Statistical Physics

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Thermodynamics

Thermodynamics is a **phenomenological** description of properties of macro-scopic systems in thermal equilibrium.

Adiabatic wall (**isolated** system): does **not** allow **heat** or **chemical substances** (mass transfer) to pass across it.

- An essential prerequisite for the measurability of energy is the existence of walls that do not permit the transfer of energy in the form of heat.

Diathermal wall (**closed** system): allows heat transfer but do **not** allow transfer of matter across it.

Open system has at least one wall that separates it from another thermodynamic system

- heat flows and it can't maintain temperature difference across itself.
- the wall being permeable to at least one chemical substance, as well as to radiation; such a wall.

State functions or **thermodynamic coordinates**: These are functions that depend only on the current equilibrium thermodynamic state of the system.

- well defined only when the system is in equilibrium.
- Example: pressure and volume

Extensive parameters: scale linearly with the system

- e.g., mass, volume, energy and entropy.

Intensive parameters: does not depend on the system size or the amount of material in the system

- e.g., temperature, T; refractive index, n; density, ρ; and hardness of an object, η.

In **thermodynamic equilibrium** there are no **net** **macroscopic** flows of matter or of energy, within a system or between systems. In a system that is in its own state of internal thermodynamic equilibrium, no **macroscopic change** occurs.

Equations of state is a thermodynamic equation relating state variables. Examples:

$$\begin{cases} \left(P + a/V^2\right)\left(V - b\right) = N k_B T & \text{(van der Waals gas)} \\ M = \left(N \mu_B^2 B\right)/\left(3 k_B T\right) & \text{(Curie paramagnet)} \\ F = \left(K + DT\right)\left(L - L_0\right) & \text{(Hooke's law for rubber)} \end{cases}$$

Laws of thermodynamics are based on a number of empirical observations. Statistical mechanics attempts to obtain these laws starting from classical or quantum mechanical equations.

Zeroth law

If two systems, A and B, are **separately** in equilibrium with a third system, C, then they are also in equilibrium with one another.

- implies the existence of an important state function, the empirical temperature Θ

Let $\{X_1, X_2, \cdots\}$ be state functions of system X. X can be A, B and C. When 2 systems are in equilibrium there is a constraint between
their coordinates.

$$f_{AC}\left(A_1, A_2, \cdots; C_1, C_2, \cdots\right) = 0$$

$$f_{BC}\left(B_1, B_2, \cdots; C_1, C_2, \cdots\right) = 0$$

assuming that we can obtain explicit function of C_1

$$C_1 = F_{AC}(A_1, A_2, \cdots; C_2, \cdots)$$
$$C_1 = F_{BC}(B_1, B_2, \cdots; C_2, \cdots)$$

$$\implies F_{AC}(A_1, A_2, \cdots; C_2, \cdots) = F_{BC}(B_1, B_2, \cdots; C_2, \cdots)$$

now the **Zeroth law states** that **we can always eliminate** $\{C_1, C_2, \cdots\}$ from the above equation and obtain

$$f_{AB}(A_1, A_2, \cdots; B_1, B_2, \cdots) = 0$$

> Zeroth law only states that the set of all states can be split into equivalence classes. We need to further assume that these equivalence classes are **ordered** similar to and have **same cardinality** as $\mathbb{R}$.

Kelvin scale is defined using water triple point. Ideal gas is $P \to 0$ real (dilute real gas).

$$T(\text{K}) \equiv 273.16 \times \left(\lim_{P \to 0}(PV)_{\text{system}} \bigg/ \lim_{P \to 0}(PV)_{\text{ice-water-gas}} \right)$$

First law

$$dE = dQ + dW$$

$$dE = \sum_i \frac{\partial E}{\partial x_i} dx_i$$

- Based on the experimental fact that if we adiabatically isolate a system then the work done only depends on the final and initial states.

- dE **is** an exact differential but dQ and dW **aren't**.

Work can in general depend on several generalized displacements and their conjugate generalized forces. $dW = \sum_i J_i \, dx_i$

System	J Force (intensive)	x Displacement (extensive)
Fluid	$-P$ pressure	V volume
Wire	T tension	L length
Film	S surface tension	A area
Magnet	H magnetic field	M magnetization
Dielectric	E electric field	P polarization
Chemical reaction	μ chemical potential	N particle number

For an ideal gas $E(V, T) = E(T)$ (Joule's free expansion experiment).

