Statistical Mechanics

Lecture notes — Baruch Horovitz and class of 2007

Contents

Reference books:

R. K. Pathria, Statistical Mechanics

Landau & Lifshitz, Statistical Physics

K. Huang, Statistical Mechanics

S.-k Ma, Statistical Mechanics

F. Mohling, Statistical Mechanics Methods and Applications

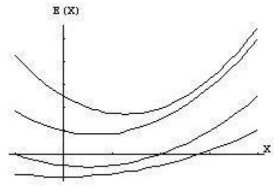
G. H. Wannier, Statistical Physics

1. ENSEMBLE THEORY

1a. Thermodynamics (Review)

Macroscopic state: Set of measurable "coordinates" of a system with many ($\to \infty$) degrees of freedom, e.g. volume V, number of particles N, energy E.
Equilibrium: A macroscopic state that is uniquely determined by a small number of external "forces", e.g. pressure P, chemical potential μ, temperature T.
Pairs of force f and coordinate x generate work $\delta W = f dx$ (δW is not necessarily an exact differential, i.e. equation may not be integrated to yield a state function W).
E.g. $\delta W = -PdV$, $\delta W = \mu dN$
Microscopic degrees of freedom contain "heat" energy Q, with S the coordinate, T the force.
$\delta Q = TdS$.
Thermodynamic limit: $N \to \infty$, $V \to \infty$ with $N/V \to$const. Macroscopic state, equilibrium etc. are defined in this limit. Define: Extensive variables that increase with N, e.g. V, E, S and intensive variables that are constants in the thermodynamic limit, e.g. N/V, P, μ.
First Law: Two ways to exchange energy, work or "heat": $\delta E = \delta Q + \delta W$; heat δQ is due to microscopic degrees of freedom. There exists an adiabatic process for which $\delta Q = 0$.
Entropy S is a thermodynamic coordinate - proof:

Adiabatic process $\delta Q = 0$. Equilibrium determines a curve $E(x)$ from $dE = f dx$. Between curves change is nonadiabatic, σ is an integration constant.



$E = E(x, \sigma)$. Curves do not cross since $f = \frac{\partial E}{\partial x}$ is unique in equilibrium. Also $E(x)$ is single valued $\Rightarrow E(x, \sigma)$ is monotonic in σ. For constant x, $\delta Q = dE = (\frac{\partial E}{\partial \sigma})_x d\sigma$

$dE = f dx + \tau d\sigma \qquad \tau = (\frac{\partial E}{\partial \sigma})_x$

σ is not unique - can choose $\bar{\sigma} = A(\sigma)$ with A(σ) monotonic. Choose σ which is extensive $\sigma \to S \sim N$, and define temperature T = $\frac{\partial E}{\partial S}$ as intensive. Assumption in proof: only one σ coordinate.

$$\Rightarrow dE = TdS - PdV + \mu dN$$

$E = E(S, V, N)$ is a (single valued) state function, $\oint dE = 0$. This is the first law.

Heat is not single valued - $\int$TdS depends on how V, N change along the path ($\oint \delta$Q $\neq 0$).

Second Law: In a closed system $S(t)$ increases with time. Exchange $dE_1 = -dE_2$ in two subsystems:

$S = S_1 + S_2$

$$\frac{dS}{dt} = \frac{dS_1}{dE_1}\frac{dE_1}{dt} + \frac{dS_2}{dE_2}\frac{dE_2}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt} > 0$$

$\Rightarrow$ energy flows from high to low T.

In equilibrium S is maximal $\Rightarrow T_1 = T_2$

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

If volumes of subsystems exchange $dV_1 = -dV_2$ with $T_1 = T_2$ (hence $\frac{\partial}{\partial E}$ terms vanish),

$dS = (\frac{\partial S_1}{\partial V_1})_{E,N}dV_1 + (\frac{\partial S_2}{\partial V_2})_{E,N}dV_2 = (\frac{P_1}{T} - \frac{P_2}{T})dV_1 \Rightarrow P_1 = P_2$ equilibrium.

Particle exchange $dN_1 = -dN_2$

$dS = (\partial S_1/\partial N_1)_{E,V}dN_1 + (\partial S_2/\partial N_2)_{E,V}dN_2 = (\mu_1/T - \mu_2/T)dN_1$

$\Rightarrow \mu_1 = \mu_2$ chemical equilibrium.

$TdS > dE + PdV - \mu dN = \delta Q$ irreversible process, i.e. S increases more than its equilibrium change.

Adiabatic process:

A process in which the energy is changed only by slow variation of external conditions so that at every instant the system is in equilibrium. Furthermore, the system is "thermally isolated" - no energy transfer except the external condition.

Adiabatic process is reversible: expand in $d\lambda/dt$, λ external condition (e.g. volume)

$\frac{dS}{dt} = a + b\frac{d\lambda}{dt} + \frac{1}{2}c(\frac{d\lambda}{dt})^2$

$a = 0$: equilibrium condition

$b = 0$: since $\frac{dS}{dt} > 0$ cannot depend on sign of $\frac{d\lambda}{dt}$

$\Rightarrow \frac{dS}{d\lambda} = \frac{1}{2}c\frac{d\lambda}{dt} + ... \rightarrow 0$ when $\frac{d\lambda}{dt} \rightarrow 0$.

$\Rightarrow dS = 0$ in adiabatic process.

Note: A reversible process in a closed system is an adiabatic process and S is constant. A reversible process in an open system is a process for which $TdS = dE + PdV - \mu dN$, i.e. heat exchange with a reservoir is allowed and $dS \neq 0$.

Thermodynamic Functions

$F = E - TS$ Helmholtz free energy

$dF = -SdT - PdV + \mu dN \Rightarrow F(T, V, N)$

If an additional variational parameter is present F is minimized to reach $dF = 0$.

T, V, N fixed: $dF = dE - TdS \leq 0$, for < 0 the process is irreversible.

$G = E - TS + PV$ Gibbs free energy

$dG = -SdT + VdP + \mu dN \Rightarrow G(T, P, N)$

T, P, N fixed: $dG = dE - TdS + PdV < 0$ and G is minimized.

$\tilde{\Omega} = F - \mu N$

$d\tilde{\Omega} = -SdT - PdV - Nd\mu \Rightarrow \tilde{\Omega}(T, V, \mu)$

T, V, μ fixed: $d\tilde{\Omega} = dE - TdS - \mu dN < 0$ and $\tilde{\Omega}$ is minimized.

Extensiveness: $\lambda E = E(\lambda S, \lambda V, \lambda N)$

$\frac{\partial}{\partial\lambda}|_{\lambda=1}$:

$$\begin{aligned} E &= TS - PV + \mu N \\ F &= -PV + \mu N \\ G &= \mu N \\ \tilde{\Omega} &= -PV \end{aligned} \qquad (1)$$

1b. Micro Canonical Ensemble (MCE)

Basic assumption:

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

Boltzman's constant: $k_B = 1.38 \cdot 10^{-16}$ erg/deg.

$\Omega(E)$ is the number of microstates for a given N, V, E, and states have equal weight :

$$\Omega(E) = \sum_{\{r\}} \delta_{E-H\{r\}}$$

$\{r\}$ are microscopic degrees of freedom of the N particles.

We shall now prove extensivity and maximum property: Consider two subsystems, neglect their interaction (justified since the number of particles near the surface is small, or surface energy $\ll$ bulk energy),

$$\begin{aligned} H\{r_1, r_2\} &= H_1\{r_1\} + H_2\{r_2\} \\ \Omega(E) &= \sum_{\{r_1,r_2\}} \delta_{E-H_1\{r_1\}-H_2\{r_2\}} \end{aligned}$$

$$= \sum_{E_1} \sum_{\{r_1\}} \delta_{E_1-H_1\{r_1\}} \sum_{\{r_2\}} \delta_{E-E_1-H_2\{r_2\}} = \sum_{E_1} \exp\left[\frac{S_1(E_1) + S_2(E-E_1)}{k_B}\right]$$

Since $S_i \sim N_i$ are large look for maximum in E_1 (equivalent to steepest descent),

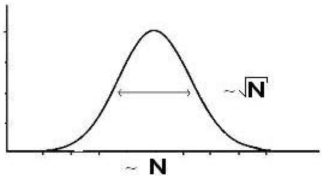
$$\begin{aligned} \frac{\partial}{\partial E_1} \left(S_1(E_1) + S_2(E-E_1)\right)|_{\bar{E}_1} &= 0 \\ \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \qquad\qquad \Rightarrow T_1 &= T_2 \end{aligned}$$

Expand to 2nd order

$$\begin{aligned} S_1(E_1) + S_2(E_2) &= S_1(\bar{E}_1) + S_2(\bar{E}_2) - \frac{1}{2k_1}(E_1 - \bar{E}_1)^2 - \frac{1}{2k_2}(E_2 - \bar{E}_2)^2 \\ \frac{1}{k_i} &= -\left(\frac{\partial^2 S}{\partial E_i^2}\right)_{E_i=\bar{E}_i} = -\frac{\partial(\frac{1}{T})}{\partial E_i} = \frac{1}{T^2 C_i} \\ C_i &= \left(\frac{\partial E_i}{\partial T}\right)_{V,N} \\ e^{S(E)/k_B} &= e^{S_1(\bar{E}_1)+S_2(\bar{E}_2)} \sum_{E_1} \exp\left(\frac{-1}{2k_1}(E_1 - \bar{E}_1)^2 - \frac{1}{2k_2}(E_2 - \bar{E}_2)^2\right) \end{aligned}$$

Probability that $E_1 \neq \bar{E}_1$ is Gaussian, $\langle (E_1 - \bar{E}_1)^2 \rangle^{1/2} \sim \sqrt{k_1} \sim \sqrt{N}$

Dominant term is $E_1 = \bar{E}_1$ with $\bar{E}_1$ such that $T_1 = T_2$.



If Δ is the spacing of E_1 levels (e.g. $\Delta \sim V^{-2/3}$ in ideal gas)

$$\begin{aligned}\sum_{E_1} \rightarrow & \int \frac{dE_1}{\Delta} \exp\left[-(\frac{1}{2k_1} + \frac{1}{2k_2})(E_1 - \bar{E}_1)^2\right] \\ = & \frac{1}{\Delta}\left(2\pi \frac{k_1 k_2}{k_1 + k_2}\right)^{1/2} \\ \Rightarrow S(E) = & S_1(\bar{E}_1) + S_2(\bar{E}_2) + O(\ln N)\end{aligned}$$

$\rightarrow$ Extensivity, ie. $\Omega(E)$ is dominated by one term: $\Omega(E) = \Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)$
(Note: The only function $f(\Omega)$ which is additive when $\Omega = \Omega_1\Omega_2$ is $f \sim \ln\Omega$)

Energy fluctuation $\sim \sqrt{k_i} = T\sqrt{C_V}$.

Similarly, separate to subsystems with $V = V_1 + V_2$ or $N = N_1 + N_2$ to obtain dominant term at $\bar{V}_i$ (hence $P_1 = P_2$) or at $\bar{N}_i$ (hence $\mu_1 = \mu_2$).

<u>Ideal Gas (no interactions)</u>

Classical: $r \rightarrow (p, q)$. For one particle energy $\epsilon(p)$: $\Omega_{cl} \sim \int d^{3N}q \int_{\sum_i \epsilon(p_i)=E} d^{3N}p \sim V^N$.
Note missing dimensional prefactor.
$\frac{P}{k_B T} = \left(\frac{\partial \ln\Omega}{\partial V}\right)_{N,E} = \frac{N}{V}$

Quantum: $r \rightarrow$ quantum numbers. Use periodic boundary conditions, e.g. $\mathrm{e}^{ip_x L/\hbar} = 1 \Rightarrow$
$p_x = \frac{h}{L}n_x$, n_x integer $-\infty < n_x < \infty$
$\epsilon = \frac{h^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$

$\Omega(E)$ is the number of solutions to $\sum_{r=1}^{3N} n_r^2 = \frac{2m}{h^2}EV^{2/3}$
$\Rightarrow S(N, V, E) = S(N, V^{2/3}E)$

In an adiabatic process $V^{2/3}E = const$, $P = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = \frac{2E}{3V}$
$\Rightarrow PV^{5/3} = const$

$\Omega(E)$ irregular - No. of points **on** surface of 3N sphere.

Instead $\Sigma(N,V,E) = \sum_{E' \leq E} \Omega(N,V,E')$ has reasonable $E \to \infty$ limit.

