/(2\chi)$ to create a dipole moment of magnitude D . Now

consider the dipolar interaction $V(r)$ emerging from two polarizable particles with polarizabilities χ_1 and χ_2 . Repeat the calculation of $Z(r)$, including the energy costs of creating the dipoles.

- The partition function is now given by

$$Z(r) = \int d^3 D_1 d^3 D_2 e^{-\beta \left(\frac{D_1^2}{2\chi_1} + \frac{D_2^2}{2\chi_2} - V \right)} = Z'_0 \left[1 - \beta \langle V \rangle'_0 + \frac{\beta^2}{2} \langle V^2 \rangle'_0 + \dots \right],$$

where $Z'_0 = (2\pi k_B T)^3 (\chi_1 \chi_2)^{3/2}$ is the partition function of non-interacting polarizable particles, while $\langle X \rangle'_0$ indicates averaging with respect to such non-interacting polarizations. The first order averages are again zero because of rotational symmetry, while the same form applies to the second order averages, i.e.

$$\langle V^2 \rangle_0 = \frac{1}{r^6} [9 \langle D_{1,r} D_{1,r} D_{2,r} D_{2,r} \rangle_0 - 6 \langle D_{1,r} D_{1,\alpha} D_{2,r} D_{2,\alpha} \rangle_0 + \langle D_{1,\beta} D_{1,\alpha} D_{2,\beta} D_{2,\alpha} \rangle_0].$$

The components of distinct dipoles are independent, while for the same dipole $\langle D_\alpha D_\beta \rangle_0 = \delta_{\alpha\beta} k_B T \chi$, resulting in

$$\langle V^2 \rangle_0 = \frac{(k_B T)^2 \chi_1 \chi_2}{r^6} [9 - 6 \delta_{\alpha r} \delta_{\alpha r} + \delta_{\alpha\beta} \delta_{\alpha\beta}] = \frac{6 D_1^2 D_2^2}{r^6},$$

leading to

$$Z(r) = Z'_0 \left(1 + \frac{3\chi_1 \chi_2}{r^6} + \dots \right) \approx Z'_0 \exp \left[\frac{3\chi_1 \chi_2}{r^6} \right].$$

(d) Find effective fluctuation-induced potential between polarizable particles at the lowest non-trivial order, and comment on its temperature dependence.

- Equating the Boltzmann weight for a potential $U'(r)$ to $Z'(r)$, we find

$$U'(r) = -k_B T \ln \frac{Z'(r)}{Z'_0} = -k_B T \frac{3\chi_1 \chi_2}{r^6}.$$

This potential now vanishes at zero temperature due to the large cost of creating dipoles, and is proportional to temperature.

5. Molecular adsorption: N diatomic molecules are stuck on a metal surface of square symmetry. Each molecule can either lie flat on the surface in which case it must be aligned to one of two directions, x and y , or it can stand up along the z direction. There is an

energy cost of $\varepsilon > 0$ associated with a molecule standing up, and zero energy for molecules lying flat along x or y directions.

(a) How many microstates have the smallest value of energy? What is the largest microstate energy?

- The ground state energy of $E = E_{min} = 0$ is obtained for 2^N configurations. The largest microstate energy is $N\varepsilon$ is unique.

(b) For *microcanonical* macrostates of energy E , calculate the number of states $\Omega(E, N)$, and the entropy $S(E, N)$.

- Let $N_z = E/\varepsilon$. Expressing Ω as the number of ways to choose the N_z excited molecules, multiplied by the number of possible configurations

$$\Omega(E, N) = \frac{N!}{N_z!(N - N_z)!} \cdot 2^{N - N_z},$$

and

$$\begin{aligned} S(E, N) &= S_{two-level\ system} + k_b(N - N_z) \ln 2 \\ &= -Nk_B \left\{ \frac{E}{N\varepsilon} \ln \frac{E}{N\varepsilon} + \left(1 - \frac{E}{N\varepsilon}\right) \ln \left(1 - \frac{E}{N\varepsilon}\right) \right\} + k_b(N - \frac{E}{\varepsilon}) \ln 2. \end{aligned}$$

(c) Calculate the heat capacity $C(T)$ and sketch it.

