Statistical Mechanics

Revision Notes

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Contents

1   Thermodynamics

Thermodynamics mainly deals with macroscopic measurements that are made on the system of interest. We will always be interested in systems that are in **equilibrium**. The various thermodynamic potentials are-

$$G(T, p, N) = U - TS - pV \qquad\qquad F(T, V, N) = U - TS$$
$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N \qquad\qquad \mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$$

$$\Phi(T, V, \mu) = U - TS - \mu N \qquad\qquad U(S, V, N) = TS - pV + \mu N$$
$$\mathrm{d}\Phi = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu \qquad\qquad \mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$$

- If U is given as a function of T and V i.e. $U(V, T)$, then

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V \Rightarrow \mathrm{d}S = \frac{p\mathrm{d}V + \mathrm{d}U}{T} = \frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_T + p\right)\mathrm{d}V + \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T$$

The state quantity Entropy for a thermodynamic process with start and end points as A and B can be written as-

$$S = \int_A^B \frac{\delta Q}{T}$$

The heat capacities are defined as incremental heat δQ absorbed by the system (with some constant control variable) when the temperature is increased by $\mathrm{d}T$

$$\delta Q\big|_p = T\mathrm{d}S\big|_p = C_p\mathrm{d}T \qquad\qquad \delta Q\big|_V = T\mathrm{d}S\big|_V = \mathrm{d}U\big|_{V,N} = C_V\mathrm{d}T$$

$$\Rightarrow C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} \qquad\qquad \Rightarrow C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} \qquad\qquad C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N}$$

Math Aside:
A derivative identity between x, y and z with a single constraint $x(y, z)$-

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{1}$$

Differential transform from $f(x, y) \to f(x, z)$ for a function $f(x, y)$ with a constraint $x = x(y, z)$-

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \tag{2}$$

Thus, for magnetic systems, the differential $\mathrm{d}U$ can be written down as-

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + H\mathrm{d}M$$

and the heat capacities can be written as-

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H \qquad\qquad C_M = T\left(\frac{\partial S}{\partial T}\right)_M$$

and then using equation (2) and Maxwell's relations-

$$\left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial S}{\partial T}\right)_M + \left(\frac{\partial S}{\partial M}\right)_T\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial T}\right)_M - \underbrace{\left(\frac{\partial H}{\partial T}\right)_M}_{\text{Maxwell}}\left(\frac{\partial M}{\partial T}\right)_H$$

$$C_H - C_M = -T\left(\frac{\partial H}{\partial T}\right)_M\left(\frac{\partial M}{\partial T}\right)_H$$

Analogously, the relation between C_p and C_V can be written as $(H \to -p, M \to V)$

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$$

The laws of thermodynamics can thus be combined together for equilibrium processes in the following way-

$$\Delta U = Q + W = Q - \int p\mathrm{d}V = \int C_V\mathrm{d}T \text{ (even when } V \neq \text{ const.)}$$

Different Thermodynamic Processes-

- For isothermal processes, $\mathrm{d}T = 0$, and for ideal gases, $\mathrm{d}U = C_V\mathrm{d}T = 0$.

- For adiabatic processes, $\delta Q = 0$, and hence $\Delta U = W$. The constrain relations for an adiabatic process are-

$$TV^{\gamma-1} = \text{ const.} \qquad pV^\gamma = \text{ const.} \qquad T^\gamma p^{1-\gamma} = \text{ const.}$$

Maxwell's relations are a consequence of thermodynamic potentials being exact differentials. For some potential $\psi(x, y)$-

$$\mathrm{d}\psi = \left(\frac{\partial \psi}{\partial x}\right)_y\mathrm{d}x + \left(\frac{\partial \psi}{\partial y}\right)_x\mathrm{d}y = A(x, y)\mathrm{d}x + B(x, y)\mathrm{d}y$$

$$\implies \left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y$$

For a Carnot Engine, the efficiency can be defined as-

$$\eta = \frac{|W|}{Q_{\text{in}}} = \frac{|W_{\text{isothermal}}|}{Q_{\text{in}}} = \frac{Q_{\text{in}} + Q_{\text{out}}}{Q_{\text{in}}} = 1 + \frac{Q_{\text{out}}}{Q_{\text{in}}}$$

but since $\frac{Q_{\text{out}}}{T_{\text{cold}}} = -\frac{Q_{\text{in}}}{T_{\text{hot}}}$, we get the expression for efficiency as

$$\eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

2 Classical Statistical Mechanics

Throughout these notes, we will assume that we are again dealing with systems in **equilibrium**. The core theme of equilibrium Statistical Mechanics is that we assume that over long periods of time, the phase space trajectory of the system takes on all the accessible microstates (Ergodic Hypothesis), and hence the essence of the subject is that

<div align="center">

Time averages $\equiv$ Ensemble Averages

</div>

Apart from this, we'll also require the fundamental postulate of statistical mechanics which states that - *In a state of equilibrium, all the accessible microstates are equally probable.*

2.1 Microcanonical Ensemble

The control variables of a closed system which is described by a microcanonical ensemble are (E, V, N). The entropy of such a system can be found out as-

$$S = k_B \ln(\Omega)$$

The number of microstates Ω are just the number of phase space cells occupied by a hypersurface shell between E and some $E + \Delta E$. Therefore, the number of microstates can be calculated as-

$$\Omega(E) = g(E)\Delta E = \frac{\partial \Sigma}{\partial E}\Delta E$$

where Σ is the number of phase space inside the hypersurface (volume/ h^{3N}) subject to the constraint $H(p,q) \leq E$.

$$\Sigma = \frac{1}{h^{3N}} \int_{H \leq E} \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \implies \Omega = \frac{1}{h^{3N}} \int_{E \leq H \leq E + \Delta E} \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p$$

We can therefore attach a phase space density to each point in the phase space. For a microcanonical ensemble, the only accessible microstates are within the region where $E \leq H \leq E + \Delta E$, and all of them have to be equally probable, so-

$$\rho_{mc} = \begin{cases} \frac{1}{\Omega} & \text{for } E \leq H \leq E + \Delta E \\ 0 & \text{elsewhere} \end{cases} \implies \frac{1}{h^{3N}} \int \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \, \rho_{mc} = 1$$

Hence, the average of a quantity can be expressed as-

$$\langle f \rangle = \frac{1}{h^{3N}} \int \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \, \rho_{mc} f(q_i, p_i) = \frac{1}{h^{3N}} \int\limits_{E \leq H \leq E + \Delta E} \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \, \frac{1}{\Omega} f(q_i, p_i)$$

In the discrete limit, the integral can be replaced by a sum-

$$\frac{1}{h^{3N}} \int \mathrm{d}^{3N}q \mathrm{d}^{3N}p \xrightleftharpoons[\text{continuum}]{\text{discrete}} \sum_{i \,\in\, \{\text{all }\Omega(N)\}} \implies \frac{1}{h^{3N}} \int\limits_{E \leq H \leq E + \Delta E} \mathrm{d}^{3N}q \mathrm{d}^{3N}p \xrightleftharpoons[\text{continuum}]{\text{discrete}} \sum_{i \,\in\, \{\Omega(E,N)\}} \quad (3)$$

We'll use this approximation (3) quite often in statistical mechanics. We will occasionally omit writing N because N is almost always fixed except for GC ensembles.