Replace Ω by $\Gamma =$ number of microstates with $E - \frac{\Delta}{2} <\text{energy}< E + \frac{\Delta}{2}$

$$\Omega \to \Gamma(N,V,E;\Delta) = \Delta \frac{\partial \Sigma}{\partial E}$$

Σ is the volume of 3N sphere with radius $R = (2mV^{2/3}E/h^2)^{1/2}$

Volume of n sphere: $V_n = C_n R^n$ with surface area $dV_n = nC_n R^{n-1} dR$

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} \cdots \int e^{-\sum_{i=1}^{n} x_i^2} \prod_i dx_i = \pi^{n/2}$$

In spherical coordinates:

$$\int_0^{\infty} e^{-r^2} nC_n r^{n-1} dr = \left(\frac{n}{2}\right)! C_n = \pi^{n/2}$$

$$\Rightarrow V_n = \frac{\pi^{n/2} R^n}{(n/2)!}$$

$$\Sigma(N,V,E) = \frac{\pi^{3N/2}}{(3N/2)!} (2mV^{2/3}E/h^2)^{3N/2} \Rightarrow \Gamma = \Delta \frac{3N\Sigma}{2E}$$

$$N \to \infty : \ln N! = N \ln N - N$$

$$\ln \Gamma = N \ln \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N + \ln \frac{3N}{2} + \ln \frac{\Delta}{E}$$

$\Delta \sim$ level spacing: $n_r \to n_r + 1$ for some r yields $E \to E + \Delta$

$$2n_r + 1 = \frac{2m}{h^2} \Delta V^{2/3} \qquad 0 \leq n_r < \left(\frac{2m}{h^2} E V^{2/3} \right)^{1/2} \sim N^{5/6}$$

$$\Rightarrow \qquad \sim N^{-2/3} < \Delta <\sim N^{1/6} \qquad \Rightarrow \qquad \ln \Delta / E = O(\ln N)$$

$$\Rightarrow \ln \Gamma = \ln \Sigma + O(\ln N)$$

Volume near surface dominates total volume for $N \gg 1$. Value of Δ is not important.

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

$$T = \left(\frac{\partial E}{\partial S} \right)_{N,V} = \frac{2E}{3Nk_B}$$

$$E = \frac{3}{2} N k_B T \Rightarrow \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} N k_B$$

$$P = - \left(\frac{\partial E}{\partial V} \right)_{N,S} = \frac{2E}{3V} \Rightarrow PV = N k_B T$$

$$C_p \equiv \left(\frac{\partial (E + PV)}{\partial T} \right)_{N,P} = \frac{5}{2} N k_B$$

$P \left(\frac{\partial V}{\partial T} \right)_{N,P}$ is excess work at constant P.

$$\Rightarrow \frac{C_p}{C_v} = \frac{5}{3}$$

Gibbs paradox:

S is not extensive. Even mixing gases 1,2 with equal T, n leads to $S_{total} \neq S_1 + S_2$

The "mixing" entropy is positive:

$$N k_B \ln V - N_1 k_B \ln V_1 - N_2 k_B \ln V_2 = k_B \left[N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] > 0$$

But this must be reversible !

Quantum mechanics - indistinguishability. Classical limit ($h \to 0$) should give $\Sigma \to \frac{1}{N!} \Sigma$

$$\Rightarrow S(N, V, E) = N k_B \ln \frac{V}{N} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

Sackur Tetrude eq. : S is extensive.

<u>Classical derivation</u> ...

$$\sum_{cl} = \frac{1}{w_0} \int d^{3N} q \int_{\sum_i p_i^2 < 2mE} d^{3N} p = \frac{1}{w_0} V^N C_{3N} (2mE)^{3N/2}$$

w_0 is chosen with $\sum \xrightarrow[\hbar \to 0]{} \sum_{cl}$

$$\sum = \frac{1}{N!} C_{3N} (\frac{2mE}{h^2})^{3N/2} \Rightarrow w_0 = N! h^{3N}$$

Where $\frac{1}{N!}$ is the Gibbs correction and h is the volume of one state in the p,q space.

Ex: evaluate w_0 for harmonic oscillator.

<u>Equipartition</u>

$x_i = q_i \quad or \quad p_i$

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle \equiv \frac{\underset{E-\frac{1}{2}\Delta<H<E+\frac{1}{2}\Delta}{\int \dots \int} x_i \frac{\partial H}{\partial x_j} d\omega}{\underset{E-\frac{1}{2}\Delta<H<E+\frac{1}{2}\Delta}{\int \dots \int} d\omega} = \frac{\Delta \frac{\partial}{\partial E} \underset{0<H<E}{\int \dots \int} x_i \frac{\partial H}{\partial x_j} d\omega}{\Delta \frac{\partial}{\partial E} \underset{0<H<E}{\int \dots \int} d\omega}$$

where $d\omega = \frac{d^{3N}q d^{3N}p}{N! h^{3N}}$. Noting that $\frac{\partial E}{\partial x_j} = 0$ and integrating by parts

$$\text{numerator} = \underset{0<H<E}{\int \dots \int} x_i \frac{\partial}{\partial x_j} (H-E) d\omega = \underset{0<H<E}{\int \dots \int} dx_{k \neq j} [x_i (H-E)]_{x_j^{(1)}}^{x_j^{(2)}} - \delta_{ij} \underset{0<H<E}{\int \dots \int} (H-E) d\omega$$

Assume $H(x_j) \to \infty$ and monotonic, e.g. $\frac{p^2}{2m}$ or at walls of container.

At boundaries, $x_j^{(1,2)}$, all energy is in x_j $\qquad H(x_j^{(1)}) = H(x_j^{(2)}) = E$

therefore, the first expression on the right side vanish. Returning to $\langle x_i \frac{\partial H}{\partial x_j} \rangle$ we have:

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \delta_{ij} \frac{\frac{\partial}{\partial E} \underset{0<H<E}{\int \dots \int} (E-H) dw}{\frac{\partial}{\partial E} \underset{0<H<E}{\int \dots \int} dw} = \delta_{ij} \frac{\underset{0<H<E}{\int \dots \int} dw}{\frac{\partial}{\partial E} \underset{0<H<E}{\int \dots \int} dw} = \frac{\delta_{ij}}{\frac{\partial}{\partial E} \ln \underset{0<H<E}{\int \dots \int} dw} = \frac{k_B \delta_{ij}}{(\frac{\partial S}{\partial E})_{N,V}} = \delta_{i,j} k_B T$$

concluding:

$\boxed{\langle x_i \frac{\partial H}{\partial x_j} \rangle = \delta_{i,j} k_B T}$ $\qquad x_j \to \infty \qquad$ with $H(x_j)$ monotonic unbounded.

E.g. (Specific examples):

$$x_i = x_j = p_i \qquad \langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \dot{q}_i \rangle = k_B T$$

$$x_i = x_j = q_i \qquad \langle q_i \frac{\partial H}{\partial q_i} \rangle = -\langle q_i \dot{p}_i \rangle = k_B T$$

for quadratic Hamiltonians (usually at high T)

$$H = \sum_j A_j p_j^2 + B_j q_j^2$$

for such systems we clearly have:

$$\sum_j (p_j \frac{\partial H}{\partial p_j} + q_j \frac{\partial H}{\partial q_j}) = 2H \Rightarrow \langle H \rangle = \frac{1}{2} f k_B T$$

f=No. of degree of freedom $\equiv$ number of quadratic terms in H.

Each harmonic term in the quadratic Hemiltonian makes a contribution of $\frac{1}{2}kT$ towards the internal energy of the system and hence a contribution of $\frac{1}{2}k$ towards the specific heat C_v.

Example: molecule with m atoms

C.M: 3 translations + 3 rotations   non co-linear molecule

3 translations + 2 rotations   co-linear

(To understand the significance of colinearity, note that quantum levels $\frac{\hbar^2 \ell(\ell+1)}{2I}$ form a classical continuum if $\frac{\hbar^2}{I} \ll k_B T$. However, if $I \to 0$ as in a colinear case, at $k_B T \ll \frac{\hbar^2}{I}$ only the single ground state is relevant)

3m coordinates $\Rightarrow$ no. of vibrations = 3m-6   non-collinear

or = 3m-5   collinear

Translation ($\frac{p_x^2}{2m}$), rotation ($\frac{L_x^2}{2I}$) - 1 quadratic term

Vibration ($\frac{p_x^2}{2m} + \frac{m\omega^2 x^2}{2}$) - 2 quadratic terms.

$$\langle H \rangle = \frac{1}{2}[6 + 2(3m-6)] N k_B T = (3m-3) N k_B T \qquad non-collinear$$

$$\langle H \rangle = \frac{1}{2}[5 + 2(3m-5)] N k_B T = (3m-5/2) N k_B T \qquad collinear$$

Virial Theorem (Clausius 1870) ...

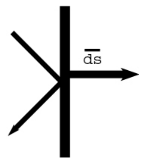
The Virial of a system is by definition, the sum of the products of the coordinates of the various particles and the representative forces acting on them:

$$\mathcal{V} \equiv \sum_{i=1}^{3N} \langle q_i \dot{p}_i \rangle = -3 N k_B T$$

E.g. ideal gas in box:

$\dot{p} \neq 0$ only from walls at $q_i = r$

$$\dot{\vec{p}} = -P\vec{ds}$$



where: P is pressure, ds is surface element and $\vec{p}$ is momentum hitting ds (of all particles)

$$\mathcal{V} = \sum_r \vec{r} \cdot \dot{\vec{p}} = -P \oint_s \vec{r} \cdot \vec{ds} = -P \int (\vec{\nabla} \cdot \vec{r}) dv = -3PV \Rightarrow PV = Nk_BT$$

Consider now classical particles i, j with 2-body interaction $u(r_{i,j}) : r_{ij} = |r_i - r_j|$.

$$\dot{\vec{p_i}} = -\frac{\partial}{\partial \vec{r_i}} \sum_j u(|r_i - r_j|)$$

$$\sum_i \vec{r_i} \cdot \dot{\vec{p_i}} = -\sum_{i,j} \vec{r_i} \cdot \frac{\partial}{\partial \vec{r_i}} u(|r_i - r_j|), \qquad \frac{\partial u(r)}{\partial \vec{r}} = \frac{\partial r^2}{\partial \vec{r}} \frac{\partial u}{\partial r^2}$$

Sum over pairs:

$$\sum_i \vec{r_i} \cdot \dot{\vec{p_i}} = \sum_{i<j} -\frac{\partial u}{\partial r_{ij}^2} [\vec{r_i} \cdot \frac{\partial (r_i - r_j)^2}{\partial \vec{r_i}} + r_j \frac{\partial (r_j - r_i)^2}{\partial \vec{r_j}}] + \text{wall pressure} =$$

$$-\sum_{i<j} \frac{\partial u}{\partial r_{ij}^2} [\overbrace{2\vec{r_i} \cdot (\vec{r_i} - \vec{r_j}) + 2\vec{r_j} \cdot (\vec{r_j} - \vec{r_i})}^{2r_{ij}^2}] = -\sum_{i<j} r_{ij} \frac{\partial u}{\partial r_{ij}} =$$

The net contribution, arising from all the $\frac{N(N-1)}{2}$ pairs of particles, $(N \gg 1)$:

$$\frac{1}{2} N(N-1) \langle -r \frac{\partial u}{\partial r} \rangle = -\frac{1}{2} N^2 \int \int r_{12} \frac{\partial u}{\partial r_{12}} g(r_1 - r_2) d^3r_1 d^3r_2 / V^2 = -\frac{N^2}{2V} \int r \frac{\partial u}{\partial r} g(r) 4\pi r^2 dr$$

g(r) pair distribution function

$$\mathcal{V} = -\frac{N^2}{2V} \int_0^\infty r \frac{\partial u}{\partial r} g(r) 4\pi r^2 dr - 3PV = -3Nk_BT$$

$$PV = NK_BT[1 - \frac{2\pi n}{3k_BT} \int_0^\infty \frac{\partial u(r)}{\partial r} g(r) r^3 dr]$$

Also:

$$E = \frac{3}{2} NK_BT[1 + \frac{4\pi n}{3k_BT} \int u(r) g(r) r^2 dr]$$

where the 1st term in the square brackets stands for the Kinetic energy.