Response functions: for characterizing the macroscopic behavior of a system. Experimentally measured.

- Heat capacities:(Heat sector) path dependent. C_P is larger since some of the heat is used up in the work done in changes of volume.

$$C_V = \frac{dQ}{dT}\bigg|_V = \frac{dE - dW}{dT}\bigg|_V = \frac{dE + P\,dV}{dT}\bigg|_V = \frac{\partial E}{\partial T}\bigg|_V$$
$$C_P = \frac{dQ}{dT}\bigg|_P = \frac{dE - dW}{dT}\bigg|_P = \frac{dE + P\,dV}{dT}\bigg|_P = \frac{\partial E}{\partial T}\bigg|_P + P\frac{\partial V}{\partial T}\bigg|_P$$

- Force constants:(Mechanical sector) ratio of displacement to force and are generalizations of the spring constant. Ex: isothermal compressibility of a gas, susceptibility of a magnet

$$\kappa_T = -\partial V / \left.\partial P\right|_T / V$$
$$\chi_T = \partial M / \left.\partial B\right|_T / V$$

- Thermal responses:(Mixed sector) change in the thermodynamic coordinates with temperature. Ex: expansivity of a gas

$$\alpha_P = \frac{\left.\frac{\partial V}{\partial T}\right|_P}{V}$$

Second law

Kelvin's statement: No process is possible whose sole result is the complete conversion of heat into work.
**Clausius's statement**: No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

Quasistatic process: It happens slowly enough for the system to remain in internal physical (but not necessarily chemical) thermodynamic equilibrium.
Reversible process: direction can be reversed by infinitesimal changes in some properties of the surroundings, such as pressure or temperature.
Cyclic process: returns to the original state.

1. All reversible processes are quasi-static but not vice versa.

2. All reversible processes are cyclic but not vice versa.
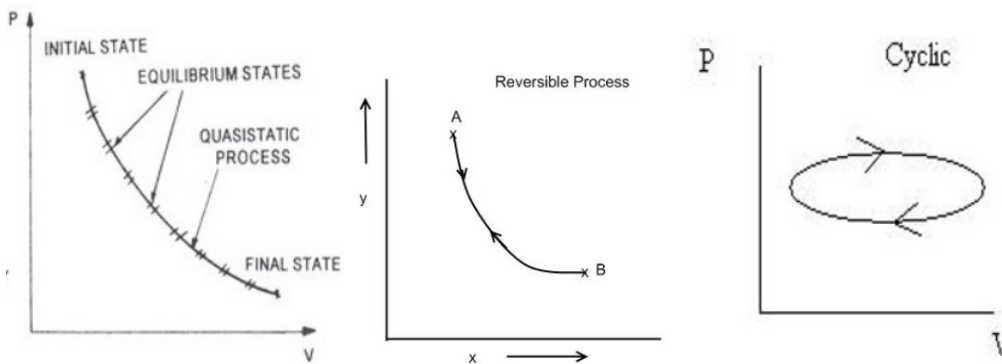
Entropy

Clausius's theorem For any cyclic transformation (reversible or not), $\oint \frac{dQ}{T_{\text{surr}}} \leq 0$, where dQ is the heat increment supplied to the system at temperature T.

- for reversible processes the equality holds. $\implies$ all reversible processes with same initial and final points will both have same change in entropy. If we consider only only reversible paths then entropy behaves like a state function. So, **for any reversible path**

$$dQ = TdS$$

$$\mathrm{d}E = TdS + \sum_i J_i \, \mathrm{d}x_i$$

Generalized "inequality of Clausius" for an infinitesimal change in entropy S applies not only to cyclic processes, but to any process that occurs in a closed system.

$$dS_{\text{sys}} \geq \frac{\delta Q}{T_{\text{surr}}}$$

Third law

The entropy of all systems at zero absolute temperature is a universal constant that can be taken to be zero.

$$\lim_{T \to 0} S(\mathbf{X}, T) = S(\mathbf{X}, 0) = 0$$

Ideal gas

For an ideal gas $E(V, T) = E(T)$ (Joule's free expansion experiment).