2.2   Canonical Ensemble

The control variables of a system immersed in a heat bath which is described by a canonical ensemble are (T, V, N). If the system is in a microstate with energy E, the heat bath can still take $\Omega_B(E_{\text{total}} - E)$ microstates, and this gives us the probability of finding the system in microstate i with energy E_i as-

$$p_i = \frac{e^{-\beta E_i}}{Z} \xrightarrow{\text{continuum}} \rho_c = \frac{e^{-\beta H(p_i, q_i)}}{Z}$$

where the normalization factor Z is called the Partition Function. Knowledge of the Partition function is enough to calculate all the thermodynamic observables [1] .

$$Z = \sum_{i \,\in\, \{\text{all }\Omega\}} e^{-\beta E_i} \xrightarrow{\text{continuum}} \frac{1}{h^{3N}} \int \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \, e^{-\beta H(p_i, q_i)}$$

The expectation value of observables can thus be written down as-

$$\langle f \rangle = \sum_{i \,\in\, \{\text{all }\Omega\}} p_i f_i = \sum_{i \,\in\, \{\text{all }\Omega\}} \frac{e^{-\beta E_i}}{Z} f_i \longrightarrow \frac{1}{h^{3N}} \int \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \, \frac{e^{-\beta H(p_i, q_i)}}{Z} f(q_i, p_i)$$

Whenever there is degeneracy in the energy levels of the microstates, we can write down the Partition function as-

$$Z = \sum_{i \in \{\text{energy levels}\}} g_i e^{-\beta E_i} \xrightarrow[g_i = g(E_i) \Delta E]{\text{in } \lim \Delta E \to 0} \int_0^\infty \mathrm{d}E \, g(E) e^{-\beta E}$$

where g_i is the degeneracy in i^{th} state, which generalises to $g(E_i)$ density of states in the continuum limit. In this way, the averages can be written as-

$$\langle f \rangle = \sum_{i \in \{\text{energy levels}\}} g_i \frac{e^{-\beta E_i}}{Z} f(E_i) \longrightarrow \frac{1}{Z} \int_0^\infty \mathrm{d}E \, g(E) e^{-\beta E} f(E)$$

---

[1] The subscripts $i \in \{\text{all }\Omega\}$ is to be interpreted as $i \in \{\text{all }\Omega$ with particle no. N$\}$ for canonical ensembles since $N = \text{const.}$

Conversely, if we know the partition function $Z(\beta)$, we can calculate the density of states as a Laplace transform-

$$g(E) = \frac{1}{2\pi i} \int_{\beta_x - i\infty}^{\beta_x + i\infty} \mathrm{d}\beta \, Z(\beta) e^{\beta E}$$

where $\beta_x > 0$ and the contour represents a straight line on the complex plane with $x = \beta_x$ and y running from $-\infty$ to $+\infty$. Then transform the straight line contour to a closed contour by adding an arc which doesn't contribute to the integral (semicircular arcs of infinite radius on either side with the straight line as the base).

Also, once the partition function is known, all thermodynamic quantities are derivable from it since we know F-

$$F = U - TS = -k_B T \ln Z$$

Since $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$, we get-

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

For classical indistinguishable particles, the partition function also has a $1/N!$ factor latched on as a Gibbs correction factor. If the system has a non-interacting Hamiltonian, then Z can be written as-

$$Z_{\text{dist}}(T, V, N) = [Z(T, V, 1)]^N \qquad\qquad Z_{\text{indist}}(T, V, N) = \frac{1}{N!}[Z(T, V, 1)]^N$$

Since a canonical ensemble doesn't have a fixed energy E, we can study its fluctuations by finding $\langle E \rangle$ and $\langle E^2 \rangle$. Plugging in E in the expression of averages, we see that we can write the mean and variances as-

$$U = \langle E \rangle = \frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial(\ln Z)}{\partial \beta} \qquad\qquad \langle E^2 \rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$$

$$\implies (\sigma E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial U}{\partial \beta} = k_B T^2 C_V$$

The relative width of the fluctuations is σE divided by the mean energy U, i.e.

$$\frac{\sigma E}{U} = \frac{\sqrt{k_B T^2 C_V}}{U} \sim \frac{1}{\sqrt{N}}$$

Thus, in the thermodynamic limit $N \to \infty$, the energy of the system looks like a delta function around the average energy $\delta(E - U)$.

Also, for a system at a given temperaure T, we can comment on the expectation values of energies of the system due to the Virial Theorem-

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} k_B T$$

where x_k runs over both position and momenta coordinates ($k = 1, 2 \dots 6N$).

Canonical Ensembles can also be used to study paramagnetic systems at a fixed temperature. For paramagnetic substances, the form of the energy of a microstate gives Z

$$E = -\vec{\mu} \cdot \vec{H} \implies Z(\beta, 1) = \frac{4\pi \sinh(\beta\mu H)}{\beta\mu H}$$

$$\langle \mu_z \rangle = \frac{1}{\beta} \frac{\partial \ln Z(\beta, 1)}{\partial H} = -\frac{\partial F(T, H, 1)}{\partial H}$$

$$\implies \langle D_z \rangle = \frac{1}{\beta} \frac{\partial \ln Z(\beta, N)}{\partial H} = -\frac{\partial F(T, H, N)}{\partial H} = N \langle \mu_z \rangle$$

2.3   Grand Canonical Ensemble

Continuing our story for open systems characterized by the control variables (T, V, μ) inside a particle and heat bath, we can use the methods of Grand Canonical ensembles. If the system is in a microstate with energy E and particle number N, the heat bath can still take $\Omega_B(E_{\text{total}} - E, N_{\text{total}} - N)$ microstates, and this gives us the probability of finding the system in microstate i with energy E_i and particle number N as-

$$p_{i,N} = \frac{e^{-\beta(E_i - \mu N)}}{\mathcal{Z}} \xrightarrow{\text{continuum}} \rho_{gc} = \frac{e^{-\beta(H - \mu N)}}{\mathcal{Z}}$$

where the normalization factor $\mathcal{Z}$ is called the Grand Canonical Partition function given by-

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{i \in \left\{ \substack{\text{all } \Omega \text{ with} \\ N \text{ particles}} \right\}} e^{-\beta(E_i - \mu N)} \xrightarrow{\text{continuum}} \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \, d^{3N}p \; e^{-\beta(H - \mu N)}$$

Then the expectation values (averages) of the observables can be written down as [2] -

$$\langle f \rangle = \sum_{i \in \{\text{all } \Omega\}} p_i f_i = \sum_{N=0}^{\infty} \sum_{i \in \{\Omega(N)\}} \frac{e^{-\beta(E_i - \mu N)}}{\mathcal{Z}} f_{i,N} \longrightarrow \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \, d^{3N}p \frac{e^{-\beta(H - \mu N)}}{\mathcal{Z}} f(q_i, p_i)$$

As a consequence of this form of observable averages in all the three formalisms (microcanonical, canonical, grand canonical), the entropy can be also be written down as-

$$S = -k_B \langle \rho \ln \rho \rangle \xrightleftharpoons[\text{continuum}]{\text{discrete}} S = -k_B \sum_{i \in \{\text{all } \Omega\}} p_i \ln p_i \tag{4}$$

This form of entropy readily generalises to von Neumann entropy in Quantum StatMech.