1c. Ensemble theory - generalities

$\rho(p,q,t)d^{3N}qd^{3N}p$ is the probability of microstate(p,q), with normalization

$$\int_{E=const} \rho(p,q,t)d^{3N}qd^{3N}p = 1$$

Average: $\langle f \rangle = \int f(p,q)\rho(p,q,t)d^{3N}qd^{3N}p$

Equilibrium: all observables $\frac{\partial <f>}{\partial t} = 0 \Rightarrow \frac{\partial \rho}{\partial t} = 0$. In mechanics we start with a point p(0),q(0) in the 6N dimensional phase space, follow trajectory and average on time.
Ergodic theorem: Long time average = ensemble average, i.e. probability concept $\rho(p,q,t)$ is equivalent to mechanics.
Liouvill's theorem
$p(t), q(t)$ satisfy Hamilton's equation and define a velocity in phase space

$$\vec{v} = (\dot{q}, \dot{p})$$

Net flow of states from volume ω, with surface σ, is $= -\frac{\partial}{\partial t}\int \rho d\omega$

$$\Rightarrow \int_\omega \rho(\vec{v}\cdot\hat{n})d\sigma = \int_\omega div(\rho\vec{v})d\omega = -\frac{\partial}{\partial t}\int_\omega \rho d\omega$$

true for any ω $\Rightarrow$. Continuity: $\frac{\partial \rho}{\partial t} + div(\rho\vec{v}) = 0$.
$\Rightarrow$ Consider $\rho(q_i, p_i, t)$ for a collection of states $q_i(t), p_i(t)$

$$\frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) + \rho\sum_i \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) = 0$$

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial H}{\partial q_i \partial p_i} = -\frac{\partial \dot{p}_i}{\partial p_i}$$

and therefore $\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) = 0$ leads to

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H]_{poisson} = 0$$

Local density as viewed on moving points, is constant, hence $\frac{d\rho}{dt} = 0$.
No. of states is conserved $\Rightarrow$ incompressible "fluid".
Equilibrium:

$$\frac{\partial \rho}{\partial t} = 0 \Rightarrow \sum_i \left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) = 0$$

solutions:

$$\rho(p,q) = \begin{cases} \text{const} & E - \frac{1}{2}\Delta < H(p,q) < E + \frac{1}{2}\Delta \ \text{ microcanonical} \\ 0 & \text{otherwise} \end{cases}$$

In general ρ can depend on constants of motion, e.g. $H(p,q)$.

$$\rho[H(q,p)] \to \text{canonical ensemble}$$

In microcanonic $\rho(p,q,t) = \frac{1}{\Omega}$

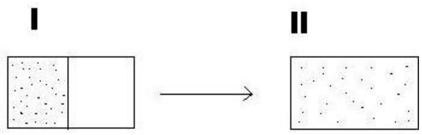
$$S = -k_B \ln \rho = -k_B \int \rho(p,q,t) \ln \rho(p,q,t) d^{3N}p d^{3N}q$$

defines entropy also in other ensembles, in equilibrium. Is this form of S valid at non-equilibrium? but then

$$\Rightarrow \frac{dS}{dt} = 0$$

which violates the second law.

Arrow of time



Consider volume expansion I→II. For $N = 10^{20}$, volume increases by factor 2.

The increase in number of states is $2^{10^{20}}$!! all states of I evolve into II, but only fraction $\frac{1}{2^{10^{20}}}$ of states in II evolve into I. Probability suggests that $S(t)$ increases.

Just probability is not sufficient:

Consider I→II→III, increasing volumes. States in II most probably go to III, but where do states in II come from - most probably also from III !? not I?

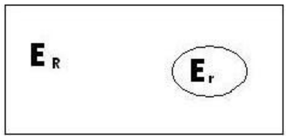
Time reversal invariance: a state x_1 in I evolves into x_2 in II. Now reverse all momenta in $x_2 \to R\vec{x}_2$.

$R\vec{x}_2$ is a state in II. It's time evolution yields x_1 in I, i.e. it is possible to find *a* state that lowers entropy.

The difficulty with $R\vec{x}_2$ is that it must be prepared accurately; a minute perturbation causes instability (chaos, the butterfly effect). Nature does not allow "perfect aiming" with accuracy $\sim 2^{10^{20}}$.

⇒ need probability + stability, i.e. information on nearby trajectories, "coarse grained", then entropy can increase with time.
Hypothesis: Universe started with low entropy, low entropy radiation from the sun produces low entropy food etc...

1d. Canonical Ensemble (CE)



Consider a system that is embedded in a larger "heat bath". Energy exchange is allowed, i.e. E_r is not fixed.
r is point in phase space of the system.
Reservoir energy E_R, $E_r << E_0$

$$E_R + E_r = E_0 = \text{const}$$

probability of state r $P_r \sim \Omega_R(E_R)$, i.e. the number of states of the reservoir.
[note: No. of all states with energy $E_r = \Omega_r(E_r)\Omega_R(E_R)$]

$$\Rightarrow P_r \sim \Omega_R(E_0 - E_r)$$

$$\ln \Omega_R(E_0 - E_r) = \ln \Omega_R(E_0) - \frac{\partial \ln \Omega_R}{\partial E}|_{E_0} E_r + \cdots = \ln \Omega_R(E_0) - \beta E_r$$

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$\beta = \frac{1}{k_B T}$ is determined by the reservoir. The partition function is defined by

$$Z_N(V,T) = \sum_r e^{-\beta E_r}$$

Define F BY $Z_N = e^{-\beta F(T,V,N)}$. Identify F:

$$0 = \frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r + \beta F} = \sum_r e^{-\beta E_r + \beta F} \left(-E_r + F + \beta \left(\frac{\partial F}{\partial \beta} \right)_V \right)$$

$$\Rightarrow F(T,V) - E(T,V) - T \left(\frac{\partial F}{\partial T} \right)_V = 0$$

solution of this differential equation is the free energy $F = E - TS$.
Alternative proof: Assume dominant energy in sum $\sum_r$:

$$Z_N(V,T) = \sum_r e^{-\beta E_r} = \sum_E \Omega(E) e^{-\beta E} = \sum_E e^{S(E)/k_B - \beta E}$$

dominant term at E^*:

$$\frac{\partial}{\partial E}(S(E)/k_B - \beta E) = 0 \Rightarrow \frac{\partial S(E)}{\partial E}|_{E^*} = \frac{1}{T}$$

E^* is such that the MCE at E^* has the temperature T.

$$S(E^*)/k_B - \beta E^* = -\beta F_{MCE}$$

where F_{MCE} is the free energy of the MCE defined with variable E^*, V, N.

Note: $S(E^*(T,V,N),V,N)$ defines $F(T,V,N)$.

Fluctuation near E^* (expanding S around E^*):

$$\frac{S(E)}{k_B} - \beta E \;=\; \frac{S(E^*)}{k_B} - \beta E^* + \frac{1}{2k_B}\frac{\partial^2 S}{\partial E^2}\bigg|_{E^*}(E-E^*)^2 + \dots\,,$$

where,

$$\frac{\partial^2 S}{\partial E^2} \;=\; \frac{\partial(1/T)}{\partial E} \;=\; -\frac{1}{T^2}\frac{1}{\partial E/\partial T} \;=\; -\frac{1}{T^2 C_V},$$

and T, C_V are for MCE.

$$Z_N(V,T) \;=\; e^{-\beta F_{MCE}} \sum_E e^{-(E-E^*)^2/2k_B T^2 C_V} \qquad \Rightarrow \qquad \text{Gaussian.}$$

The weight of $E \neq E^*$ decreases rapidly with width,

$$\frac{\sqrt{\langle (E-E^*)^2 \rangle}}{E^*} \;=\; \frac{\sqrt{k_B T^2 C_V}}{E^*} \sim \frac{1}{\sqrt{N}} \;\to\; 0.$$

To find the partition function, we replace the Sum with Integral,

$$\sum_E \;\to\; \frac{1}{\Delta}\int dE,$$

where Δ is the energy level spacing (as above $\Delta \propto N^a \to \ln \Delta \sim \ln N$), and

$$Z_N(V,T) \;=\; \frac{e^{-\beta F_{MCE}}}{\Delta}\int e^{-E^2/2k_B T^2 C_V} dE \;=\; \frac{e^{-\beta F}\sqrt{2\pi k_B T^2 C_V}}{\Delta} \;=\; e^{-\beta F_{CE}},$$

$$\Rightarrow \qquad F_{CE} \;=\; F_{MCE} + \mathcal{O}(\ln N),$$

where $F_{CE}, F_{MCE} \sim \mathcal{O}(N)$.

Insensitivity of thermodynamic results to type of ensemble due to:

1. $\Omega(E) \sim \mathrm{e}^{(\dots)N} \sim \mathrm{e}^{(\dots)E} \;\to\; \infty$: exponential increase.

2. Thermodynamic limit: $E, N \rightarrow \infty$.

E.g. for ideal gas, $\Omega(E)e^{-\beta E} \sim e^{(3/2)N\ln E - \beta E}$ with maximum at $E^* = \frac{3}{2}Nk_BT$. For $E \neq E^*$, $\Omega(E)e^{-\beta E}$ practically vanishes.

Note: The energy fluctuations can also be identified by evaluating the specific heat:

$$C_V = \frac{\partial}{\partial T}\langle E\rangle = \frac{-1}{k_BT^2}\frac{\partial}{\partial\beta}\frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{-1}{k_BT^2}\left(-\langle E^2\rangle + \langle E\rangle^2\right),$$

where

$$\left\langle (E - \langle E\rangle)^2\right\rangle = \left\langle E^2 - \langle E\rangle^2\right\rangle = k_BT^2C_V \sim N.$$

Examples:

- Classical systems: the general expression for the partition function,

$$Z_N(V,T) = \frac{1}{N!h^{3N}}\int e^{-\beta\mathcal{H}(p,q)}d^{3N}qd^{3N}p,$$

  where, $N!$ is Gibbs normalization, and h corresponds to a volume of one state in the q, p phase space.

- Ideal gas: $\mathcal{H} = \sum_i p_i^2/2m$,

$$Z_N(V,T) = \frac{V^N}{N!h^{3N}}\left(\int_0^\infty e^{-\beta p^2/2m}4\pi p^2 dp\right)^N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N,$$

  where,

$$\lambda \equiv \frac{h}{\sqrt{2\pi m k_BT}}, \qquad \text{the thermal wavelength.}$$

  This λ corresponds to a deBroiglie wavelength for momentum $\approx \sqrt{mk_BT}$ i.e. $\lambda \sim h/\sqrt{\langle p^2\rangle} = h/\sqrt{mk_BT}$.

$$\begin{aligned}
F &= -k_BT\ln Z_N = Nk_BT\left(\ln N\lambda^3/V - 1\right),\\
P &= -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{Nk_BT}{V},\\
S &= -\left(\frac{\partial F}{\partial T}\right)_{N,V} = Nk_B\left(\ln V/N\lambda^3 + 5/2\right), \quad \text{as in MCE},\\
\mu &= \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_BT\ln N\lambda^3/V.
\end{aligned}$$

- Consider N noninteracting molecules with internal energies ϵ_i, n_i molecules at level ϵ_i are indistinguishable.

$$
\begin{aligned}
Z_N(V,T) &= \sum_{\{n_i\}} \frac{1}{n_0!n_1!...} e^{-\beta \sum_i \epsilon_i n_i} \left(\underbrace{\int e^{-\beta p^2/2m} d^3p d^3q}_{\text{center of mass}} \right)^N \\
&= \frac{V^N}{N!\lambda^{3N}} \left(\sum_i e^{-\beta\epsilon_i} \right)^N , \qquad \text{using multinomial expansion} \\
&= \frac{1}{N!} \left(Z_1(V,T) \right)^N , \qquad Z_1 \equiv \frac{V}{\lambda^3} \sum_i e^{-\beta\epsilon_i} \quad \text{partition of one molecule.}
\end{aligned}
$$

Note: The multinomial expansion is:

$$
\left(\sum_i a_i \right)^N = N! \sum_{\{n_i\}} \frac{1}{n_1!n_2!...} a_1^{n_1} a_2^{n_2} ... ,
$$

where the sum on distributions $\{n_i\}$ is restricted by $\sum_i n_i = N$.