$$\kappa_T = \frac{1}{P}$$

$$C_P - C_V = Nk_B$$

$$\alpha_P = \frac{1}{T}$$

$$\mu = -\left.\frac{\partial S}{\partial N}\right|_{E,V} T = Tk_B \ln\left[\frac{V}{N}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right]$$

$$\Omega(N, E, V) = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{(3N/2 - 1)!}(2mE)^{(3N-1)/2}\Delta_R$$

$$S = k_B N \ln\left[\frac{V}{N}\left(\frac{4\pi em}{3}\frac{E}{N}\right)^{3/2}\right]$$

$$\frac{S}{k_B N} = \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right] + \frac{5}{2}$$

$$\lambda(T) = \frac{h}{\sqrt{2\pi mk_B T}},$$

Thermodynamic potentials

Name	Definition	Differential
Enthalpy	$H = E - \mathbf{J} \cdot \mathbf{x}$	$dH = T\,dS - \mathbf{x} \cdot d\mathbf{J}$
Helmholtz free energy	$F = E - TS$	$dF = -S\,dT + \mathbf{J} \cdot d\mathbf{x}$
Gibbs free energy	$G = E - TS - \mathbf{J} \cdot \mathbf{x}$	$dG = -S\,dT - \mathbf{x} \cdot d\mathbf{J}$
Grand potential ($\mathcal{G}$ or Ω)	$\mathcal{G} = E - TS - \mu \cdot \mathbf{N}$	$d\mathcal{G} = -S\,dT + \mathbf{J} \cdot d\mathbf{x} - \mathbf{N} \cdot d\mu$

Use of potentials: $dW \leq \mathbf{J} \cdot \delta\mathbf{x}$ (Equality is achieved for a quasi-static change but there is generally some loss of the external work to dissipation). If $dQ = 0$ then $\delta E \leq \mathbf{J} \cdot \delta\mathbf{x}$ and

$$\delta H \leq 0$$

Condition	$dQ = 0$	Constant T
dW=0	$dS \geq 0$	$dF \leq 0$
Constant $\mathbf{J}$	$dH \leq 0$	$dG \leq 0$

Maxwell relations

Schwarz' theorem

$$\frac{\partial}{\partial x_j}\left(\frac{\partial \Phi}{\partial x_i}\right) = \frac{\partial}{\partial x_i}\left(\frac{\partial \Phi}{\partial x_j}\right)$$

$$+\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V}$$

$$+\left(\frac{\partial T}{\partial P}\right)_S = +\left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P}$$

$$+\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V}$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = +\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial P}$$

Each equation can be re-expressed using the relationship

$$\left(\frac{\partial y}{\partial x}\right)_z = 1 \bigg/ \left(\frac{\partial x}{\partial y}\right)_z$$

Gibbs–Duhem relation

$$dE = T\, dS + \mathbf{J} \cdot d\mathbf{x} + \mu \cdot d\mathbf{N}$$

$$E(\lambda S, \lambda \mathbf{x}, \lambda \mathbf{N}) = \lambda E(S, \mathbf{x}, \mathbf{N})$$

$$\frac{\partial E}{\partial S}\bigg|_{\mathbf{x},\mathbf{N}} S + \sum_i \frac{\partial E}{\partial x_i}\bigg|_{S, x_{j\neq i}, \mathbf{N}} x_i + \sum_\alpha \frac{\partial E}{\partial N_\alpha}\bigg|_{S, \mathbf{x}, N_{\beta \neq \alpha}} N_\alpha = E(S, \mathbf{x}, \mathbf{N})$$

Now from the 1st equation we can substitute the partial derivatives

$$E = TS + \mathbf{J} \cdot \mathbf{x} + \mu \cdot \mathbf{N}$$

$$SdT + \mathbf{x} \cdot d\mathbf{J} + \mathbf{N} \cdot d\mu = 0$$

Probability

One random variable

Probability density function (PDF)

$$p(x) = \mathrm{prob}(E \subset [x, x + dx])$$

Cumulative probability function (CPF)

$$P(x) = \mathrm{prob}(E \subset [-\infty, x])$$

$$p(x) \equiv dP(x)/dx$$

Expectation value

$$\langle F(x) \rangle = \int_{-\infty}^{\infty} dx\, p(x) F(x)$$

$$p_F(f)df = \sum_i p(x_i)\, dx_i, \implies p_F(f) = \sum_i p(x_i) \left|\frac{dx}{dF}\right|_{x=x_i}$$