- The temperature dependence of the energy is obtained from the relation

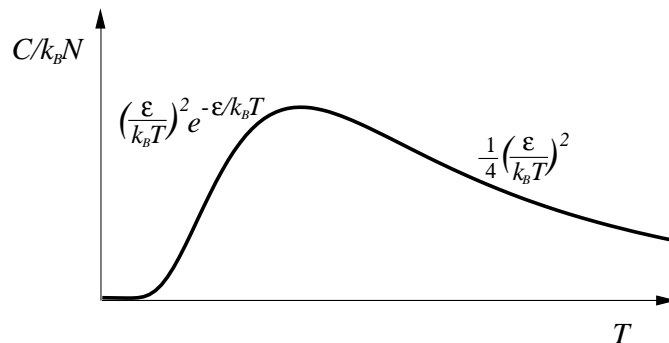
$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_N = -\frac{k_B}{\varepsilon} \ln \left(\frac{E}{N\varepsilon - E} \right) - \frac{k_B}{\varepsilon} \ln 2,$$

whence

$$E = \frac{N\varepsilon}{\exp\left(\frac{\varepsilon}{k_B} \left(\frac{1}{T} + \frac{k_B}{\varepsilon} \ln 2\right)\right) + 1} = \frac{N\varepsilon}{2 \exp\left(\frac{\varepsilon}{k_B T}\right) + 1},$$

and

$$C = \frac{dE}{dT} = Nk_B \left(\frac{\varepsilon}{k_B T}\right)^2 \frac{2 \exp\left(\frac{\varepsilon}{k_B T}\right)}{(1 + 2 \exp\left(\frac{\varepsilon}{k_B T}\right))^2}.$$



(d) What is the probability that a specific molecule is standing up?

- The probability that a specific molecule is standing up is

$$\begin{aligned}
 p(\vec{r}_1 = \hat{z}) &= \frac{\Omega(E - \epsilon, N - 1)}{\Omega(E, N)} \\
 &= \frac{(N - 1)!}{(N_z - 1)!((N - 1) - (N_z - 1))!} 2^{(N-1)-(N_z-1)} \frac{N_z!(N - N_z)!}{N!} \frac{1}{2^{N-N_z}} \\
 &= \frac{N_z}{N} = \frac{E}{N\epsilon} \\
 &= \frac{1}{2 \exp \frac{\epsilon}{k_B T} + 1}.
 \end{aligned}$$

(e) What is the largest possible value of the internal energy at any positive temperature?

- Since $\frac{dE}{dT} > 0$ for all $T > 0$, the energy is largest for $\rightarrow \infty$, i.e.

$$E_{max} = \frac{N\epsilon}{3}.$$

6. Curie susceptibility: Consider N non-interacting quantized spins in a magnetic field $\vec{B} = B\hat{z}$, and at a temperature T . The work done by the field is given by BM_z , with a magnetization $M_z = \mu \sum_{i=1}^N m_i$. For each spin, m_i takes only the $2s + 1$ values $-s, -s + 1, \dots, s - 1, s$.

(a) Calculate the Gibbs partition function $\mathcal{Z}(T, B)$. (Note that the ensemble corresponding to the macrostate (T, B) includes magnetic work.)

- The Gibbs partition function is

$$\mathcal{Z} = \sum_{\{m_i\}} \exp(\beta \vec{B} \cdot \vec{M}) = \sum_{\{m_i\}} \exp\left(\beta B \mu \sum_{i=1}^N m_i\right) = \left[\sum_{m_i=-s}^{m_i=s} \exp(\beta \mu B \cdot m_i) \right]^N.$$

Thus we obtain the series

$$\mathcal{Z} = [\exp(-\beta B \mu s) + \exp(-\beta B \mu (s - 1)) + \dots + \exp(\beta B \mu (s - 1)) + \exp(\beta B \mu s)]^N.$$

In general, to evaluate a geometrical series of the form

$$S = x^{-s} + x^{-(s-1)} + \dots + x^{s-1} + x^s,$$

increase the order of the series by one,

$$Sx = x^{-s+1} + \dots + x^s + x^{s+1},$$

and subtract from the original series:

$$(1-x)S = x^{-s} - x^{s+1}, \quad \implies \quad S = \frac{x^{-s} - x^{s+1}}{1-x}.$$

(Note that the same result is obtained whether s is an integer or half-integer quantity.)