- Diatomic gas:

$$
\begin{aligned}
\mathcal{H} &= \underbrace{\varepsilon_0}_{\text{electron}} + \underbrace{\hbar\omega(\nu + 1/2)}_{\text{vibration}} + \underbrace{\hbar^2 k(k+1)/2I}_{\text{rotation}}, \\
Z &= e^{-\beta\varepsilon_0} \sum_{\nu=0}^{\infty} e^{-\beta\hbar\omega(\nu+1/2)} \sum_{k=0}^{\infty} (2k+1) e^{-\beta\hbar^2 k(k+1)/2I} \underbrace{\sum_s (2s+1)}_{\text{nonidentical atoms}} ,
\end{aligned}
$$

where s is the spin of the two atoms.

$$
\begin{aligned}
Z_{rot} &\overset{T\to\infty}{=} \int_0^\infty 2k e^{-\beta\hbar^2 k^2/2I} dk = 2I/\beta\hbar^2, \\
Z_{rot-class} &= \frac{1}{h^2} \int e^{-\beta(M_x^2+M_y^2)/2I} dM_x dM_y d\theta_x d\theta_y = 2I/\beta\hbar^2,
\end{aligned}
$$

The two atom axis is $\hat{z}$ and $d\theta_x d\theta_y = d\Omega \to 4\pi$ is the solid angle.

If the two atoms are identical, we need QM:

There is a constraint: $s+k$ needs to be even. [Orbital exchange has $(-)^k$, spin exchange has $(-)^{s-s_1-s_2}$, hence both Fermion and Boson symmetries are obeyed for $s+k$ even].

	Spin	k	degeneracy $= 2s+1$	
H_2	$s=1$	odd	3	orthohydrogen
	$s=0$	even	1	parahydrogen
D_2	$s=2$	even	5	
	$s=1$	odd	3	
	$s=0$	even	1	

$$
\begin{aligned}
Z_{rot}^{H_2} &= 3\sum_{\text{k odd}}(2k+1)e^{-\beta\hbar^2 k(k+1)/2I} + \sum_{\text{k even}}(2k+1)e^{-\beta\hbar^2 k(k+1)/2I}, \\
Z_{rot}^{D_2} &= 3\sum_{\text{k odd}} ... + 6\sum_{\text{k even}} ... \\
&\overset{T\to\infty}{\to} \frac{1}{2}\frac{2I}{\beta\hbar^2}\sum_s (2s+1).
\end{aligned}
$$

In the last equation, the $\frac{1}{2}$ is the classical reduction of angular integration by factor of 2, for identical atoms.

Equipartition:

$$
\left\langle x_i \frac{\partial H}{\partial x_j}\right\rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega},
$$

$$
\text{numerator} = \int x_i \frac{\partial H}{\partial x_j} \mathrm{e}^{-\beta H} d\omega = \frac{-1}{\beta}\int dx_{i\neq j} x_i \mathrm{e}^{-\beta H}\Big|_{x_j^{(1)}}^{x_j^{(2)}} + \frac{1}{\beta}\int \mathrm{e}^{-\beta H} d\omega \delta_{ij}.
$$

In general, the energy $H(x_j^{(1,2)}) \to \infty$ at the boundaries of $x_j \Rightarrow \left\langle x_i \frac{\partial H}{\partial x_j}\right\rangle = \delta_{ij} k_B T$.
E.g. ideal gas:

$$
\begin{aligned}
\left\langle p_{ix}\frac{\partial}{\partial p_{ix}}\frac{\vec{p_i}^2}{2m}\right\rangle &= \frac{1}{m}\left\langle p_{ix}^2\right\rangle = k_B T, \\
E &= \sum_i \left\langle \frac{\vec{p_i}^2}{2m}\right\rangle = \frac{3}{2}N k_B T.
\end{aligned}
$$

Extreme relativistic: $H = \sum_i c\,|\vec{p_i}|$,

$$
\begin{aligned}
\dot{q}_{ix} &= \frac{\partial H}{\partial p_{ix}} = \frac{\partial}{\partial p_{ix}} c\sqrt{p_{ix}^2 + p_{iy}^2 + p_{iz}^2} = \frac{c p_{ix}}{|\vec{p_i}|}, \\
\left\langle \sum_i \vec{p_i}\dot{\vec{q_i}}\right\rangle &= \left\langle \sum_i c\,|\vec{p_i}|\right\rangle = \langle H\rangle = 3N k_B T \quad (> \frac{3}{2}N k_B T),
\end{aligned}
$$

as the power of p smaller, the energy is higher for given temperature.

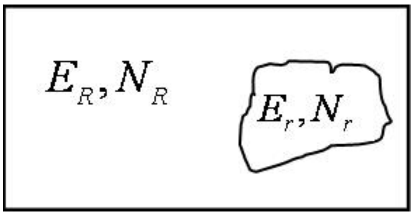
1e. Grand Canonical Ensemble (GCE)

System in heat bath *and* particle reservoir.

$$E_r \ll E_R, \qquad N_r \ll N_R$$

$$E_r + E_R = E_0 = Const.$$

$$N_r + N_R = N_0 = Const.$$



The combined system is microcanonic.

r is a point in phase space of the system, which now includes all N_r ($\ll N_0$). The probability of a point r with E_r, N_r is P_r

$$P_r \propto \Omega_R(N_0 - N_r, E_0 - E_r)$$

$$\begin{aligned}\ln P_r &\approx \ln \Omega_R(N_0, E_0) - \frac{\partial \ln \Omega_R}{\partial N}|_{N_0} N_r - \frac{\partial \ln \Omega_R}{\partial E}|_{E_0} E_r \\ &= \ln \Omega_R(N_0, E_0) + \beta\mu N_r - \beta E_r\end{aligned}$$

$\beta = 1/k_B T$, μ is imposed by the resevoir

$$\Rightarrow P_r = e^{\beta\mu N_r - \beta E_r}/\mathcal{L}$$

The grand partition function is

$$\mathcal{L}(\mu, T, V) = \sum_r e^{\beta\mu N_r - \beta E_r} \equiv e^{-\beta\widetilde{\Omega}(\mu,T,V)}$$

Identify $\widetilde{\Omega}$:

$$0 = \frac{\partial}{\partial\beta} \sum_r e^{\beta\mu N_r - \beta E_r + \beta\widetilde{\Omega}} = \sum_r \left(\mu N_r - E_r + \widetilde{\Omega} + \beta \frac{\partial\widetilde{\Omega}}{\partial\beta} \right) P_r$$

$$= \mu N - E + \widetilde{\Omega} - T\frac{\partial\widetilde{\Omega}}{\partial T}$$

The energy $E(\mu, T, V)$ shows that the solution to this differential equation is the theromodynamic potential, since $\widetilde{\Omega} = F - \mu N = E - \mu N - TS = E - \mu N + T\frac{\partial\widetilde{\Omega}}{\partial T}$

Alternatively, if $\sum_N$ is dominated by one term

$$\mathcal{L} \approx e^{\beta\mu N} \sum_{r, N fixed} e^{-\beta E_r} = e^{\beta\mu N - \beta F} \Rightarrow \widetilde{\Omega} = F - \mu N = -PV$$

Define fugacity $\zeta = e^{\beta\mu}$

$$\mathcal{L}(\zeta, T, V) = \sum_{N=0}^{\infty} \zeta^N Z_N(V, T)$$

So that the weight of each $N = \zeta^N Z_N / \mathcal{L}$.

$$N = \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{L}(\zeta, T, V)|_{T,V}$$

$$E = -\frac{\partial}{\partial \beta} \ln \mathcal{L}(\zeta, T, V)|_{\zeta,V} \qquad etc.$$

<u>Ideal gas:</u> with internal energies ϵ_i for each particle,

$$Z_1 = \frac{V}{\lambda^3} \sum_i e^{-\beta\epsilon_i} = \frac{V}{\lambda^3} a(T)$$

$$Z_N = \frac{1}{N!} Z_1^N \Rightarrow \quad \mathcal{L} = \sum_N \zeta^N \frac{1}{N!} Z_1^N = e^{\zeta Z_1}$$

$$\frac{PV}{k_B T} = \zeta Z_1 = e^{\beta\mu} \frac{V}{\lambda^3} a(T) \Rightarrow \mu = k_B T \ln \frac{P\lambda^3}{k_B T a(T)}$$

$$N = \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{L}(\zeta, V, T) = \zeta Z_1 = \frac{PV}{k_B T} \Rightarrow \mu = k_B T \ln(\frac{n\lambda^3}{a(T)}) \xrightarrow{n\lambda^3 \ll 1} -\infty$$

Particle (N) fluctuations:

Weight $W(N) = e^{\beta\mu N - \beta F(N,V,T)}/\mathcal{L}$

Maximum at $\overline{N}$ such that $\mu = \frac{\partial F}{\partial N}|_{\overline{N}}$, i.e. $\mu_{can} = \frac{\partial F}{\partial N}$ equals μ if N is chosen at this maximum, $N = \overline{N}$.

For maximum need $\frac{\partial^2 F}{\partial N^2}|_{\overline{N}} > 0$:

$$F(N, V, T) = N f(v) \qquad v = \frac{V}{N}$$

For fixed V, $\frac{\partial}{\partial N} = \frac{-v}{N} \frac{\partial}{\partial v}$, hence

$$\frac{\partial F}{\partial N} = f(v) - v \frac{\partial f}{\partial v} \Rightarrow \frac{\partial^2 F}{\partial N^2} = \frac{v^2}{N} \frac{\partial^2 f}{\partial v^2}$$

Since $P(v) = -\frac{\partial f}{\partial v} \Rightarrow \gamma \equiv \frac{\partial^2 F}{\partial N^2}|_{\bar{N}} = -\frac{v^2}{N} \frac{\partial P}{\partial v}$ (or $= \frac{\partial \mu}{\partial N}$) we need $(\frac{\partial P}{\partial v})|_T < 0$ for $W(\overline{N})$ being a maximum (this is Van Hove's theorem, Huang first edition p.321 - general proof; Huang second edition p.206 - for the special case of hardcore interaction).

Physically obvious: if $P > P_{ext}$ the net force increases V; now if $\frac{\partial P}{\partial V} > 0$ P increases even more and equilibrium ($P = P_{ext}$) is further away.

CE and GCE are equivalent by this thermodynamic stability criterion $(\frac{\partial P}{\partial v})|_T < 0$.
Note however, that at a 1st order phase transition, e.g. the gas-liquid transition, $\partial P/\partial v = 0$ and GCE is not equivalent to CE, hence large N fluctuations are expected.

$$W(N) \approx W(\bar{N}) e^{-\frac{1}{2}\beta\gamma(N-\overline{N})^2} \Rightarrow \left\langle \Delta N^2 \right\rangle^{\frac{1}{2}} = \sqrt{\frac{k_B T N}{v^2(-\partial P/\partial v)}} \sim \sqrt{N}$$

$$\left\langle \Delta N^2 \right\rangle^{\frac{1}{2}} / N \propto 1/\sqrt{N} \to 0$$

Energy fluctuations:

$$\overline{E} = \sum_r E_r P_r = -\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{\zeta,V}$$

$$\overline{E^2} = \frac{1}{\mathcal{L}}\left(\frac{\partial^2 \mathcal{L}}{\partial \beta^2}\right)_{\zeta,V} \Rightarrow \overline{\Delta E^2} = \overline{E^2} - \overline{E}^2 = \left(\frac{\partial^2}{\partial \beta^2}\ln \mathcal{L}\right)_{\zeta,V} = -\left(\frac{\partial \overline{E}}{\partial \beta}\right)_{\zeta,V} = k_B T^2 \frac{\partial \overline{E}}{\partial T}|_{\zeta,V}$$

$$\frac{\partial E\left(N\left(\zeta,T,V\right),T,V\right)}{\partial T} = \left(\frac{\partial E}{\partial T}\right)_{N,V} + \left(\frac{\partial E}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{\zeta,V} = C_V + \left(\frac{\partial E}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{\zeta,V}$$

$$dE = TdS - PdV + \mu dN \Rightarrow \left(\frac{\partial E\left(S\left(N,T,V\right),V,N\right)}{\partial N}\right)_{T,V} = \mu + T\left(\frac{\partial S}{\partial N}\right)_{T,V}$$

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

Chain rule $(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x(\frac{\partial z}{\partial x})_y = -1$
prove by $dx = (\frac{\partial x}{\partial y})_z dy + (\frac{\partial x}{\partial z})_y dz = 0$ which yields $(\frac{\partial y}{\partial z})_x$.

$$\left(\frac{\partial N(\mu(T,\zeta),T,V)}{\partial T}\right)_{\zeta,V} = \left(\frac{\partial N}{\partial T}\right)_{\mu,V} + \left(\frac{\partial N}{\partial \mu}\right)_{T,V}\left(\frac{\partial \mu}{\partial T}\right)_{\zeta} = -\left(\frac{\partial N}{\partial \mu}\right)_{T,V}\left(\frac{\partial \mu}{\partial T}\right)_{N,V} + \left(\frac{\partial N}{\partial \mu}\right)_{T,V}\frac{\mu}{T}$$

$$= \frac{1}{T}\left(\frac{\partial N}{\partial \mu}\right)_{T,V}\left[\mu - T\left(\frac{\partial \mu}{\partial T}\right)_{N,V}\right] = \frac{1}{T}\left(\frac{\partial N}{\partial \mu}\right)_{T,V}\left(\frac{\partial E}{\partial N}\right)_{T,V} \text{ from } (*)$$

$$\Rightarrow \overline{\Delta E^2} = k_B T^2 C_V + k_B T\left(\frac{\partial N}{\partial \mu}\right)_{T,V}\left[\left(\frac{\partial E}{\partial N}\right)_{T,V}\right]^2$$

$$= (\overline{\Delta E^2})_{can} + \overline{\Delta N^2}\left[\left(\frac{\partial E}{\partial N}\right)_{T,V}\right]^2 > (\overline{\Delta E^2})_{can}$$

$(\overline{\Delta E^2})^{\frac{1}{2}}/\overline{E} \approx 1/\sqrt{N} \to 0$ except at Phase transitions.