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[2] The $i \in \{\text{all } \Omega\}$ is indeed going over all microstates with N also changing.

Once the grand canonical partition function is known, we also have the grand potential $\Phi(T, V, \mu)$ and all thermodynamic observables can be derived form it-

$$\Phi = U - TS - \mu N = -k_B T \ln \mathcal{Z}$$

Since $\mathrm{d}\Phi = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu$, we get-

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} \qquad p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} \qquad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

If the particles are distinguishable and have a Hamiltonian which is separable, then-

$$\mathcal{Z}_{\text{dist}} = \sum_{N=0}^{\infty} (e^{\beta\mu})^N \frac{1}{h^{3N}} \int \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \, e^{-\beta H} = \sum_{N=0}^{\infty} z^N Z(T, V, N) = \sum_{N=0}^{\infty} z^N [Z(T, V, 1)]^N$$

where z is called *fugacity*. Similarly, if the particles were indistinguishable, we get an additional $1/N!$ factor

$$\mathcal{Z}_{\text{indist}} = \sum_{N=0}^{\infty} \frac{1}{N!} z^N Z(T, V, N) = \sum_{N=0}^{\infty} \frac{1}{N!} z^N [Z(T, V, 1)]^N = \exp[z \, Z(T, V, 1)]$$

Again, as in the canonical ensemble, if there is degenracy in the energy levels of the microstates, then we can write down the probability of the system to be in the energy level (migh not be a single microstate) with energy E and particle number N as-

$$p_{i,N}(E, N) = \frac{1}{\mathcal{Z}} g(E, N) e^{-\beta(E-\mu N)} \qquad \text{where } \mathcal{Z} = \sum_{N=0}^{\infty} \int_0^\infty \mathrm{d}E \, g(E, N) e^{-\beta(E-\mu N)}$$

$$\implies \langle f \rangle = \sum_{i,N} p_{i,N} f_{i,N} \longrightarrow \int_0^\infty \mathrm{d}E \, g(E, N) \frac{e^{-\beta(E-\mu N)}}{\mathcal{Z}} f(E, N)$$

Therefore, we can use the above formula for averages to study the fluctuations in N and E in the system. For energy E fluctuations-

$$\langle E \rangle = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{z,V} \qquad \langle E^2 \rangle = \frac{1}{\mathcal{Z}}\left(\frac{\partial^2 Z}{\partial \beta^2}\right)_{z,V}$$

$$\implies (\sigma E)^2 = \left(\frac{\partial^2 \ln \mathcal{Z}}{\partial \beta^2}\right)_{z,V} = -\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z,V}$$

For particle number N fluctuations in the grand canonical ensemble-

$$\langle N \rangle = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V} \qquad \langle N^2 \rangle = \frac{1}{\beta^2 \mathcal{Z}}\left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right)_{T,V}$$

$$\implies (\sigma N)^2 = \frac{1}{\beta^2}\left(\frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2}\right)_{T,V} = \frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V}$$

3   Quantum Statistical Mechanics

When we talk about a classical system of particles, we can describe the average properties of the system using the phase space density ρ. Similarly, when we have a quantum system with a large number of particles, we can calculate the ensemble averages of the system using a "quantum" density operator.

$$\hat{\rho} = \sum_i p_i \hat{\rho}_i = \sum_i p_i \left| \psi_i \right\rangle \left\langle \psi_i \right| .$$

where $\{\left| \psi_i \right\rangle\}$ are the possible states that the system can take with probablities p_i. The density operator (or density matrix) is a Hermitian operator with $\mathrm{Tr}(\rho) = 1$. The expectation values of observables can be calculated as

$$\langle \hat{O} \rangle = \mathrm{Tr}(\hat{\rho}\,\hat{O}).$$

For an ensemble, we can describe the notion of pure and mixed states as follows. A system is said to be in a pure state if it the system is certainly known to be in the state $\left| \psi \right\rangle$ (therefore, there are no probabilities involved).

$$\hat{\rho}_{\mathrm{pure}} = \left| \psi \right\rangle \left\langle \psi \right| ,$$

Mixed states however, model the scenario where the ensemble of states are distributed such that the state $\left| \psi_i \right\rangle$ is found with probability p_i

$$\hat{\rho}_{\mathrm{mixed}} = \sum_i p_i \left| \psi_i \right\rangle \left\langle \psi_i \right| .$$

One can also check that since $\hat{\rho}_{\mathrm{pure}}$ is projector,

$$\hat{\rho}_{\mathrm{pure}}^2 = \hat{\rho}_{\mathrm{pure}} \implies \mathrm{Tr}(\hat{\rho}_{\mathrm{pure}}^2) = \mathrm{Tr}(\hat{\rho}_{\mathrm{pure}}) = 1.$$

For mixed states however, $\hat{\rho}_{\mathrm{mixed}}^2 \neq \hat{\rho}_{\mathrm{mixed}}$, and one can check that

$$\mathrm{Tr}(\hat{\rho}_{\mathrm{mixed}}^2) < 1.$$

The time evolution of the density matrix is described by the von Neumann equation

$$i\hbar \frac{\mathrm{d}\hat{\rho}(t)}{\mathrm{d}t} = [\hat{H}, \hat{\rho}],$$

and for time independent Hamiltonians, the von Neumann equation can be easily solved to yield

$$\rho(t) = e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar}.$$

Coming back to the different types of ensembles of statistical mechanics, we can extend the definition of the densities from classical picture to density operators in the quantum world

$$\hat{\rho}_{\mathrm{mc}} = \frac{\delta(\hat{H} - E\hat{I})}{\mathrm{tr}\left[\delta(\hat{H} - E\hat{I})\right]} \qquad \hat{\rho}_{\mathrm{canon}} = \frac{e^{-\beta\hat{H}}}{\mathrm{tr}\left[e^{-\beta\hat{H}}\right]} \qquad \hat{\rho}_{\mathrm{gc}} = \frac{e^{-\beta(\hat{H} - \mu\hat{N})}}{\mathrm{tr}\left[e^{-\beta(\hat{H} - \mu\hat{N})}\right]} .$$

3.1   Density Matrix calculations for free particles

Let's start by calculating the matrix elements of the density matrix of a <u>single free particle</u>.