Moments of the PDF

$$m_n \equiv \langle x^n \rangle = \int dx\, p(x) x^n$$

Many random variables

Change of variables

$$dy_1 \cdots dy_n = \left| \frac{\partial(y_1, \ldots, y_n)}{\partial(x_1, \ldots, x_n)} \right| dx_1 \cdots dx_n$$

Here the substitution function needs to be injective and continuously differentiable, and the differentials transform as above.

$$|\mathbf{J}_{ij}| = \left| \frac{\partial y_i}{\partial x_j} \right|$$

$$\int_{\varphi(U)} f(\mathbf{v}) \, d\mathbf{v} = \int_U f(\varphi(\mathbf{u})) \left| \frac{\partial v_i}{\partial u_j} \right| d\mathbf{u}.$$

For orthogonal coordinates

$$J = \left| \frac{\partial \mathbf{r}}{\partial q^1} \cdot \left(\frac{\partial \mathbf{r}}{\partial q^2} \times \frac{\partial \mathbf{r}}{\partial q^3} \right) \right| = \left| \frac{\partial(x, y, z)}{\partial(q^1, q^2, q^3)} \right| = h_1 h_2 h_3$$

Central limit theorem

If $X_1, X_2, \ldots, X_n$ are n random samples drawn from a population with overall mean μ and finite variance σ^2, and if $\bar{X}_n$ is the sample mean, then the limiting form of the distribution

$$Z = \lim_{n \to \infty} \sqrt{n} \left(\frac{\bar{X}_n - \mu}{\sigma} \right) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2}$$

is a **standard** normal distribution.

Rules for large numbers

Saddle point integration

$$\mathcal{J} = \int dx \exp(N\phi(x))$$

$$\mathcal{J} \approx e^{N\phi(x_{\max})} \int dx \exp\left[-\frac{N}{2} |\phi''(x_{\max})| (x - x_{\max})^2 \right] \approx \sqrt{\frac{2\pi}{N |\phi''(x_{\max})|}} e^{N\phi(x_{\max})}$$

When there are multiple maxima take maximum among them.

Stirling's approximation

Let $\phi(x) = \ln x - x/N$ in the Saddle point integration then we get

$$\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N) + \mathcal{O}\left(\frac{1}{N} \right)$$

Classical Statistical Mechanics

Higher dimension areas and volumes

$$S_{n-1} = \frac{n\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2} + 1\right)} R^{n-1} = \frac{2\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2}\right)} R^{n-1}$$

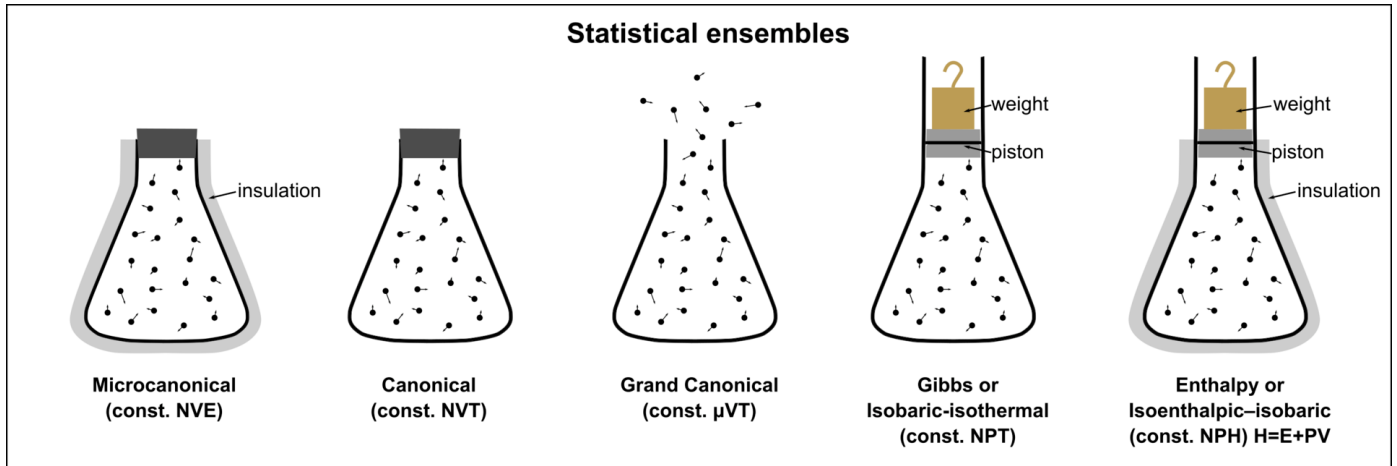$$V_n(R) = \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2} + 1\right)} R^n$$