Summary: Thermodynamics:

$$E(S,V,N) \qquad\qquad dE = TdS - PdV + \mu dN$$

$$E - TS = F(T,V,N) \qquad dF = -SdT - PdV + \mu dN$$

$$F - \mu N = \widetilde{\Omega}(T,V,\mu) \qquad d\widetilde{\Omega} = -SdT - PdV - Nd\mu$$

Statistical Mechanics:

$$\Omega = \sum_{r \ \ (E,N fixed)} 1 = e^{S(E,V,N)/k_B} \qquad MCE$$

$$Z = \sum_{r \ \ (N fixed)} e^{-\beta E_r} = e^{-F(T,V,N)/k_B T} \qquad CE$$

$$\mathcal{L} = \sum_r e^{\beta\mu N_r - \beta E_r} = e^{-\widetilde{\Omega}(T,V,\mu)/k_B T} \qquad GCE$$

2. QUANTUM STATISTICAL MECHANICS

A system of N particles is described by a wave function $\psi(r_1, r_2, ...)$. Since the particles are indistinguishable, upon exchange of particles $r_i \leftrightarrow r_j$ the wave function acquires a phase $e^{i\theta}$

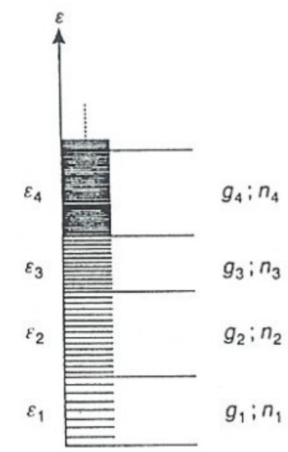
$$\psi(\cdots, r_i, \cdots, r_j, \cdots) = e^{i\theta}\psi(\cdots, r_j, \cdots, r_i, \cdots).$$

This particle exchange is equivalent to a rotation by π in the relative coordinate $r_i - r_j$. Exchanging the particles i, j twice is equivalent to a 2π rotation, which in 3-dimensions is equivalent to the identity operator [a circle on a sphere can be smoothly deformed into a point]. Hence $e^{2i\theta} = 1$ and there are two types of particles in nature:
$\theta = 0$ symmetric ψ for bosons (Bose Einstein statistics (BE))
$\theta = \pi$ antisymmetric ψ for fermions (Fermi Dirac statistics (FD)).
In particular fermions obey pauli's exclusion principle [antisymmetric wavefunction at $r_i = r_j$ vanishes]. Note also the spin-statistics connection, i.e. integer spin particles are bosons, half integer particles are fermions. Note also that in 2-dimensions other statistics are allowed; since the 2π rotation is now a circle with a singular point $r_i = r_j$ at its center, the circle cannot be deformed into an identity operation. In 3-dimension one "escapes in the 3rd dimension" avoiding the $r_i = r_j$ singularity.
We also define a "'Boltzman statistics"' (MB) where only the particles at the same energy level are indistinguishable, i.e. for each energy level ϵ we add a factor of $\frac{1}{n_\epsilon!}$.

2a. Ensembles for ideal quantum gases

<u>**Micro Canonical Ensemble**</u>

We group the different states into energy levels ϵ_i with degeneracy of g_i. Each level is occupied with n_i particles. For the statistical treatment we assume $g_i, n_i >> 1$.



$$\Omega(N, V, E) = \sum_{\{n_i\}}{}' W(\{n_i\}) \text{where} W(\{n_i\}) = \prod_i W(i) \quad \text{for a given distribution} \{n_i\}$$

The prime on the sum denotes the following constraints:

$$\sum_i n_i = N \quad \text{and} \quad \sum_i n_i \epsilon_i = E$$

For bosons, each energy level can be occupied with n_i particles within g_i folders with $g_i - 1$ divisions. Hence we choose n_i particles from $n_i + g_i - 1$ objects, $W(i) = \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$ and for all energy levels we have

$$W_{B.E.} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

For fermions we choose n_i sites from the g_i available ones, so

$$W_{F.D.} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \quad g_i \geq n_i >> 1$$

For the Boltzman statistics any particle can occupy any of the states up to the Gibbs correction $(\frac{1}{n_i!})$ for the indistinguishability of the particles in each energy level

$$W_{M.B.} = \prod_i \frac{(g_i)^{n_i}}{n_i!}$$

The Gibbs factor correctly accounts for permutations of particles in differen quantum states, but also unnecessarily corrects for particles that are in the same quantum state where correction is not necessary (e.g. one symmetric state only). Therefore $n_i!$ is an "over-correction" and is valid when the density is low $n_i << g_i$ and there is a small chance of all particles being in the same quantum state. This is also reflected in the possible situation $g_i^{n_i}/n_i! < 1$. E.g., consider two particles in two states n=g=2:

$$\begin{aligned}
W_{BE} &= 3 \qquad \left\{ |aa\rangle,\ |bb\rangle,\ \frac{1}{\sqrt{2}}(|ab\rangle + |ba\rangle) \right\} \\
W_{FD} &= 1 \qquad \frac{1}{\sqrt{2}}(|ab\rangle - |ba\rangle) \\
W_{MB} &= \frac{2^2}{2!} = 2 \qquad \tfrac{1}{2} \quad \text{of} \quad |aa\rangle \quad \text{or of} \quad |bb\rangle \quad \text{is ad hoc.}
\end{aligned}$$

The entropy of the quantum gas will be

$$S = k_B \ln \left(\sum_{\{n_i\}}' W(\{n_i\}) \right).$$

We now find the distribution n_i^* that maximizes S. Using the method of lagrange multipliers we demand

$$\delta\left[\ln W(\{n_i\}) - \alpha\sum_i n_i - \beta\sum_i n_i\epsilon_i\right] = 0.$$

with α, β to be determined below. Rewrite our 3 cases as

$$\ln\left(W(\{n_i\})\right) = \sum_i n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a}\ln\left(1 - a\frac{n_i}{g_i}\right)$$

where a is defined by $a = -1$ (BE), $a = +1$ (FD) and $a \to 0$ (MB).
Performing the variation yields

$$\sum_i\left[\ln\left(\frac{g_i}{n_i^*} - a\right) - \alpha - \beta\epsilon_i\right]\delta n_i = 0$$

so that S is maximized by the distribution

$$\frac{n_i*}{g_i} = \frac{1}{e^{\alpha+\beta\epsilon_i} + a}$$

The value of S at its maximum is therefore

$$S/k_B = \ln W(\{n_i^*\}) = \sum_i n_i^*(\alpha + \beta\epsilon_i) + \frac{g_i}{a}\ln\left(1 + ae^{-\alpha-\beta\epsilon_i}\right)$$

The coefficients α and β are determined by the constraints on N and E:

$$\begin{aligned}\frac{-\mu}{k_BT} &= \frac{1}{k_B}\left(\frac{\partial S}{\partial N}\right)_{E,V} = N\left(\frac{\partial\alpha}{\partial N}\right)_{E,V} + \alpha + E\left(\frac{\partial\beta}{\partial N}\right)_{E,V} \\ &+ \sum\frac{g_i}{a}\frac{-ae^{-\alpha-\beta\epsilon_i}}{1+ae^{-\alpha-\beta\epsilon_i}}\left[\left(\frac{\partial\alpha}{\partial N}\right)_{E,V} + \epsilon_i\left(\frac{\partial\beta}{\partial N}\right)_{E,V}\right] = \alpha\end{aligned}$$

since the last sum is $-N\left(\frac{\partial\alpha}{\partial N}\right)_{E,V} - E\left(\frac{\partial\beta}{\partial N}\right)_{E,V}$. The coefficient β is identified by

$$\begin{aligned}\frac{1}{k_BT} &= \frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)_{N,V} = N\left(\frac{\partial\alpha}{\partial E}\right)_{N,V} + E\left(\frac{\partial\beta}{\partial E}\right)_{N,V} + \beta \\ &+ \sum_i\frac{g_i}{a}\frac{-ae^{-\alpha-\beta\epsilon_i}}{1+ae^{-\alpha-\beta\epsilon_i}}\left[\left(\frac{\partial\alpha}{\partial E}\right)_{N,V} + \epsilon_i\left(\frac{\partial\beta}{\partial E}\right)_{N,V}\right] = \beta\end{aligned}$$

The equation of state is obtained by

$$\frac{1}{a}\sum_i g_i\ln(1 + ae^{-\alpha-\beta\epsilon_i}) = \frac{S}{k_B} + \frac{\mu N - E}{k_BT} = \frac{PV}{k_BT}$$

so that finally

$$PV = \left\{ \begin{array}{ll} \mp k_B T \sum g_i \ln \left[1 \mp e^{(\mu-\epsilon_i)/k_B T}\right] & a = \mp 1 \\ \\ k_B T \sum g_i e^{-\alpha-\beta\epsilon_i} = k_B T \sum n_i^* = k_B T N & a = 0 \\ \end{array} \right\} .$$

Canonical and Grand-Canonical ensembles

In the GCE there are no constraints on N, E. Hence we label by i all quantum numbers that completely specify a state so that $g_i = 1$ and

$$W_{BE}\{n_i\} = 1$$

$$W_{FD}\{n_i\} = 1 \text{ (if all } n_i = 0{,}1) \text{ or 0 otherwise}$$

$$W_{MB}\{n_i\} = \prod_i \frac{1}{n_i!}$$

notice that $W_{FD} < W_{MB} < W_{BE}$. E.g. with $N = 2$ particles in two states

$$\begin{array}{llr} \text{BE:} & |aa\rangle,\ |bb\rangle,\ \frac{1}{\sqrt{2}}(|ab\rangle + |ba\rangle) & \text{3 states} \\ \text{FD:} & \frac{1}{\sqrt{2}}(|ab\rangle - |ba\rangle) & \text{1 state} \\ \text{MB:} & \frac{1}{2}|aa\rangle, \quad \frac{1}{2}|bb\rangle, \quad |ab\rangle & \text{2 states.} \end{array}$$

Consider briefly the CE constrained with $\sum_i n_i = N$,

$$Z_N = {\sum_{\{n_i\}}}' W(\{n_i\}) e^{-\beta \sum_i n_i \epsilon_i}$$

and for the MB distribution

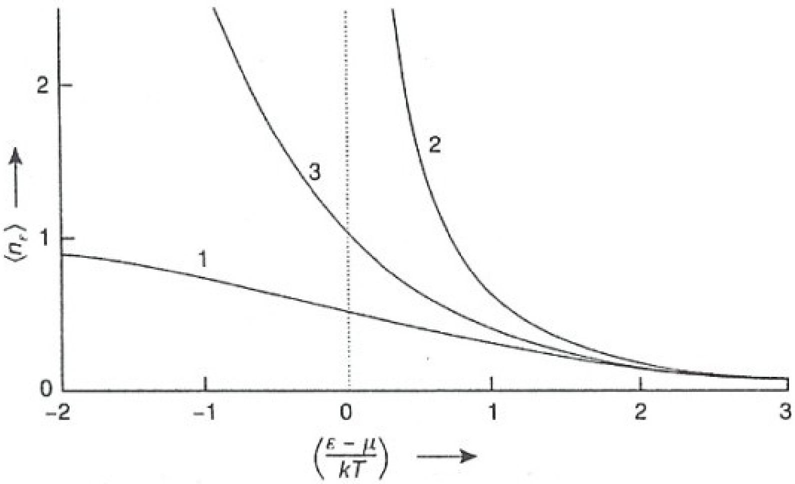
$$Z_N = {\sum_{\{n_i\}}}' \prod_i \left(\frac{N!}{n_i!} e^{-\beta\epsilon_i n_i}\right) \frac{1}{N!} = \text{using multinomial expansion} = \left(\sum_i e^{-\beta\epsilon_i}\right)^N \frac{1}{N!} = \frac{1}{N!} \left(Z_1(V,T)\right)^N$$