1. In momentum representation

$$
\left\langle \vec{k}' \middle| \rho \middle| \vec{k} \right\rangle = \frac{\left\langle \vec{k}' \middle| e^{-\beta H} \middle| \vec{k} \right\rangle}{Z_1(T,V,1)} = \boxed{\frac{e^{-\beta \hbar^2 \vec{k}^2 / 2m}}{V/\lambda^3} \delta_{\vec{k},\vec{k}'}}.
\tag{5}
$$

2. In position representation

$$
\langle \vec{r}' | \rho | \vec{r} \rangle = \sum_{\vec{k}',\vec{k}} \left\langle \vec{r}' \middle| \vec{k}' \right\rangle \left\langle \vec{k}' \middle| \rho \middle| \vec{k} \right\rangle \left\langle \vec{k} \middle| \vec{r} \right\rangle = \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}'-\vec{r})} \frac{\lambda^3}{V^2} e^{-\beta \hbar^2 \vec{k}^2/2m}
$$

$$
\approx \left(\frac{1}{V} e^{-\frac{\pi}{\lambda^2}(\vec{r}-\vec{r}')^2} \right) \cdot \frac{V/\lambda^3}{V/\lambda^3} = \boxed{\frac{1}{\lambda^3} e^{-\frac{\pi}{\lambda^2}(\vec{r}'-\vec{r})^2} \frac{1}{V/\lambda^3} \equiv \frac{f(\vec{r}'-\vec{r})}{V/\lambda^3}}.
\tag{6}
$$

where we have used an important approximation

$$
\sum_{\vec{k}} \approx \frac{V}{(2\pi)^3} \int \mathrm{d}^3 k.
\tag{7}
$$

Let's now calculate the density matrix elements of the density matrix of <u>N free particles</u>.

1. In momentum representation

$$
\left\langle \vec{k_1}' \dots \vec{k_N}' \middle| \rho \middle| \vec{k_1} \dots \vec{k_N} \right\rangle = \frac{\left\langle \vec{k_1}' \dots \vec{k_N}' \middle| e^{-\beta \hat{H}} \middle| \vec{k_1} \dots \vec{k_N} \right\rangle}{\sum_{\{\vec{k_i}\}} \left\langle \vec{k_1}' \dots \vec{k_N}' \middle| e^{-\beta \hat{H}} \middle| \vec{k_1} \dots \vec{k_N} \right\rangle}
$$

$$
= \frac{e^{-\beta \hbar^2 / 2m \sum_{i=1}^{N} \vec{k_i}^2} \delta_{\vec{k_1}',\vec{k_1}} \cdots \delta_{\vec{k_N}',\vec{k_N}}}{\underbrace{\prod_{i=1}^{N} \sum_{\{\vec{k_i}\}} \left\langle \vec{k_i}' \middle| e^{-\beta \hat{H}} \middle| \vec{k_i} \right\rangle}_{Z(T,V,1)=V/\lambda^3}} = \boxed{\frac{e^{-\beta \hbar^2 / 2m \sum_{i=1}^{N} \vec{k_i}^2}}{(V/\lambda^3)^N} \delta_{\vec{k_1}',\vec{k_1}} \cdots \delta_{\vec{k_N}',\vec{k_N}}}.
\tag{8}
$$

2. In position representation

$$
\left\langle \vec{r_1}' \dots \vec{r_N}' \middle| \rho \middle| \vec{r_1} \dots \vec{r_N} \right\rangle
$$

$$
= \sum_{\{\vec{k_i},\vec{k_i}'\}} \left\langle \vec{r_1}' \dots \vec{r_N}' \middle| \vec{k_1}' \dots \vec{k_N}' \right\rangle \left\langle \vec{k_1}' \dots \vec{k_N}' \middle| e^{-\beta \hat{H}} \middle| \vec{k_1} \dots \vec{k_N} \right\rangle \left\langle \vec{k_1} \dots \vec{k_N} \middle| \vec{r_1} \dots \vec{r_N} \right\rangle
$$

$$
= \prod_{i=1}^{N} \left(\sum_{\{\vec{k_i}\}} \frac{e^{i\vec{k_i}\cdot(\vec{r_i}'-\vec{r_i})}}{V} \cdot \frac{\lambda^3}{V} e^{-\beta \hbar^2 \vec{k_i}^2/2m} \right) = \boxed{\prod_{i=1}^{N} \frac{1}{V} e^{-\frac{\pi}{\lambda^2}(\vec{r_i}'-\vec{r_i})^2} = \frac{1}{(V/\lambda^3)^N} \prod_{i=1}^{N} f(\vec{r_i}'-\vec{r_i})}.
\tag{9}
$$

3.2   Density Matrix calculations for identical free particles

Once we go to quantum mechanics, we really have to deal with identical particles. The identical particle wavefunctions are given by

$$\left|\vec{k}_1 \dots \vec{k}_N\right\rangle^{\text{A,S}} = \frac{1}{\sqrt{N! \prod_{k=1}^{\infty} n_k!}} \sum_P \eta^{E(P)} \left|\vec{k}_{P_1} \dots \vec{k}_{P_N}\right\rangle \tag{10}$$

where n_k are the occupation numbers associated to state $\vec{k}$, $\sum_P$ is sum over $N!$ permutations of states $\{\vec{k}_i\}$, and $\eta^{\text{A,S}} = \pm 1$ with $E(P)$ denoting the number of exchanges in the permutation P.

> **Important Trick:**
> Two fold sum over permutations $= N! \times$ sum over all permutations
>
> $$\sum_{P,P'} \eta^{E(P)} \eta^{E(P')} \left\langle \vec{k'}_{P'_1} \dots \vec{k'}_{P'_N} \middle| \vec{k}_{P_1} \dots \vec{k}_{P_N} \right\rangle = \sum_P \eta^{E(P)} \underbrace{\sum_{P'} \eta^{E(P')} \left\langle \vec{k'}_{P'_1} \dots \vec{k'}_{P'_N} \middle| \vec{k}_{P_1} \dots \vec{k}_{P_N} \right\rangle}_{N! \left\langle \vec{k'}_1 \dots \vec{k'}_N \right|}$$

Using the above trick, the normalization for identical particle wavefunctions is-

$$^{\text{A,S}}\left\langle \vec{k'}_1 \dots \vec{k'}_N \middle| \vec{k}_1 \dots \vec{k}_N \right\rangle^{\text{A,S}} = \sum_P \eta^{E(P)} \delta_{\vec{k'}_1 \vec{k}_{P_1}} \cdots \delta_{\vec{k'}_N \vec{k}_{P_N}}$$

The trace of an operator $\hat{O}$ using this method can be calculated as-

$$\text{Tr}(\hat{O}) = \frac{1}{N!} \sum_{\{\vec{k}_i\}} {}^{\text{A,S}}\left\langle \vec{k}_1 \dots \vec{k}_N \middle| \hat{O} \middle| \vec{k}_1 \dots \vec{k}_N \right\rangle^{\text{A,S}} \tag{11}$$

Let's now calculate the matrix elements of density matrix of <u>N identical particles</u> forming an ideal gas (assuming every particle occupies a different $\vec{k}$ state)-