$$\Gamma(x + 1) = x!$$

$$\Gamma(1/2) = (-1/2)! = \sqrt{\pi}$$

Ensembles

- in the thermodynamic limit $N \to \infty$ all these ensembles are in fact equivalent. They describe the same systems but through different variables.
  Note: for example in the grand canonical N is not fixed. But the probability of N is almost a delta function and average=most probable. This logic won't for Maxwell Boltzmann distribution because it is completely different. There you are talking about single particle not an ensemble. It is microscopic quantity not macroscopic.

Statistical ensembles

Microcanonical (const. NVE) — Canonical (const. NVT) — Grand Canonical (const. μVT) — Gibbs or Isobaric-isothermal (const. NPT) — Enthalpy or Isoenthalpic–isobaric (const. NPH) H=E+PV

The microcanonical ensemble

- macrostate $M \equiv (E, \mathbf{x})$
- (E, V, N) is constant among microstates and parametrize the system.

Find $\Omega(E, \mathbf{x})$ and find $S(E, \mathbf{x}) = k_{\mathrm{B}} \log \Omega(E, \mathbf{x})$ and using entropy we can find any other function.

Gibbs paradox

For an ideal gas

$$\Omega(N, E, V) = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{(3N/2 - 1)!} (2mE)^{(3N-1)/2} \Delta_R$$

- Ideal gas in **not consistent with classical mechanics** because the entropy is not extensive.
- Once we use the the fact that the **particles are identical** from quantum mechanics then the inconsistency is gone.

The canonical ensemble

$$F(T, \mathbf{x}) = -k_B T \ln Z(T, \mathbf{x})$$

$$p_{(T,\mathbf{x})}(\mu) = \frac{\mathrm{e}^{-\beta \mathcal{H}(\mu)}}{Z(T, \mathbf{x})}$$

$$Z(T, \mathbf{x}) = \sum_{\{\mu\}} \mathrm{e}^{-\beta \mathcal{H}(\mu)} = \sum_{\mathcal{E}} \mathrm{e}^{-\beta F(\mathcal{E})} = \approx \mathrm{e}^{-\beta F(E^*)}$$

$$p(\mathcal{E}) = \sum_{\{\mu\}} p(\mu)\delta(\mathcal{H}(\mu) - \mathcal{E}) = \frac{\Omega(\mathcal{E})\mathrm{e}^{-\beta \mathcal{E}}}{Z} = \frac{1}{Z} \exp\left[-\frac{F(\mathcal{E})}{k_B T}\right]$$

$$E = \langle \mathcal{H} \rangle = \sum_{\mu} \mathcal{H}(\mu) \frac{\mathrm{e}^{-\beta \mathcal{H}(\mu)}}{Z} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{\mu} \mathrm{e}^{-\beta \mathcal{H}} = -\frac{\partial \ln Z}{\partial \beta}$$

- macrostate $M \equiv (T, \mathbf{x})$

- $\mathrm{d}W = 0$ but $\mathrm{d}Q \neq 0$
- (T, V, N) is constant among microstates and parametrize the system.
- thermodynamic limit of $N \to \infty$, the canonical energy probability is so sharply peaked around the average energy that the ensemble becomes essentially indistinguishable from the microcanonical ensemble at that energy.

Ideal gas

$$\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}\sum_{i,j=1}^{n} A_{ij} x_i x_j\right) d^n x = \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} x^\mathsf{T} A x\right) d^n x = \sqrt{\frac{(2\pi)^n}{\det A}} = \sqrt{\frac{1}{\det(A/2\pi)}} = \sqrt{\det(2\pi A^{-1})}$$

using the above integral we get

$$
\begin{aligned}
Z(T, V, N) &= \int \frac{1}{N!} \prod_{i=1}^{N} \frac{\mathrm{d}^3 \vec{q}_i \, \mathrm{d}^3 \vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] \\
&= \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} = \frac{1}{N!}\left(\frac{V}{\lambda(T)^3}\right)^N,
\end{aligned}
$$