Using this expression, we get

$$\begin{aligned} \mathcal{Z} &= \left(\frac{\exp(-\beta B\mu s) - \exp(\beta B\mu(s+1))}{1 - \exp(\beta B\mu)} \right)^N \\ &= \left(\frac{\exp(-\beta B\mu(s+1/2)) - \exp(-\beta B\mu(s+1/2))}{\exp(-\beta B\mu/2) - \exp(-\beta B\mu/2)} \right)^N. \end{aligned}$$

Substituting in the proper trigonometric identity,

$$\mathcal{Z} = \left[\frac{\sinh(\beta\mu B(s+1/2))}{\sinh(\beta\mu B/2)} \right]^N.$$

(b) Calculate the Gibbs free energy $G(T, B)$, and show that for small B ,

$$G(B) = G(0) - \frac{N\mu^2 s(s+1)B^2}{6k_B T} + \mathcal{O}(B^4).$$

- The Gibbs free energy is

$$\begin{aligned} G &= E - BM = -k_B T \ln \mathcal{Z} \\ &= -Nk_B T \ln[\sinh(\beta\mu B(s+1/2))] + Nk_B T \ln[\sinh(\beta\mu B/2)]. \end{aligned}$$

Using an approximation of $\sinh \theta$ for small θ ,

$$\sinh \theta = \frac{1}{2} (e^\theta - e^{-\theta}) \approx \frac{1}{2} \left(2\theta + 2\frac{\theta^3}{3!} \right) + \mathcal{O}(\theta^5), \quad \text{for } \theta \ll 1,$$

we find (setting $\alpha = \beta\mu B$),

$$G \approx -Nk_B T \left\{ \ln \left[\alpha \left(s + \frac{1}{2} \right) \left(1 + \frac{\alpha^2}{6} \left(s + \frac{1}{2} \right)^2 \right) \right] - \ln \left[\frac{\alpha}{2} \left(1 + \frac{\alpha^2}{24} \right) \right] + \mathcal{O}(\alpha^4) \right\}.$$

Using the expansion $\ln(1+x) = x - x^2/2 + x^3/3 - \dots$, we find

$$\begin{aligned} G &\approx -Nk_B T \left[\ln(2s+1) + \frac{1}{6} (\alpha(s+1/2))^2 - \frac{1}{6} (\alpha/2)^2 + \mathcal{O}(\alpha^4) \right] \\ &\approx -Nk_B T \ln(2s+1) - Nk_B T \alpha^2 \frac{(s^2+s)}{6} \\ &= G_0 - \frac{N\mu^2 B^2 s(s+1)}{6k_B T} + \mathcal{O}(B^4). \end{aligned}$$

(c) Calculate the zero field susceptibility $\chi = \partial M_z / \partial B|_{B=0}$, and show that it satisfies *Curie's law*

$$\chi = c/T.$$

• The magnetic susceptibility, $\chi = \partial M_z / \partial B$, is obtained by noting that the average magnetization is

$$\langle M_z \rangle = k_B T \frac{\partial \ln \mathcal{Z}}{\partial B} = -\frac{\partial G}{\partial B}.$$

Thus

$$\chi = \frac{\partial \langle M_z \rangle}{\partial B} = -\frac{\partial}{\partial B} \frac{\partial G}{\partial B} = \frac{N\mu^2 s(s+1)}{3k_B T},$$

which obeys *Curie's law*, $\chi = c/T$, with $c = N\mu^2 s(s+1)/3k_B$.

(d) Show that, to leading order in B , $C_B - C_M = cB^2/T^2$ where C_B and C_M are heat capacities at constant B and M respectively.

• Since,

$$C_B = T \left. \frac{\partial S}{\partial T} \right|_B, \quad C_M = T \left. \frac{\partial S}{\partial T} \right|_B + T \left. \frac{\partial S}{\partial B} \right|_T \left. \frac{\partial B}{\partial T} \right|_M,$$

we get,

$$C_B - C_M = -T \left. \frac{\partial S}{\partial B} \right|_T \left. \frac{\partial B}{\partial T} \right|_M.$$

Using the Maxwell relation,

$$\left. \frac{\partial S}{\partial B} \right|_T = \left. \frac{\partial M}{\partial T} \right|_B,$$

and the fact that $\langle M \rangle = cB/T$ up to leading order in B , we get,

$$C_B - C_M = -T \left. \frac{\partial M}{\partial T} \right|_B \left. \frac{\partial B}{\partial T} \right|_M = -T \frac{-cB}{T^2} \frac{B}{T} = \frac{cB^2}{T^2}.$$

7. Langmuir isotherms: An ideal gas of particles is in contact with the surface of a catalyst.

(a) Show that the chemical potential of the gas particles is related to their temperature and pressure via $\mu = k_B T [\ln(P/T^{5/2}) + A_0]$, where A_0 is a constant.