1. In momentum representation

$$^{\text{A,S}}\left\langle \vec{k'}_1 \dots \vec{k'}_N \middle| \hat{\rho} \middle| \vec{k}_1 \dots \vec{k}_N \right\rangle^{\text{A,S}} = \frac{1}{N!} \sum_P \eta^{E(P)} \sum_{P'} \eta^{E(P')} \left\langle \vec{k'}_{P'_1} \dots \vec{k'}_{P'_N} \middle| \frac{e^{-\beta \hat{H}}}{Z} \middle| \vec{k}_{P_1} \dots \vec{k}_{P_N} \right\rangle$$

$$= \frac{1}{N!} N! \left\langle \vec{k'}_1 \dots \vec{k'}_N \middle| \sum_P \eta^{E(P)} \frac{e^{-\beta \hat{H}}}{Z} \middle| \vec{k}_{P_1} \dots \vec{k}_{P_N} \right\rangle = \sum_P \eta^{E(P)} \left\langle \vec{k'}_1 \dots \vec{k'}_N \middle| \frac{e^{-\beta \hat{H}}}{Z} \middle| \vec{k}_{P_1} \dots \vec{k}_{P_N} \right\rangle$$

$$= \boxed{\frac{1}{Z} \sum_P \eta^{E(P)} e^{-\beta \frac{\hbar^2}{2m} \sum_\alpha \vec{k}_\alpha^2} \delta_{\vec{k'}_1 \vec{k}_{P_1}} \cdots \delta_{\vec{k'}_N \vec{k}_{P_N}}}$$

where the partition function $Z = \mathrm{Tr}(e^{-\beta \hat{H}})$ expanded in momentum basis evaluates to

$$Z = \frac{1}{N!} \sum_{\vec{k}_i} {}^{\mathrm{A,S}} \left\langle \vec{k}_1 \ldots \vec{k}_N \middle| e^{-\beta \hat{H}} \middle| \vec{k}_1 \ldots \vec{k}_N \right\rangle^{\mathrm{A,S}} = \sum_{\vec{k}_i} e^{-\beta \frac{\hbar^2}{2m} \sum_\alpha \vec{k}_\alpha^{\,2}} \sum_P \eta^{E(P)} \delta_{\vec{k}_1 \vec{k}_{P_1}} \cdots \delta_{\vec{k}_N \vec{k}_{P_N}}$$

2. In position representation

$$^{\mathrm{A,S}} \left\langle \vec{r_1}' \ldots \vec{r_N}' \middle| \hat{\rho} \middle| \vec{r_1} \ldots \vec{r_N} \right\rangle^{\mathrm{A,S}} = \sum_P \eta^{E(P)} \left\langle \vec{r_1}' \ldots \vec{r_N}' \middle| \frac{e^{-\beta \hat{H}}}{Z} \middle| \vec{r}_{P_1} \ldots \vec{r}_{P_N} \right\rangle$$

Using the N distinguishable particle matrix element from equation (9), we get

$$^{\mathrm{A,S}} \left\langle \vec{r_1}' \ldots \vec{r_N}' \middle| \hat{\rho} \middle| \vec{r_1} \ldots \vec{r_N} \right\rangle^{\mathrm{A,S}} = \sum_P \frac{\eta^{E(P)}}{Z} \prod_{i=1}^N e^{-\frac{\pi}{\lambda^2} (\vec{r_i}' - \vec{r}_{P_i})^2} \cdot \frac{1}{\lambda^3} = \boxed{\sum_P \frac{\eta^{E(P)}}{Z} \prod_{i=1}^N f(\vec{r_i}' - \vec{r}_{P_i})}$$

$$(12)$$

where the partition function $Z = \mathrm{Tr}(e^{-\beta \hat{H}})$ expanded in position basis evaluates to

$$Z = \frac{1}{N!} \int \mathrm{d}^3 r_1 \ldots \mathrm{d}^3 r_N {}^{\mathrm{A,S}} \left\langle \vec{r_1} \ldots \vec{r_N} \middle| e^{-\beta \hat{H}} \middle| \vec{r_1} \ldots \vec{r_N} \right\rangle^{\mathrm{A,S}} = \frac{1}{N!} \sum_P \eta^{E(P)} \int \mathrm{d}^3 r_1 \ldots \mathrm{d}^3 r_N \prod_{i=1}^N f(\vec{r_i} - \vec{r}_{P_i})$$

3.3   Grand Canonical Formalism for identical particles

For indistinguishable particles, the occupation number basis is an equivalent but more natural basis to work with. The occupation numbers n_k satisfy

$$\sum_{k=1}^\infty n_k = N, \qquad \sum_{k=1}^\infty n_k \varepsilon_k = E$$

and the wavefunctions can be written equivalently as

$$|k_1 \ldots k_N\rangle \equiv |n_1 \, n_2 \, n_3 \ldots\rangle$$

In the occupation number basis, the density matrix elements for a canonical ensemble can be written as

$$^{\mathrm{A,S}} \langle n_1' \, n_2' \ldots | \hat{\rho} | n_1 \, n_2 \ldots \rangle^{\mathrm{A,S}} = \frac{1}{Z} \langle n_1' \, n_2' \ldots | e^{-\beta \hat{H}} | n_1 \, n_2 \ldots \rangle = \frac{1}{Z} e^{-\beta \sum_{k=1}^\infty n_k \varepsilon_k} \delta_{n_1, n_1'} \delta_{n_2, n_2'} \cdots$$

where the canonical partition function

$$Z^{\mathrm{BE/FD}} = \sum_{\{n_k\}}' e^{-\beta \sum_{k=1}^\infty n_k \varepsilon_k}$$

with the prime denoting a restricted sum which respects $\sum_{k=1}^{\infty} n_k = N$.

If we do the above calculations of <u>density matrix elements for a grand canonical ensemble</u>, we get the following

$$^{\text{A,S}}\langle n_1' \, n_2' \ldots | \frac{e^{-\beta(\hat{H} - \mu\hat{N})}}{\mathcal{Z}} | n_1 \, n_2 \ldots \rangle^{\text{A,S}} = \frac{1}{\mathcal{Z}} e^{-\beta \sum_{k=1}^{\infty} n_k(\varepsilon_k - \mu)} \, \delta_{n_1', n_1} \delta_{n_2', n_2} \cdots$$

where the grand canonical partition function is of the form

$$\mathcal{Z}(T, V, \mu) = \text{Tr}(e^{-\beta(\hat{H} - \mu\hat{N})}) = \sum_{\{n_k\}} e^{-\beta \sum_{k=1}^{\infty} n_k(\varepsilon_k - \mu)}$$

and we see that the restricted sum disappears in the partition function of a GC ensemble.