The Gibbs canonical ensemble

- macrostate $M \equiv (T, \mathbf{J})$
- $\mathrm{d}W \neq 0$, $\mathrm{d}Q \neq 0$
- (N, P, T) is constant among microstates and parametrize the system.

$$\mathcal{Z}(N, T, \mathbf{J}) = \sum_{\mu_S, \mathbf{x}} \mathrm{e}^{\beta \mathbf{J} \cdot \mathbf{x} - \beta \mathcal{H}(\mu_S)}$$

$$G(N, T, \mathbf{J}) = -k_B T \ln \mathcal{Z}$$

$$H = \langle \mathcal{H} - \mathbf{x} \cdot \mathbf{J} \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

The grand canonical ensemble

- macrostate $M \equiv (T, \mu, \mathbf{x})$
- $\mathrm{d}W \neq 0$, $\mathrm{d}Q \neq 0$
- (T, V, μ) is constant among microstates and parametrize the system.

$$\mathcal{Q}(T, \mu, \mathbf{x}) = \sum_{\mu_S} \mathrm{e}^{\beta \mu N(\mu_S) - \beta \mathcal{H}(\mu_S)}$$

$$\mathcal{G}(T, \mu, \mathbf{x}) = E - TS - \mu N = -k_B T \ln \mathcal{Q}$$

$$\langle \mathcal{N} \rangle = \frac{\partial \ln \mathcal{Q}}{\partial \beta \mu}$$

Quantum statistical mechanics

Density matrix

$$\rho = \sum_{j} p_j |\psi_j\rangle\langle\psi_j|$$

$$\langle A \rangle = \mathrm{tr}(\rho A)$$

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho] \text{ (Schrödinger picture)}$$

A simple criterion for checking whether a density matrix is describing a pure or mixed state is that the trace of ρ^2 is equal to **1 if the state is pure**, and less than 1 if the state is mixed. Another, equivalent, criterion is that the **von Neumann entropy** is 0 for a pure state, and strictly positive for a mixed state. Also for a pure state, $\rho = |\psi\rangle\langle\psi| \Rightarrow \rho = \rho^2$.

Fugacity

$$Z = e^{\beta\mu}$$

Microcanonical ensemble

$$\rho(E) = \frac{\delta(\mathcal{H} - E)}{\Omega(E)}$$

$$\langle n|\rho|m\rangle = \sum_\alpha p_\alpha \langle n \mid \Psi_\alpha\rangle \langle \Psi_\alpha \mid m\rangle = \begin{cases} \frac{1}{\Omega} & \text{if } \mathcal{E}_n = E, \text{ and } m = n, \\ 0 & \text{if } \mathcal{E}_n \neq E, \text{ or } m \neq n. \end{cases}$$

Canonical ensemble

$$\rho(\beta) = \frac{\exp(-\beta\mathcal{H})}{Z(\beta)}$$

$$Z = \operatorname{tr}\left(e^{-\beta\mathcal{H}}\right) = \sum_n e^{-\beta\mathcal{E}_n}$$

Grand canonical ensemble

$$\rho(\beta, \mu) = \frac{e^{-\beta\mathcal{H}+\beta\mu N}}{\mathcal{Q}}$$

$$\mathcal{Q}(\beta, \mu) = \operatorname{tr}\left(e^{-\beta\mathcal{H}+\beta\mu N}\right) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta)$$

Here we expressed it in terms of canonical partition function.

Bosons and Fermions

- For both B–E and M–B statistics, more than one particle can occupy the same state, unlike F–D statistics.

Appendix

Useful mathematical results

-
$$\int_{-\infty}^{\infty} e^{-a(x+b)^2} \, dx = \sqrt{\frac{\pi}{a}}$$

- Let $f(x, y, z) = 0$ and let w be function 2 of them:

$$\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z$$

$$\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w = \left(\frac{\partial x}{\partial z}\right)_w$$

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

$$\frac{\partial^2 w}{\partial x \partial y} = \frac{\partial^2 w}{\partial y \partial x}$$

- Euler's homogeneous function theorem:

  If f is a (partial) function of n real variables that is positively homogeneous of degree k, and continuously differentiable in some open subset of $\mathbb{R}^n$, then it satisfies in this open set the partial differential equation

  $$\sum_{i=1}^{n} x_i \frac{\partial f}{\partial x_i}(x_1, \ldots, x_n) = k\, f(x_1, \ldots, x_n)$$