[Note: with $\epsilon_i \to 0$ we have $\sum_{n_i} W_{MB}\{n_i\} = N^N/N!$ for N particles in N states]. For the BE and FD statistics one has to proceed to the GCE, to avoid the $\sum n_i = N$ constraint.

$$\mathcal{L}(\zeta, V, T) = \sum_{N=0}^{\infty} \zeta^N Z_N(V.T) = \sum_{N=0}^{\infty} {\sum_{\{n_i\}}}' \prod_i \left(\zeta e^{-\beta\epsilon_i}\right)^{n_i} \qquad \text{with } \zeta = e^{\beta\mu}$$

here the first sum determines the constraint N on the second sum. However, since anyway we some on all occupations, we can sum them on each level independently,

$$\mathcal{L} = \sum_{n_0, n_1, \ldots} \left(\zeta e^{-\beta\epsilon_0}\right)^{n_0} \left(\zeta e^{-\beta\epsilon_1}\right)^{n_1} \cdots = \prod_i \left[\sum_{n_i} \left(\zeta e^{-\beta\epsilon_i}\right)^{n_i}\right]$$



now using $\sum_n x^n = \frac{1}{1-x}$ we get the result for each of the distributions

$$\mathcal{L} = \left\{ \begin{array}{lll} \prod_i \frac{1}{1-\zeta e^{-\beta\epsilon_i}} & BE & \\ & & \\ \prod_i \left(1+\zeta e^{-\beta\epsilon_i}\right) & FD & \\ & & \\ \ln L = \zeta Z_1 = \zeta \sum_i e^{-\beta\epsilon_i} & MB & \text{using } \sum \frac{x^n}{n!} = e^x \end{array} \right\}.$$

The GCE relation is

$$\ln \mathcal{L} = \frac{PV}{k_B T} = \frac{1}{a} \sum_i \ln\left(1 + a\zeta e^{-\beta\epsilon_i}\right)$$

and recall $a = -1$ for BE, $a = 1$ for FD and $a \to 0$ for MB. For N, E we have :

$$N = \zeta \left(\frac{\partial(\ln \mathcal{L})}{\partial \zeta}\right)_{V,T} = \sum_i \frac{1}{\frac{1}{\zeta} e^{\beta\epsilon_i} + a}$$

$$E = -\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{\zeta,V} = \sum_i \frac{\epsilon_i}{\frac{1}{\zeta} e^{\beta\epsilon_i} + a}$$

The mean occupation number is given by

$$\begin{aligned} \langle n_i \rangle &= \frac{1}{\mathcal{L}} \sum_N \sum_{\{n_j\}} n_i \zeta^N e^{-\beta \sum_j n_j \epsilon_j} \\ &= -\frac{1}{\beta} \left(\frac{\partial \ln \mathcal{L}}{\partial \epsilon_i}\right)_{\zeta,T,j\neq i} = \frac{1}{\frac{1}{\zeta} e^{\beta\epsilon_i} + a} = \frac{1}{e^{\beta(\epsilon_i - \mu)} + a} \end{aligned}$$

The figure illustrates the various cases. For FD, if $\mu > \epsilon$ and low temperatures the mean occupation tends to 1. For the BE case, the condition $\mu < \epsilon$ must be valid for all ϵ to maintain $\langle n_i \rangle \geq 0$; this leads (see below) to BE condensation. The MB distribution is valid only when $\langle n_i \rangle << 1$ which means $\frac{\epsilon_i - \mu}{k_B T} >> 1$ for all ϵ_i, hence $\mu < 0$ and $|\mu| \gg k_B T$ or $\zeta \ll 1$. The condition on the density is $N \cong \zeta \sum_i e^{-\beta \epsilon_i} = \zeta \frac{V}{\lambda^3}$ which implies high temperature or low density limit. Note that both BE and FD approach MB at this limit of $\zeta \ll 1$.

2b. Ideal Bose gas

Here $\epsilon_i = \vec{p}^2/2m$ and the summation index is $i = \vec{p}$.
A note on momentum summations: The sum $\sum_p$ actually stands for a sum on integers n_x, n_y, n_z that define p_x, p_y, p_z via periodic boundary conditions. E.g. $\mathrm{e}^{ip_x L_x/\hbar} = 1$ with L_x the length in the x direction, $p_x = \frac{2\pi\hbar}{L_x} n_x$, hence for any function $f(p)$

$$\sum_{n_x, n_y, n_z} f(p) = \int \frac{L_x L_y L_z}{h^3} f(p) d^3p = \frac{V}{h^3} \int f(p) d^3p$$

In radial coordinates we then have

$$\frac{P}{k_B T} = -\frac{4\pi}{h^3} \int_0^\infty p^2 \ln(1 - \zeta \mathrm{e}^{-\beta p^2/2m}) dp - \frac{1}{V} \ln(1 - \zeta)$$

$$\frac{N}{V} = \frac{4\pi}{h^3} \int_0^\infty p^2 \left[\frac{1}{\zeta} \mathrm{e}^{\beta p^2/2m} - 1 \right]^{-1} dp + \frac{1}{V} \frac{\zeta}{1 - \zeta}$$

The $p = 0$ term in the original sum is singled out. It is the number of particles $N_0 = \frac{\zeta}{1-\zeta}$ in the single state $p = 0$. [Equivalently, need $\zeta \mathrm{e}^{-\beta \epsilon_i} < 1$ to allow convergence for $\mathcal{L}$.]
The crucial property of bosons is $\zeta \leq 1$ so as to keep all state occupations $\langle n_p \rangle \geq 0$. For a given density the integral term decreases with T for a fixed ζ; to keep N/V fixed ζ must increase, but it is bound by $\zeta = 1$. The integral is bound at $\zeta = 1$, hence below some T_c the integral becomes $< N/V$ and a macroscopic part of N must populate the $p = 0$ state. This is *Bose Einstein condensation.*
The correction in the pressure equation is negligible:

$$1 - \zeta = \frac{1}{1 + < N_0 >} \Rightarrow -\frac{1}{V} \ln(1 - \zeta) = \frac{1}{V} \ln(< N_0 > + 1) \stackrel{always}{\rightarrow} 0$$

The boson thermodynamics are then given by

$$\frac{P}{k_B T} = \frac{1}{\lambda^3} g_{5/2}(\zeta)$$

$$\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(\zeta) + \frac{< N_0 >}{V}$$

$$g_n(\zeta) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1} dx}{\frac{1}{\zeta} e^x - 1} = \sum_{\ell=1}^\infty \frac{\zeta^\ell}{\ell^n}$$

For small ζ we use the expansion to eliminate ζ:

$$\Rightarrow \frac{PV}{NkT} = \sum_{\ell=1}^\infty a_\ell (n\lambda^3)^{\ell-1}$$

(a_ℓ = virial coefficient)

$$a_1 = 1, \quad a_2 = -\frac{1}{4\sqrt{2}} = -0.176, \quad a_3 = -0.0033 \quad .....$$

For specific heat:

$$E = -(\frac{\partial}{\partial \beta} \ln \mathcal{L})_{\zeta,V} = k_B T^2 \left[\frac{\partial}{\partial T} \frac{V g_{5/2}(\zeta)}{\lambda^3}\right]_{\zeta,V} = \frac{3}{2} k_B T \frac{PV}{k_B T} = \frac{3}{2} PV$$

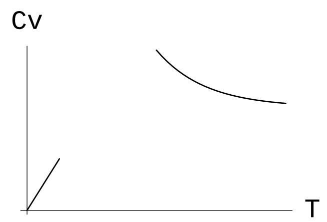
since the virial expansion for PV has $T(\lambda^3)^{\ell-1} \sim T^{5/2-3\ell/2}$ terms.

$$\frac{C_V}{Nk} = \frac{1}{Nk} \left(\frac{\partial E}{\partial T}\right)_{N,V} = \frac{3}{2} \left(\frac{\partial}{\partial T} \frac{PV}{Nk}\right)_{N,V} = \frac{3}{2} \sum_{\ell=1}^\infty \frac{5-3\ell}{2} a_\ell (n\lambda^3)^{\ell-1}$$

$$= \frac{3}{2}(1 + 0.0884 n\lambda^3 + 0.0066 (n\lambda^3)^2 + ...)$$

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_{N,V} \xrightarrow{T \to 0} 0$$

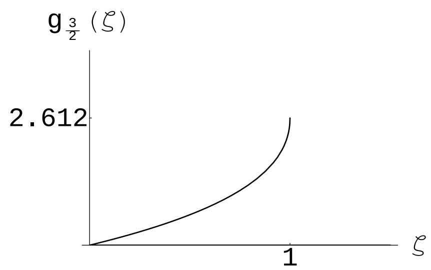
hence C_V looks roughly as:



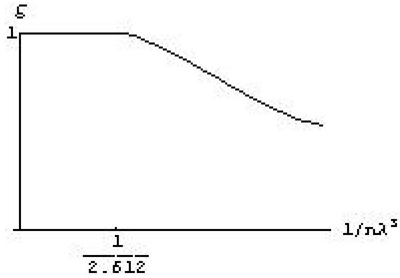
If $n\lambda^3 < g_{3/2}(1) = \zeta(\frac{3}{2}) = 2.612$

$$0 < \zeta < 1 \quad \text{and} \quad \frac{< N_0 >}{V} = 0$$

If $n\lambda^3 > g_{3/2}(1)$ $\quad \frac{<N_0>}{V} = n - \frac{g_{\frac{3}{2}}(1)}{\lambda^3} > 0$



with $\zeta = 1$ and finite density at the single $\epsilon = 0$ level.



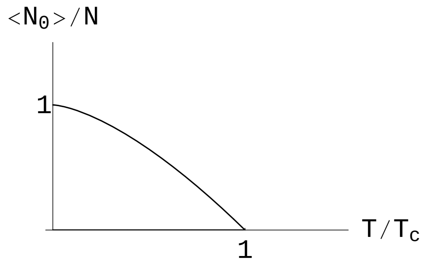
Transition at $n\lambda^3 = g_{\frac{3}{2}}(1) \Rightarrow kT_c = \frac{2\pi\hbar^2}{m[g_{3/2}(1)]^{\frac{2}{3}}} n^{2/3}$

When $\zeta = 1$, $< N_1 >$ is negligible since $\epsilon_1 \sim h^2/V^{2/3}$

$$\frac{< N_1 >}{V} = \frac{1}{V}\frac{1}{e^{\beta\epsilon_1 - 1}} \sim \frac{1}{V}\frac{V^{2/3}}{\beta h^2} \overset{V\to\infty}{\longrightarrow} 0$$

At $T \leq T_c$, $\frac{<N_0>}{N} = 1 - \frac{g_{3/2}(1)}{\lambda^3 n}$

$$= 1 - \left[\frac{T}{T_c(n)}\right]^{3/2} = 1 - \frac{n_c(T)}{n}$$

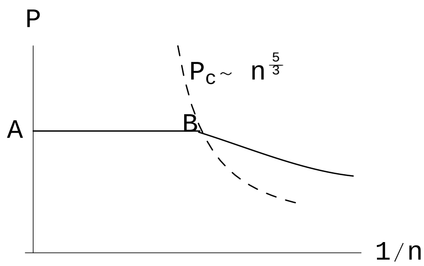


Two fluid concept: $< N_0 >$ condensate, $\frac{g_{\frac{3}{2}}(1)}{\lambda^3}$ normal component.

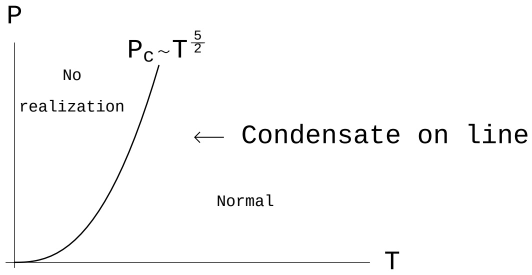
$$\frac{P}{kT} = \begin{cases} \frac{1}{\lambda^3} g_{5/2}(\zeta) & n < n_c \text{ (normal)} \\ \frac{1}{\lambda^3} g_{5/2}(1) & n > n_c \text{ (condensed phase)} \end{cases}$$

$$P_c \sim T^{\frac{5}{2}} \sim n^{\frac{5}{3}}$$

all excess particles beyond n_c occupy $p = 0$, $< N_0 > = N - N_c(T)$, even at $n \to \infty$ with no contribution to P. Along AB $\frac{\partial P}{\partial n} = 0$, two phases coexist with phase A that has $n \to \infty$.