One can also use the occupation number basis for Maxwell-Boltzmann (MB) statistics, which is used to describe distinguishable particles. The canonical partition function for MB statistics can be written as

$$Z_{\text{MB}} = \frac{1}{N!} \sideset{}{'}\sum_{\{n_k\}} \langle n_1 \, n_2 \ldots | e^{-\beta\hat{H}} | n_1 \, n_2 \ldots \rangle \cdot (\text{Permutations of the ordered set } \{k_i\})$$

$$= \sideset{}{'}\sum_{n_1, n_2 \ldots = 0}^{N} \frac{1}{n_1! \, n_2! \, \ldots} \, e^{-\beta \sum_{k=1}^{\infty} n_k \varepsilon_k}$$

Therefore, by defining a statistical weight $g\{n_k\}$ such that

$$g\{n_k\} = \begin{cases} \frac{1}{n_1! \, n_2! \, \ldots}, & \text{MB statistics} \\ 1, & \text{BE statistics} \\ \begin{cases} 1, & \text{if } n_k = 0, 1 \, \forall \, k \\ 0, & \text{otherwise} \end{cases}, & \text{FD statistics} \end{cases}$$

we can write down the general form of the partition functions as

$$\boxed{\begin{aligned} Z &= \sideset{}{'}\sum_{\{n_k\}} g\{n_k\} \, e^{-\beta \sum_{k=1}^{\infty} n_k \varepsilon_k} \qquad \text{(Canonical)} \\ \mathcal{Z} &= \sum_{\{n_k\}} g\{n_k\} \, e^{-\beta \sum_{k=1}^{\infty} n_k(\varepsilon_k - \mu)} \quad \text{(Grand Canonical)} \end{aligned}}$$

$$\tag{13}$$
$$\tag{14}$$

A similar method can also be employed to find the expectation value of observables in both canonical and grand canonical settings

$$\boxed{\begin{aligned} \langle O \rangle &= \frac{1}{Z} \sideset{}{'}\sum_{\{n_k\}} g\{n_k\} \, e^{-\beta \sum_{k=1}^{\infty} n_k \varepsilon_k} \, \langle n_1 \, n_2 \ldots | \hat{O} | n_1 \, n_2 \ldots \rangle \qquad \text{(Canonical)} \\ \langle O \rangle &= \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} g\{n_k\} \, e^{-\beta \sum_{k=1}^{\infty} n_k(\varepsilon_k - \mu)} \, \langle n_1 \, n_2 \ldots | \hat{O} | n_1 \, n_2 \ldots \rangle \quad \text{(Grand Canonical)} \end{aligned}}$$

$$\tag{15}$$
$$\tag{16}$$

Similarly, the trace of the operators in the canonical and grand canonical cases evaluates to

$$\text{Tr}(\hat{O}) = {\sum_{\{n_k\}}}' \langle n_1 \, n_2 \dots | \hat{O} | n_1 \, n_2 \dots \rangle \, g\{n_k\} \qquad \text{(Canonical)}$$

$$\text{Tr}(\hat{O}) = \sum_{\{n_k\}} \langle n_1 \, n_2 \dots | \hat{O} | n_1 \, n_2 \dots \rangle \, g\{n_k\} \qquad \text{(Grand Canonical)}$$

Depending on whether the particles are distinguishable, or indistinguishable (in which case either fermions or bosons), the grand canonical partition function is of the following forms

$$\mathcal{Z}_{\text{BE}} = \prod_{k=1}^{\infty} \frac{1}{1 - z \, e^{-\beta \varepsilon_k}}, \quad \mathcal{Z}_{\text{FD}} = \prod_{k=1}^{\infty} (1 + z \, e^{-\beta \varepsilon_k}), \quad \mathcal{Z}_{\text{MB}} = \prod_{k=1}^{\infty} \exp\left(z \, e^{-\beta \varepsilon_k} \right) \qquad (17)$$

These expressions can be summarized succinctly in the following expression

$$\ln(\mathcal{Z}) = \frac{1}{a} \sum_{k=1}^{\infty} \ln\left(1 + az \, e^{-\beta \varepsilon_k} \right) \qquad \text{where } a = \begin{cases} +1, & \text{F.D.} \\ -1, & \text{B.E.} \\ \lim_{a \to 0}, & \text{M.B.} \end{cases} \qquad (18)$$

Here, $z = e^{-\beta\mu}$ is commonly referred as the *fugacity*. Using the partition function, the expectation values of the observables can be calculated.

$$\langle \hat{N} \rangle = N(T, V, \mu) = k_B T \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)_{T,V} = \sum_{k=1}^{\infty} \frac{1}{z^{-1} e^{\beta \varepsilon_k} + a}$$

$$\langle \hat{H} \rangle = U(T, V, \mu) = - \left(\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right)_{z,V} = \sum_{k=1}^{\infty} \frac{\varepsilon_k}{z^{-1} e^{\beta \varepsilon_k} + a}$$

$$\langle \hat{n}_k \rangle = -\frac{1}{\beta} \left(\frac{\partial \ln \mathcal{Z}}{\partial \varepsilon_k} \right)_{z,V,\varepsilon_{i \neq k}} = \frac{1}{z^{-1} e^{\beta \varepsilon_k} + a}$$

In the grand canonical ensemble, the fluctuations in the occupation numbers n_k can thus be calculated as

$$(\sigma \, n_k)^2 = \frac{1}{\beta^2} \frac{\partial^2 \ln \mathcal{Z}}{\partial \varepsilon_k{}^2} = -\frac{1}{\beta} \frac{\partial \langle n_k \rangle}{\partial \varepsilon_k} = \frac{e^{\beta(\varepsilon_k - \mu)}}{\left(e^{\beta(\varepsilon_k - \mu)} + a \right)^2}$$

$$\implies \frac{(\sigma \, n_k)^2}{\langle \hat{n}_k \rangle^2} = \frac{1}{\langle n_k \rangle} - a$$

In the general case where the quantum state (or the energies) of the particles of an ensemble depend not just on a single quantum number k_i (like a 1-D free particle), but on M quantum numbers $(\alpha_1 \, \alpha_2 \dots \alpha_M)$ (like a M-D QHO), then the partition function becomes-

$$\ln(\mathcal{Z}) = \frac{1}{a} \sum_{\alpha_1, \alpha_2 \dots \alpha_M = 0}^{\infty} \ln\left(1 + az \, e^{-\beta \varepsilon_{\alpha_1, \alpha_2, \dots \alpha_M}} \right)$$

3.4   Ideal Bose Gas

As calculated earlier, the grand canonical partition function for a Bose gas is given by

$$\mathcal{Z}_{\text{Bose}}(T, V, \mu) = \prod_{k=1}^{\infty} \frac{1}{1 - z\, e^{-\beta\varepsilon_k}} \qquad q_{\text{Bose}} \equiv \ln \mathcal{Z} = -\sum_k \ln\left(1 - z\, e^{-\beta\varepsilon_k}\right)$$