- For convenience, we begin by defining the characteristic length,

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}},$$

in terms of which the free energy of ideal gas is given by,

$$F = -N k_B T \ln \left(\frac{V e}{N \lambda^3} \right).$$

Then using the equation of state of ideal gas we get,

$$\begin{aligned} \mu = \frac{\partial F}{\partial N} &= -k_B T \ln \left(\frac{V}{N \lambda^3} \right) = -k_B T \ln \left(\frac{k_B T}{P \lambda^3} \right) \\ &= k_B T \left[\ln(P T^{-5/2}) + \ln \left(\frac{h^3}{k_B^{5/2} 2^{3/2} \pi^{3/2} m^{3/2}} \right) \right]. \end{aligned}$$

(b) If there are \mathcal{N} distinct adsorption sites on the surface, and each adsorbed particle gains an energy ϵ upon adsorption, calculate the grand partition function for the two dimensional gas with a chemical potential μ .

- We have,

$$Q(T, \mu) = \sum_{n=0}^{\mathcal{N}} \binom{\mathcal{N}}{n} e^{n\beta\mu} e^{-n\beta\epsilon} = \left(1 + e^{\beta(\mu-\epsilon)} \right)^{\mathcal{N}}.$$

(c) In equilibrium, the gas and surface particles are at the same temperature and chemical potential. Show that the fraction of occupied surface sites is then given by $f(T, P) = P/(P + P_0(T))$. Find $P_0(T)$.

- Since the average number of absorption sites occupied is,

$$\langle N \rangle = k_B T \frac{\partial \ln Q}{\partial \mu} = \mathcal{N} \frac{e^{\beta(\mu-\epsilon)}}{1 + e^{\beta(\mu-\epsilon)}},$$

and the fraction of occupied sites is given by,

$$f(T, P) = \frac{e^{\beta(\mu-\epsilon)}}{1 + e^{\beta(\mu-\epsilon)}}.$$

Since the gas and surface particles have the same temperature and chemical potential, the relation in (a), namely,

$$e^{\beta\mu} = \frac{P\lambda^3}{k_B T}$$

holds. Plugging this into the formula for f we obtain,

$$f(T, P) = \frac{P}{P + P_0(T)}, \quad \text{with} \quad P_0(T) = \frac{k_B T}{\lambda^3} e^{\beta\epsilon}.$$

(d) In the grand canonical ensemble, the particle number N is a random variable. Calculate its characteristic function $\langle \exp(-ikN) \rangle$ in terms of $\mathcal{Q}(\beta\mu)$, and hence show that

$$\langle N^m \rangle_c = -(k_B T)^{m-1} \left. \frac{\partial^m \mathcal{G}}{\partial \mu^m} \right|_T,$$

where \mathcal{G} is the grand potential.

- Note that in calculating $\mathcal{Q}(\beta\mu)$ the term for N particles is proportional to $e^{\beta\mu N}$. In calculating the average of e^{-ikN} , we just replace the initial factor with $e^{(\beta\mu - ik)N}$, and hence

$$\langle e^{-ikN} \rangle = \frac{\mathcal{Q}(\beta\mu - ik)}{\mathcal{Q}(\beta\mu)}.$$

For the cumulant generating function, we get

$$\ln \langle e^{-ikN} \rangle = \ln \mathcal{Q}(\beta\mu - ik) - \ln \mathcal{Q}(\beta\mu) = -\beta \mathcal{G}(\beta\mu - ik) + \beta \mathcal{G}(\beta\mu).$$

Hence,

$$\begin{aligned} \langle N^m \rangle_c &= \frac{\partial^m}{\partial (-ik)^m} (-\beta \mathcal{G}(\beta\mu - ik)) \Big|_T \\ &= -\beta \left. \frac{\partial^m \mathcal{G}}{\partial (\beta\mu)^m} \right|_T = -\beta^{1-m} \left. \frac{\partial^m \mathcal{G}}{\partial \mu^m} \right|_T \\ &= -(k_B T)^{m-1} \left. \frac{\partial^m \mathcal{G}}{\partial \mu^m} \right|_T. \end{aligned}$$

(e) Using the characteristic function, show that

$$\langle N^2 \rangle_c = k_B T \left. \frac{\partial \langle N \rangle}{\partial \mu} \right|_T.$$