This corresponds to a first order phase transition, $1/n$ jumps by $\Delta(1/n) = 1/n_c$ as pressures increases.



Note that there is no realization of $P > P_c(T)$. The equation of state defines a 2-dimensional surface in P, T, n; the figure is a projection of this surface on the P, T plane. There are no points on the surface that project onto the region $P > P_c(T)$. Consider a fixed n and an initial high temperature where $P = nk_BT$ and $P \ll P_c(T)$. Now as T decreases P approaches $P_c(T)$ at T_c, and upon further decrease of T, P stays on the critical curve $P(T) = P_c(T)$ for all $T < T_c$. This feature is an artifact of the ideal gas; once hard core repulsion is added, at sufficiently high density (in a constant T trajectory) the pressure will start to increase.

<u>Clausius Clapeyron</u>:

$$\frac{dP_c}{dT} = \frac{\Delta S/N}{\Delta(\frac{1}{n})}$$

ΔS is the jump in entropy. We will evaluate S directly:

$$\frac{S}{Nk_B} = \frac{PV}{Nk_BT} + \frac{E}{Nk_BT} - \frac{\mu}{kT} = \frac{5}{2}\frac{PV}{Nk_BT} - \frac{\mu}{k_BT} = \begin{cases} \frac{5}{2}\frac{g_{5/2}(\zeta)}{n\lambda^3} - \ln\zeta & T > T_c \\ \frac{5}{2}\frac{g_{5/2}(1)}{n\lambda^3} = \frac{5}{2}\frac{g_{5/2}(1)}{g_{3/2}(1)}\frac{N-<N_0>}{N} & T \le T_c \end{cases}$$

At $T < T_c$, $\;S \sim N- < N_0 >= N_{norm}$, no entropy for the condensate. Above the $P_c(T)$ line $S/N \to 0$, while just below this line

$$N = \frac{V}{\lambda^3}g_{3/2}(1) \Rightarrow \frac{S}{N} = \frac{5k_B}{2}\frac{g_{5/2}(1)}{g_{3/2}(1)}\,, \qquad \Delta(1/n) = 1/n_c = \lambda^3/g_{3/2}(1)$$

Consider now the derivative

$$\frac{dP_c}{dT} = \frac{5}{2}k\frac{g_{5/2}(1)}{\lambda^3} \quad \text{obtained from} \quad P_c = \frac{kT}{\lambda^3}g_{5/2}(1)$$

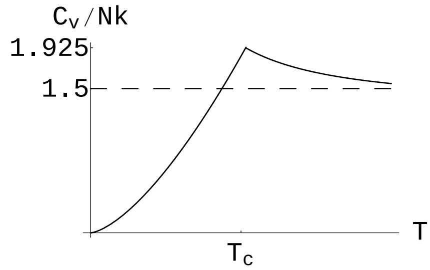
This proves the Clausius Clapeyron relation.

Note that ΔS implies a "Latent heat" $T\Delta S \Rightarrow$ 1st order transition.

Specific heat ($T < T_c$):

$$\frac{C_v}{Nk} = \frac{3V}{2N} g_{5/2}(1) \frac{d}{dT}\left(\frac{T}{\lambda^3}\right) = \frac{15}{4}\frac{\zeta(\frac{5}{2})}{n\lambda^3} \sim T^{3/2}$$

At $T > T_c$, $\dfrac{dC_v}{dT} \sim \dfrac{dg_{3/2}(\zeta)}{d\zeta} = \dfrac{g_{1/2}(\zeta)}{\zeta} \xrightarrow{\zeta \to 1} \infty$

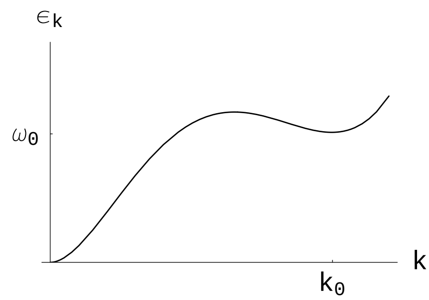


The shape of $C_V(T)$ is similar to the "λ transition" of ^{4}He, which looks like the letter λ.

For ^4He by this theory $T_c = 3.13°K$, by experimental results $T_c = 2.19°K$.

Note: In a real superfluid there is a finite critical velocity v_c below which there is no dissipation to the flow. This implies that at momentum k and frequency ω the current states have excitations $\omega = vk$ (note the transformation to the moving frame $\mathrm{e}^{vtd/dx}$) which cannot decay into the excitations $\omega(k)$ of the system at rest, hence $v_c = \min\{\omega(k)/k\}$. The ideal gas is therefore not a real superfluid since excitation energies are $\epsilon_k = \hbar^2 k^2/2m$, so that $v_c = 0$ at $k \to 0$.

With repulsive weak interaction g one has at $k \to 0$ $\epsilon_k = \hbar k \left(\frac{Ng}{Vm}\right)^{1/2}$, and critical current is finite either from this limit or from a "roton" minimum (see figure) so that $v_c = \omega_0/k_0$.



Black body radiation

Photons in thermal equilibrium correspond to bosons with $\mu = 0$ since there is no conservation law for photons, hence N minimizes F, i.e. $\partial F/\partial N = 0 = \mu$.

Photon spectrum is $\hbar\omega_k = \hbar ck$ with $|\mathbf{k}| = k$. Photons have two polarization states, $\epsilon = \pm 1$.

$$Z = \sum_{\{n_k,\epsilon\}} \mathrm{e}^{-\beta\sum_{n,\epsilon}\hbar\omega_k n_{k,\epsilon}} = \prod_{k,\epsilon}\sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega_k n} = \prod_k \frac{2}{1-\mathrm{e}^{-\beta\hbar\omega_k}}$$

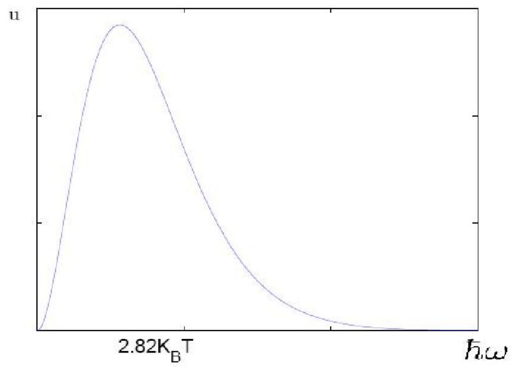
$\ln Z = -2\sum_k \ln(1 - \mathrm{e}^{-\beta\hbar\omega_k})$, same as the GCE $\mathcal{L}$ with $\mu = 0$. (Note $F = \tilde{\Omega}$ when $\mu = 0$).

$$\langle n_k \rangle = \frac{-1}{\beta}\frac{\partial}{\partial(\hbar\omega_k)}\ln Z = \frac{2}{\exp(\beta\hbar\omega_k) - 1}$$

$n(\omega)$ is the number of photons with the frequency ω.

$$\sum_k \langle n_k \rangle = \frac{V}{(2\pi)^3}\int 4\pi k^2 \langle n_k \rangle dk = \frac{4\pi V}{(2\pi)^3}\int (\frac{\omega}{c})^2 d(\frac{\omega}{c})\langle n_k \rangle \equiv \int_0^\infty n(\omega) d\omega$$

$$u(\omega) = \hbar\omega n(\omega) = \frac{\omega^3}{\exp(\beta\hbar\omega) - 1}\frac{\hbar}{\pi^2 c^3}$$



This is the Planck's formula for energy density.

The total energy

$$\frac{E}{V} = \int_0^\infty \hbar\omega n(\omega) d\omega = \frac{\pi^2 k_B^4}{15\hbar^3 c^3}T^4$$

$c_V \propto T^3$ is unbounded as $\omega \to \infty$ can contribute.

R is the rate of radiation through a small hole in a cavity. We need to average only velocities with $v_z > 0$

$$\langle v_z \rangle_{v_z > 0} = c\int_0^{\pi/2} \cos\theta d(\cos\theta) / \int_0^\pi d(\cos\theta) = \frac{c}{4}$$

$$\Rightarrow R = \frac{E}{V}\frac{c}{4} = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}T^4 \equiv \sigma T^4$$

where σ is Stefan's constant (1879) $\sigma = 5.670 \cdot 10^{-8}$ Watt/(meter)^2(Kelvin)^4.

We use periodic boundary quantization where $\vec{n}$ has integer entries,

$$\epsilon_k = \hbar c|\vec{k}| = \frac{\hbar c 2\pi |\vec{n}|}{V^{1/3}} \Rightarrow \frac{\partial \epsilon_k}{\partial V} = -\frac{1}{3}\frac{\epsilon_k}{V}$$

Therefore

$$P = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{3V}\Sigma_k \hbar\omega_k \langle n_k \rangle \Rightarrow PV = \frac{1}{3}E \Rightarrow P = \frac{4\sigma}{3c}T^4$$

(for nonreletavistic bosons $\epsilon_k \sim V^{-2/3} \Rightarrow \frac{\partial \epsilon_k}{\partial V} = \frac{-2}{3}\frac{\epsilon_k}{V} \Rightarrow PV = \frac{2}{3}E$).

$$\text{Note that} \qquad (\frac{\partial P}{\partial V})_T = 0 \Rightarrow \langle \Delta n^2 \rangle \to \infty$$

If the photon had a mass m ,then at $k_B T \ll mc^2$ Stefan's constant σ would change by a factor 3/2, inconsistent with experiment $\Rightarrow$ photon mass $= 0$ (i.e. less than the experimental $k_B T/c^2$.)

<u>Phonons</u>

Consider N atoms in a lattice that have $3N$ vibration modes, labeled by phonons with wavevector $\vec{k}$ and 3 polarizations. In the Debye model: $\omega = c|\vec{k}|$, $\omega < \omega_m$

$$3N = \Sigma_k 3 = 3\frac{V}{(2\pi)^3}\int 4\pi k^2 dk \equiv \int_0^{\omega_m} f(\omega)d\omega, \qquad f(\omega) = \frac{3\omega^2}{2\pi^2 c^3}V$$

Integrating $f(\omega)$ yields the cutoff frequency $\omega_m = c(6\pi^2 n)^{1/3}$; the Debye temprature is T_D : $k_B T_D = \hbar\omega_m$.

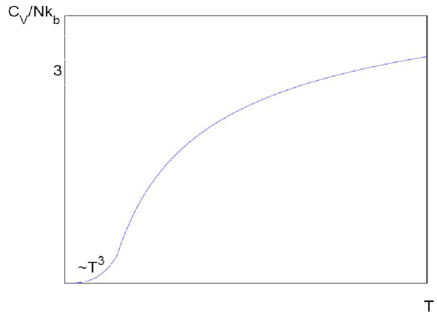
$$Z = \sum_{n_i} \mathrm{e}^{(-\beta\sum_i \hbar\omega_i n_i)} = \prod_{i=1}^{3N} \frac{1}{1-\mathrm{e}^{-\beta\hbar\omega_i}}$$

where $i = \{\vec{k}, \text{polarization}\}$.

$$\langle n_i \rangle = -\frac{1}{\beta}\frac{\partial}{\partial(\hbar\omega_i)}\ln Z = \frac{1}{\exp(\beta\hbar\omega_i)-1}$$

$$E = -\frac{\partial}{\partial\beta}\ln Z = \sum_i \hbar\omega_i\langle n_i\rangle = \int_0^{\omega_m} \hbar\omega\frac{f(\omega)}{\exp(\beta\hbar\omega)-1}d\omega =$$

$$E = \begin{cases} 3Nk_B T(1-\frac{3}{8}\frac{T_D}{T}+...) & T \gg T_D \\ 3Nk_B T\frac{\pi^4}{5}(\frac{T}{T_D})^3 + O(\exp(-\frac{T_D}{T})) & T \ll T_D \end{cases}$$



Experiments on specific heat confirm that noninteracting phonons are normal modes of solids at low T.