From this, the obervable expectation values become

$$\langle \hat{N} \rangle = \frac{1}{\beta} \frac{\partial q(T, V, \mu)}{\partial \mu} = \sum_k \langle n_k \rangle \xrightarrow{\text{continuum}} \int_0^{\infty} d\varepsilon\, g(\varepsilon)\, \langle n_\varepsilon \rangle$$

$$\langle \hat{H} \rangle = -\frac{\partial q(T, V, \mu)}{\partial \beta} = \sum_k \varepsilon_k \langle n_k \rangle \xrightarrow{\text{continuum}} \int_0^{\infty} d\varepsilon\, g(\varepsilon)\, \varepsilon \, \langle n_\varepsilon \rangle$$

$$\langle \hat{n_k} \rangle = -\frac{1}{\beta} \frac{\partial q(T, V, \mu)}{\partial \varepsilon_k} = \frac{1}{z^{-1}e^{\beta\varepsilon_k} + a}$$

where $\langle n_\varepsilon \rangle$ is a shorthand for $\langle n \rangle$ is a function of ε, and we have assumed regular BCs to approximate $\sum_k$ as

$$\sum_k \approx g_d \left(\frac{L}{2\pi}\right)^n \int d^n k = \int d\varepsilon\, g(\varepsilon)$$

where g_d is the degeneracy factor. For an n-dimensional system,

$$g(\varepsilon)\, d\varepsilon = \underbrace{g_d \frac{V}{h^n} \frac{2\pi^{n/2} p^{n-1}}{\Gamma(n/2)}}_{\tilde{g}(p)}\, dp$$

and in the general case where the dispersion relation is of the form $\varepsilon = \alpha p^s$, the density of states is of the form

$$g(\varepsilon) = g_d \frac{V}{s h^n} \frac{2\pi^{n/2}}{\Gamma(n/2)} \frac{\varepsilon^{n/s-1}}{\alpha^{n/s}}$$

For $\varepsilon = p^2/2m$, i.e. $n = 3, s = 2$ and $g_d = 1$, one can evaluate $\langle \hat{N} \rangle = N(T, V, \mu)$

$$N(T, V, z) = \frac{V}{\lambda^3} g_{3/2}(z) + N_0(z)$$

Here $N_e \equiv \frac{V}{\lambda^3} g_{3/2}(z)$ is the number of particles in the excited state, $N_0(z) = z/(1-z)$ is the number of particles in the ground state, and $g_n(z)$'s are the Bose-Einstein functions-

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^{\infty} dx\, \frac{x^{n-1}}{z^{-1}e^x - 1} \qquad \Longrightarrow \qquad g_n^{\text{max}} = g_n(z = 1) = \zeta(n)$$

Therefore, the maximum number of particles that the excited states can hold are

$$N_e^{\text{max}} = \frac{V}{\lambda^3} g_{3/2}^{\text{max}} = \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right) = V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \zeta\left(\frac{3}{2}\right) \sim V T^{3/2}$$

When the total number of particles N far exceeds N_e^{max}, i.e. $N_0 \gg N_e^{\text{max}}$, then most of the particles are in the $\varepsilon = 0$ ground state. The $N_0 \gg N_e^{\text{max}}$ condition implies that

$$N \approx N_0 = \frac{z}{1-z} \implies z = \frac{N_0}{N_0 + 1} \approx 1 - \frac{1}{N_0}$$

This is known as Bose-Einstein condensation. The condition for the onset of BEC is therefore given by $N > N_e^{\text{max}}$ or $z \approx 1$.

$$\boxed{N > N_e^{\text{max}} \implies N > VT^{3/2}\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\zeta\left(\frac{3}{2}\right)\right]}$$

Holding N and V constant, the onset temperature is-

$$T < T_C = \frac{h^2}{2\pi m k_B}\left[\frac{N}{V\zeta(3/2)}\right]^{2/3}$$

3.5   Ideal Fermi Gas

As calculated earlier, the grand canonical partition function for a Fermi gas is given by

$$\mathcal{Z}_{\text{Fermi}}(T, V, \mu) = \prod_{k=1}^{\infty}(1 + z\, e^{-\beta\varepsilon_k}) \qquad q_{\text{Fermi}} \equiv \ln\mathcal{Z} = \sum_k \ln\left(1 + z\, e^{-\beta\varepsilon_k}\right)$$

From this, the obervable expectation value for the average number of particles becomes

$$\langle\hat{N}\rangle = N(T, V, \mu) = \frac{1}{\beta}\frac{\partial\ln\mathcal{Z}}{\partial\mu} = \sum_k\frac{1}{z^{-1}e^{\beta\varepsilon_k} + 1} = \sum_k\langle n_k\rangle$$

Since we are dealing with fermions, $0 \leq \langle n_k\rangle \leq 1 \implies z^{-1}e^{\beta\varepsilon_k} = e^{\beta(\varepsilon_k - \mu)} \geq 0$. This implies any value of μ is allowed.

Again, approximating the sum as an integral, we have

$$q(T, V, z) = \int_0^{\infty}d\varepsilon\, g(\varepsilon)\ln\left(1 + z\, e^{-\beta\varepsilon}\right)$$

$$N(T, V, z) = \int_0^{\infty}d\varepsilon\, g(\varepsilon)\frac{1}{z^{-1}e^{\beta\varepsilon} + 1}$$

where $g(\varepsilon) = g_d\left[\frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2}\right]$. Shoving this into the integral, we get

$$q(T, V, z) = \frac{g_d V}{\lambda^3}f_{5/2}(z) \qquad\qquad N(T, V, z) = \frac{g_d V}{\lambda^3}f_{3/2}(z)$$

where $f_n(z)$ are the Fermi-Dirac functions defined as

$$f_n(z) = \frac{1}{\Gamma(n)}\int_0^{\infty}dx\,\frac{x^{n-1}}{z^{-1}e^x + 1} \qquad 0 \leq z \leq \infty$$

Using the Fermi-Dirac functions, one can write down the fundamental equation of the Fermi gas

$$U = \frac{3}{2}Nk_BT\,\frac{f_{5/2}(z)}{f_{3/2}(z)} \xrightarrow[N\lambda^3/(gV)\ll 1]{\text{in the classical limit}} p = \frac{2}{3}\frac{U}{V}$$

3.5.1   Degenerate Fermi Gas

Degenerate Fermi gases occur at low temperature and high densities limit. At $T = 0$, the average occupation number (with chemical potential $\mu\big|_{T=0} = \mu_0$) is

$$\langle n_\varepsilon \rangle \bigg|_{\mu=\mu_0,\, T=0} = \frac{1}{e^{\,\beta(\varepsilon-\mu)}+1}\bigg|_{\mu=\mu_0,\, \beta\to\infty} = \begin{cases} 0, & \text{if } \varepsilon > \mu_0 \\ 1, & \text{if } \varepsilon < \mu_0 \end{cases} = \Theta(\mu_0 - \varepsilon) \qquad (19)$$

$$\implies \boxed{\langle n_\varepsilon \rangle \bigg|_{\mu=\mu_0,\, T=0} = \Theta(\mu_0 - \varepsilon)} \qquad (20)$$

At $T = 0$, all the states with energies $\varepsilon \leq \mu_0$ are completely filled with exactly one particle per energy state (modulo any degeneracies). For $\varepsilon > \mu_0$, there is zero occupancy. $\therefore$ The Fermi energy ε_F of this system is $\varepsilon_F = \mu_0$.