•

$$\langle N^2 \rangle_c = -k_B T \left. \frac{\partial^2 \mathcal{G}}{\partial \mu^2} \right|_T = k_B T \left. \frac{\partial \langle N \rangle}{\partial \mu} \right|_T.$$

(f) Show that fluctuations in the number of adsorbed particles satisfy

$$\frac{\langle N^2 \rangle_c}{\langle N \rangle_c^2} = \frac{1-f}{\mathcal{N}f}.$$

• By definition of f ,

$$\langle N \rangle_c = - \left. \frac{\partial \mathcal{G}}{\partial \mu} \right|_T = \mathcal{N}f,$$

and since,

$$\left. \frac{\partial f}{\partial \mu} \right|_T = \left. \frac{\partial}{\partial \mu} \frac{e^{-\beta\epsilon}}{e^{-\beta\mu} + e^{-\beta\epsilon}} \right|_T = \frac{\beta e^{-\beta\mu} e^{-\beta\epsilon}}{(e^{-\beta\mu} + e^{-\beta\epsilon})^2} = \beta f(1-f),$$

we get,

$$\langle N^2 \rangle_c = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} = \frac{1}{\beta} \mathcal{N} \frac{\partial f}{\partial \mu} = \mathcal{N} f(1-f),$$

leading to the equality,

$$\frac{\langle N^2 \rangle_c}{\langle N \rangle_c^2} = \frac{1-f}{\mathcal{N}f}.$$

8. (Optional) One dimensional polymer: Consider a polymer formed by connecting N disc shaped molecules into a one dimensional chain. Each molecule can align either along its long axis (of length $2a$) or short axis (length a). The energy of the monomer aligned along its shorter axis is higher by ε , i.e. the total energy is $\mathcal{H} = \varepsilon U$, where U is the number of monomers standing up.

(a) Calculate the partition function, $Z(T, N)$, of the polymer.

•

$$Z = \sum_{\mu_s} e^{-\beta \mathcal{H}(\mu_s)} = \sum_{\mu_s} e^{-\beta \varepsilon U} = \sum_{U=0}^N \binom{N}{U} e^{-\beta \varepsilon U} = (1 + e^{-\beta \varepsilon})^N.$$

(b) Find the relative probabilities for a monomer to be aligned along its short or long axis.

- The probabilities for a monomer to be aligned along its short/long axis are,

$$\frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}, \quad \frac{1}{1 + e^{-\beta\epsilon}},$$

respectively.

(c) Calculate the average length, $\langle L(T, N) \rangle$, of the polymer.

- Since $L = 2aN - aU$,

$$\langle L \rangle = \langle 2aN - aU \rangle = 2aN - a\langle U \rangle = 2aN + a \frac{\partial}{\partial \beta\epsilon} \ln Z = aN \left(\frac{2 + e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \right).$$

(d) Obtain the variance, $\langle L(T, N)^2 \rangle_c$.

- By definition:

$$\langle L^2 \rangle_c = \langle (2aN - aU)^2 \rangle_c = a^2 \langle U^2 \rangle_c.$$

Since the distribution of U is a binomial distribution

$$\langle U^2 \rangle_c = N \left(\frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \right) \left(\frac{1}{1 + e^{-\beta\epsilon}} \right),$$

we get

$$\langle L^2 \rangle_c = \frac{a^2 N e^{-\beta\epsilon}}{(1 + e^{-\beta\epsilon})^2}.$$

(e) What does the central limit theorem say about the probability distribution for the length $L(T, N)$?

- The length contribution for each link of the chain is an independent variable. Hence in the large N limit, the probability distribution function of $L(T, N)$ becomes Gaussian, as

$$p(L) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[-\frac{(L - \bar{L})^2}{2\sigma^2} \right],$$

where

$$\sigma^2 = \frac{a^2 N e^{-\beta\epsilon}}{(1 + e^{-\beta\epsilon})^2}, \quad \text{and} \quad \bar{L} = aN \left(\frac{2 + e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \right).$$

9. (Optional) Classical virial theorem: Let $\bar{X} = \{\vec{q}_i, \vec{p}_i\}$ denote any of the $6N$ coordinates of phase space, and consider any function $f(\bar{X})$.

(a) Show that in a canonical ensemble governed by a Hamiltonian $\mathcal{H}(\bar{X})$

$$\left\langle \frac{\partial f}{\partial X_i} \right\rangle = \beta \left\langle f \frac{\partial \mathcal{H}}{\partial X_i} \right\rangle,$$

where $\beta = 1/(k_B T)$.

- The following integral is clearly zero as its integrand is a derivative

$$I = \int \prod_j dX_j \frac{\partial}{\partial X_i} \left[f(\bar{X}) e^{-\beta \mathcal{H}} \right] = 0.$$

Carrying out the derivatives inside the integrand yields

$$I = \int \prod_j dX_j \left[\frac{\partial f}{\partial X_i} - \beta f \frac{\partial \mathcal{H}}{\partial X_i} \right] e^{-\beta \mathcal{H}} = 0.$$

Dividing the above equation by the partition function normalizes the Boltzmann weight and yields

$$I = \left\langle \frac{\partial f}{\partial X_i} \right\rangle - \beta \left\langle f \frac{\partial \mathcal{H}}{\partial X_i} \right\rangle = 0.$$

(b) Find the two forms of the virial theorem obtained by substituting $f = q_j$ and $X_i = q_i$ and $X_i = p_i$ in the general expression.

- For $X_i = q_i$ we obtain

$$\beta \left\langle q_j \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = \delta_{ij},$$

while for $X_i = p_i$, we get

$$\beta \left\langle q_j \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = 0.$$

10. (Optional) Disordered glass: The heat capacity of many disordered materials vanishes linearly at low temperatures. A commonly used model such glassy materials is a collection of N non-interacting defects in thermal equilibrium at temperature T . Each defect is assumed to have two possible energies ϵ_i and $\epsilon_i + \delta_i$, with different values of ϵ_i and δ_i for each defect.

(a) Compute the partition function $Z(T)$, the average energy $E(T)$, and the contribution to heat capacity $C(T)$ from these independent defects.

- Since the defects are independent

$$Z = \prod_i Z_i = \prod_i [e^{-\beta\epsilon_i} (1 + e^{-\beta\delta_i})].$$

The energy and the heat capacity are additive and given by

$$E(T) = -\frac{\partial \ln Z}{\partial \beta} = \sum_i \left[\epsilon_i + \frac{\delta_i}{1 + e^{\beta\epsilon_i}} \right],$$

and

$$C(T) = \frac{dE}{dT} = k_B \sum_{i=1}^N (\beta\delta_i)^2 \frac{e^{\beta\delta_i}}{(1 + e^{\beta\delta_i})^2}.$$

(b) The number of defects with excitation energies between δ and $\delta + d\delta$ is given by $\rho(\delta)d\delta$, where $\rho(\delta)$ is the density of states of defects as a function of excitation energy. Assuming that $\rho(\delta)$ is uniformly distributed between energies of 0 and Δ , find the defect heat capacity $C(T)$, and comment on its behavior at low and high temperatures.

- By considering the contribution to heat capacity of defects with excitation energy δ , we get

$$C(T) = \int \rho(\delta) d\delta C(\delta, T).$$

With $C(\delta, T)$ computed above, and a density $\rho(\delta) = N/\Delta$, we find

$$C(T) = \frac{Nk_B}{\Delta} \int_0^\Delta d\delta (\beta\delta)^2 \frac{e^{\beta\delta_i}}{(1 + e^{\beta\delta})^2} = \frac{Nk_B}{\beta\Delta} \int_0^{\beta\Delta} dx \left(\frac{x}{e^{x/2} + e^{-x/2}} \right)^2.$$

- For low temperatures ($k_B T \ll \Delta$), the upper limit of integration can be set to infinity, resulting in a definite integral which evaluates to $\pi^2/6$, and

$$C(T \rightarrow 0) \simeq \frac{\pi^2}{6} \frac{Nk_B^2}{\Delta} T,$$

giving rise to a linear heat capacity.

- For high temperatures ($k_B T \gg \Delta$), the integrand only contributes close to zero, and

$$C(T \rightarrow \infty) \simeq \frac{Nk_B}{3} \left(\frac{\Delta}{k_B T} \right)^2.$$

(c) A uniform density of states may not be realistic. What feature of $\rho(\delta)$ will ensure $C \propto T$ at low temperatures?

- At low temperatures only defects with $\delta \leq k_B T$ are excited. A linearly vanishing heat capacity requires the number of excited defects to be proportional to T , and hence a density of defect states $\rho(\delta)$ that goes to a constant as $\delta \rightarrow 0$.