The average particle number N and internal energy U can be directly calculated using the step function for average occupation number as in equation (20).

$$\langle \hat{N} \rangle = N = \int_0^\infty d\varepsilon\, g(\varepsilon)\, \Theta(\varepsilon_F - \varepsilon) = g_d V \left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{4}{3\sqrt{\pi}} \varepsilon_F^{3/2}$$

$$\langle \hat{H} \rangle = U = \int_0^\infty d\varepsilon\, g(\varepsilon)\, \varepsilon\, \Theta(\varepsilon_F - \varepsilon) = g_d V \left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{4}{5\sqrt{\pi}} \varepsilon_F^{5/2}$$

$$\implies \frac{U}{N} = \frac{3}{5}\varepsilon_F$$

One can also evaluate the observable expectation values in terms of the Fermi momentum p_F

$$\langle \hat{N} \rangle = N = \int_0^\infty d\varepsilon\, g(\varepsilon)\, \langle n_\varepsilon \rangle = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon) = \int_{-p_F}^{p_F} dp\, \tilde{g}(p)$$

$$\langle \hat{H} \rangle = U = \int_0^\infty d\varepsilon\, g(\varepsilon)\, \varepsilon\, \langle n_\varepsilon \rangle = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)\, \varepsilon = \int_{-p_F}^{p_F} dp\, \tilde{g}(p)\, \varepsilon(p)$$

4   Ising Model

Take a periodic chain of spin dipoles which can take either $\uparrow$ ($S_i = +1$) or $\downarrow$ ($S_i = -1$) and can only interact with the nearest neighbours. The energy of such an Ising chain in 1D can be written as

$$E = -H \sum_{i=1}^{N} S_i - J \sum_{i=1}^{N} S_i \cdot S_{i+1} = -\frac{H}{2} \sum_{i=1}^{N} (S_i + S_{i+1}) - J \sum_{i=1}^{N} S_i \cdot S_{i+1}$$

The partition function of this system is given by

$$Z = \sum_{j \in \{\text{states}\}} e^{-\beta E_j}$$

where the {states} are the 2^N possible configurations of the lattice.

$$Z = \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} e^{\beta \frac{H}{2} \sum_{k=1}^N (S_k + S_{k+1})} \, e^{\beta J \sum_{k=1}^N S_k \cdot S_{k+1}}$$

Introduce an operator $\hat{T}$ in the spin space with $|S_i = +1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|S_i = -1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Now for any i, we can define the number

$$T(S_i, S_{i+1}) = \exp\left[\beta \frac{H}{2}(S_i + S_{i+1}) + \beta J S_i \cdot S_{i+1}\right]$$

Since both S_i and S_{i+1} can take values ± 1, we can have four possible values for T. We write them down as $T_{++}, T_{+-}, T_{-+}, T_{--}$ and collect them in a matrix

$$\begin{pmatrix} T_{++} & T_{+-} \\ T_{-+} & T_{--} \end{pmatrix}$$

where $T_{++} = e^{\beta(H+J)}$, $T_{+-} = T_{-+} = e^{-\beta J}$, and $T_{--} = e^{\beta(-H+J)}$. Thinking of $\hat{T}$ as an operator, we can write the above matrix elements as

$$T_{++} = \langle S_i = +1|\hat{T}|S_{i+1} = +1\rangle \qquad T_{-+} = \langle S_i = -1|\hat{T}|S_{i+1} = +1\rangle$$
$$T_{+-} = \langle S_i = +1|\hat{T}|S_{i+1} = -1\rangle \qquad T_{--} = \langle S_i = -1|\hat{T}|S_{i+1} = -1\rangle$$

Thus, we can think of $T(S_i, S_{i+1}) = \langle S_i|\hat{T}|S_{i+1}\rangle$. Using this, the partition function becomes

$$Z = \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \prod_{i=1}^N \underbrace{\exp\left[\beta \frac{H}{2}(S_i + S_{i+1}) + \beta J S_i \cdot S_{i+1}\right]}_{T(S_i, S_{i+1})}$$

$$= \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \langle S_1|\hat{T}|S_2\rangle \, \langle S_2|\hat{T}|S_3\rangle \ldots \langle S_N|\hat{T}|S_1\rangle$$

The spin eigenkets corresponding to each site i also forms a complete basis, i.e. $|S_i = -1\rangle\langle S_i = -1| + |S_i = +1\rangle\langle S_i = +1| = \mathbb{I}$

$$\implies Z = \sum_{S_1=\pm 1} \langle S_1|\underbrace{\hat{T}\ldots\hat{T}}_{\text{n times}}|S_1\rangle = \sum_{S_1=\pm 1} \langle S_1|\hat{T}^N|S_1\rangle = \text{Tr}(\hat{T}^N)$$

If $\lambda_\pm$ are the eigenvalues of $\hat{T}$, then $\text{Tr}(\hat{T}^N) = \lambda_+^N + \lambda_-^N$. The $\hat{T}$ matrix is given by

$$\begin{pmatrix} e^{\beta(H+J)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(-H+J)} \end{pmatrix}$$

The eigenvalues of this matrix can be calculated using the secular equation and come out to be

$$\lambda_\pm = e^{\beta J}\left(\cosh(\beta H) \pm \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}\right)$$

Since $\lambda_+ > \lambda_- \implies \lambda_+^N \gg \lambda_-^N$ as $N \longrightarrow \infty$. Therefore,

$$\boxed{Z = \left[e^{\beta J} \left(\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}} \right) \right]^N}$$

The free energy per spin of the Ising Model system is then given by

$$\frac{F}{N} = -\frac{1}{N}\frac{1}{\beta} \ln(Z) = -\frac{1}{N}\frac{N}{\beta} \left[\beta J + \ln \left(\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}} \right) \right]$$

$$= -J - k_B T \ln \left(\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}} \right)$$

Similarly, the internal energy of the system can be calculated as

$$U = -\frac{\partial \ln Z}{\partial \beta} = -N \left[J + \frac{H \sinh(\beta H)}{\sqrt{e^{-4\beta J} + \sinh^2(\beta H)}} \right.$$

$$\left. - \frac{2J e^{-4\beta J}}{\left(\cosh(\beta H) + \sqrt{e^{-4\beta J} + \sinh^2(\beta H)} \right) \sqrt{e^{-4\beta J} + \sinh^2(\beta H)}} \right]$$

The magnetization per spin of the system can also be calculated

$$\frac{M}{N} = \frac{1}{N}\frac{\langle \mu \rangle}{V} = \frac{1}{NV}\frac{1}{\beta}\frac{\partial \ln Z}{\partial H} = \frac{e^{\beta J}}{V \lambda_+} \left[\sinh(\beta H) + \sinh \frac{2\beta H}{2\sqrt{e^{-4\beta J} + \sinh^2(\beta H)}} \right]$$

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