2c. Ideal Fermi gas

$$\frac{PV}{kT} = \ln\mathcal{L} = \sum_{p,spin}\ln(1+\zeta\exp(-\beta p^2/2m))$$

Where $\zeta = \exp(\beta\mu)$ and

$$\langle n_p\rangle = \frac{1}{\frac{1}{\zeta}\mathrm{e}^{\beta p^2/2m}+1}$$

so that $N = \sum_{p,spin}\langle n_p\rangle$.

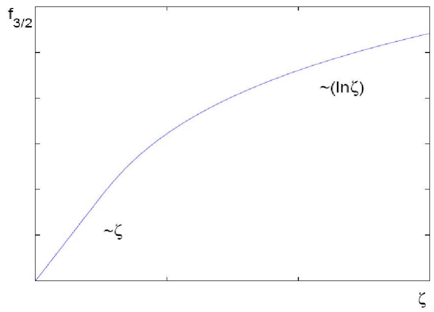
$$\frac{P}{k_BT} = \frac{4\pi}{h^3} g \int_0^\infty dp p^2 \ln\left(1 + \zeta \exp\left(-\beta p^2/2m\right)\right) = \frac{g}{\lambda^3} f_{5/2}(\zeta)$$

where $g = 2s + 1$ is the number of spin states

$$n = \frac{4\pi}{\hbar^3} g \int_0^\infty dp p^2 \frac{1}{\frac{1}{\zeta} e^{\beta p^2/2m} + 1)} = \frac{g}{\lambda^3} f_{3/2}(\zeta)$$

$$f_n(\zeta) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{\frac{1}{\zeta}\exp(x) + 1} dx$$

$$= \sum_{l=1}^{\infty} (-)^{l+1} \frac{\zeta^l}{l^n}$$



$0 < \zeta < \infty$ (unlike bosons!)

For $n\lambda^3 \ll 1$ or $\zeta \ll 1$:

$$n\lambda^3/g = \zeta - \zeta^2/2^{3/2} + \ldots, \qquad [\langle n_p \rangle \to \frac{1}{g} n\lambda^3 \exp\left(-\beta\epsilon_p\right) \text{ is MB form}]$$

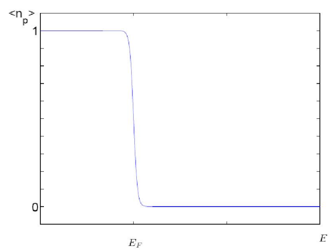
$$\frac{P}{nk_BT} = \frac{g}{n\lambda^3}(\zeta - \zeta^2/2^{5/2} + \ldots) = 1 + \frac{1}{g2^{5/2}} n\lambda^3 + \ldots$$

This is the virial expansion. Consider next $n\lambda^3 \gg 1$

$$\frac{1}{g} n\lambda^3 = \frac{4}{3\sqrt{\pi}}[(\ln\zeta)^{3/2} + \frac{\pi^2}{8}(\ln\zeta)^{-1/2} + \ldots] + O(1/\zeta)$$

Where $\zeta \to e^{\beta\epsilon_F}$, so that by comparing $T \to 0$ terms

$$\epsilon_F = \frac{\hbar^2}{2m}(\frac{6\pi^2 n}{g})^{2/3}$$



To confirm the $T = 0$ result $\langle n_p \rangle \to \frac{1}{\exp\left(\beta(\epsilon_p - \epsilon_F)\right) - 1}$ so that all the states with $\epsilon_p < \epsilon_F$ are occupied. Therefore

$$N = g\frac{V}{h^3} \int_{\epsilon_p < \epsilon_F} d^3p = \frac{gV}{(2\pi\hbar)^3} \frac{4\pi}{3} p_F^3 \Rightarrow \epsilon_F = p_F^2/2m$$

confirming the result $\epsilon_F = \frac{\hbar^2}{2m}(\frac{6\pi^2 n}{g})^{2/3}$.

Expansion at $k_BT \ll \epsilon_F$:

$$\mu = \epsilon_F[1 - \frac{\pi^2}{12}(\frac{k_BT}{E_F})^2 + \ldots]$$

$$E = \frac{3}{5} N\epsilon_F [1 + \frac{5}{12}(\frac{k_B T}{E_F})^2 + ...] = \frac{3}{2} PV.$$

The first term is $g \sum_{|p|<p_F} p^2/2m$. The second term corresponds to a fraction $k_B T/\epsilon_F$ of excited particles with energy $k_B T$, hence excess energy is $\sim T^2$ and $c_V \sim T$.

At T=0 the pressure is due to occupied states that have $\vec{p} \neq 0$.

2d. Non- Ideal gases

Atoms have on average $\langle \text{dipole} \rangle_{\text{time}} = 0$ (time average is also equivalent to ensemble average). However, the dipole moment of one atom induces a dipole on a neighboring atom such that $\langle \text{dipole} \cdot \text{dipole} \rangle_{\text{time}} \neq 0$. This energy is $\sim -\frac{1}{r^6}$.

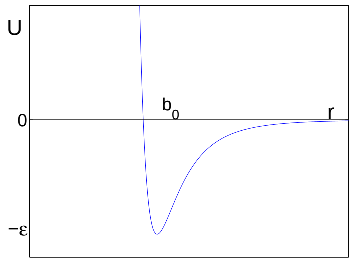
Lennard - Jones potential:

$U = \epsilon[(\frac{b_0}{r})^{12} - 2(\frac{b_0}{r})^6]$

$b_0 \approx 2 - 5 \quad \text{Å}$,

$\epsilon \approx (1 - 40) \cdot 10^{-22}$Joule

$\approx (1 - 40) \cdot 0.1°K$

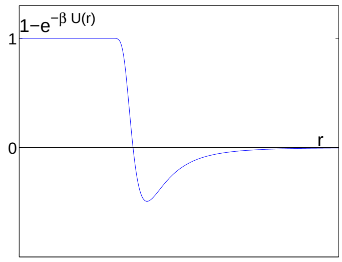


Virial expansion:

$$\begin{aligned}
Z &= \frac{1}{N!h^{3N}} \int d^{3N}p d^{3N}r \mathrm{e}^{-\beta[\sum_i p_i^2/2m + \sum_{i<j} U(r_i - r_j)]} \\
&= Z_0 \frac{1}{V^N} \int d^{3N}r \mathrm{e}^{-\beta \sum_{i<j} U(r_i - r_j)} \\
&= Z_0 \frac{1}{V^N} \int d^{3N}r [(\mathrm{e}^{-\beta \sum_{i<j} U(r_i - r_j)} - 1) + 1]
\end{aligned}$$

where Z_0 is the non interacting partition function.

For low density, each pair contributes independently:
$Z = Z_0[\frac{N(N-1)}{2}\int(\frac{d^3r_1d^3r_2}{V^2}\mathrm{e}^{-\beta U(r_1-r_2)}-1)+1]$



$$\begin{aligned}
F &= F_0 - \frac{1}{2}k_BT\frac{N^2}{V^2}\int(\mathrm{e}^{-\beta U(r_1-r_2)}-1)d^3r_1d^3r_2 \\
B(T) &\equiv \frac{1}{2}\int(1-\mathrm{e}^{-\beta U(r)})d^3r \\
F &= F_0 + k_BT\frac{N^2}{V}B(T) \\
P &= -\frac{\partial F}{\partial V} = \frac{Nk_BT}{V}(1+\frac{N}{V}B(T))
\end{aligned}$$

assuming convergence ($U \neq \frac{1}{r}$).

$$\begin{aligned}
B &\approx \overbrace{\int_0^{b_0}...}^{>0} + \overbrace{\int_{b_0}^{\infty}...}^{<0} = b - a/T \\
P &= \frac{Nk_BT}{V}(1+\frac{N}{V}b) - a(\frac{N}{V})^2 \\
&\approx \frac{Nk_BT}{V-bN} - a(\frac{N}{V})^2 \Rightarrow \text{Van der Waals equation}
\end{aligned}$$

where $V-bN$ is the excluded volume and the second term, $-a(\frac{N}{V})^2$, is the pressure reduction from the attractive part of the interaction.

GCE formulation

Low density $\longrightarrow$ low fugacity ζ

$$\mathcal{L} = \sum_N \zeta^N Z_N(V,T) = 1 + \zeta Z_1 + \zeta^2 Z_2 + ...$$

for both classical and quantum theories define partition functions for $N = 1,2$ particles:

$$\begin{aligned}
\ln\mathcal{L} &= \zeta Z_1 + \zeta^2(Z_2 - \frac{1}{2}Z_1^2) + ... = \frac{PV}{k_BT} \\
N &= \zeta\frac{\partial}{\partial\zeta}(\ln(\mathcal{L})) = \zeta Z_1 + 2\zeta^2(Z_2 - \frac{1}{2}Z_1^2)
\end{aligned}$$

eliminate $\zeta \Rightarrow$

$$\begin{aligned}
\frac{PV}{k_BT} &= N - \left(\frac{N}{Z_1}\right)^2(Z_2 - \frac{1}{2}Z_1^2) \equiv N\left[1 + B\frac{N}{V}\right] \\
B &= -V\frac{1}{Z_1^2}(Z_2 - \frac{1}{2}Z_1^2)
\end{aligned}$$

Evaluate now Z_1, Z_2: For Z_1 there are no effects of interactions or of quantum statistics, i.e.

$$Z_1 = \sum_p \mathrm{e}^{-\beta p^2/2m} = \frac{V}{\lambda^3} \qquad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Consider next $Z_2 = \mathrm{Tr}\ \mathrm{e}^{-\beta\mathcal{H}}$ for $N = 2$, first the classical problem:

$$\begin{aligned} Z_2 &= \frac{1}{2!}\left(\int d^3p\mathrm{e}^{-\beta p^2/2m}\right)^2 \cdot \frac{1}{h^6}\int d^3r_1 d^3r_2 \mathrm{e}^{-\beta U(r_1-r_2)} \\ &= \frac{V}{2\lambda^6} \cdot \int d^3r\mathrm{e}^{-\beta U(r)} \end{aligned}$$

From the expression above for B we obtain $B(T) = -\frac{1}{2}\int(\mathrm{e}^{-\beta U(r_1-r_2)} - 1)d^3r_1 d^3r_2$ as in the previous derivation.

Consider next the quantum problem with the 2-particle Hamiltonian

$$\mathcal{H} = \frac{-\hbar^2}{2m}\left(\nabla^2_{r_1} + \nabla^2_{r_2}\right) + U(r_1 - r_2) = -\frac{\hbar^2}{4m}\nabla^2_R - \frac{\hbar^2}{m}\nabla^2_r + U(r)$$

where $r = r_1 - r_2$, $R = \frac{1}{2}(r_1 + r_2)$. The eigenvalues of $\mathcal{H}$ are $\frac{P^2}{4m} + E_n$ where P is the center of mass momentum, hence

$$Z_2 = \sum_P \mathrm{e}^{-\beta P^2/4m} \cdot \sum_n \mathrm{e}^{-\beta E_n} = \frac{2^{3/2}}{\lambda^3}V \cdot \sum_n \mathrm{e}^{-\beta E_n}$$

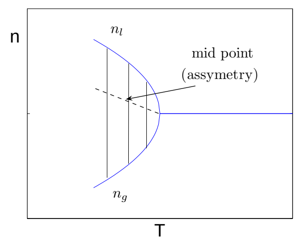
Note that E_n contain information on statistics, i.e. E_n is restricted to eigenfunctions that are symmetric in r for bosons, or to antisymmetric ones for fermions.

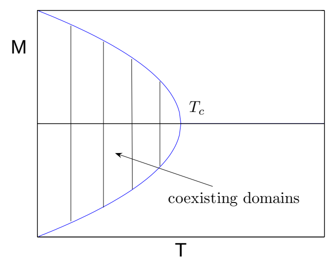
3. PHASE TRANSITIONS

	Order Parameter	Example	$T_c(^\circ K)$
Liquid-gas	density	H_2O	647
Ferromagnetic	magnetization	Fe	1044
Antiferromagnetic	sublattice magnetization	FeF_2	78
Bose condensation	superfluid amplitude	^4He	2
Superconductivity	electron pair amplitude	$YBa_2Ca_3O_7$	90
Binary fluid	concentration of one fluid	$CCl_4 - C_7F_{14}$	302
Binary alloy	density of one kind on a sublattice	$Cu - Zn$	739
Ferroelectric	polarization	$Triglycine - sulfate$	322
Ferroelastic	$q = 0$ distortion	$Ni - Ti$	
charge density wave	$q \neq 0$ distortion	$NbSe_3$	59
Metal-Insulator			
Percolation	fraction of sites in percolating cluster		

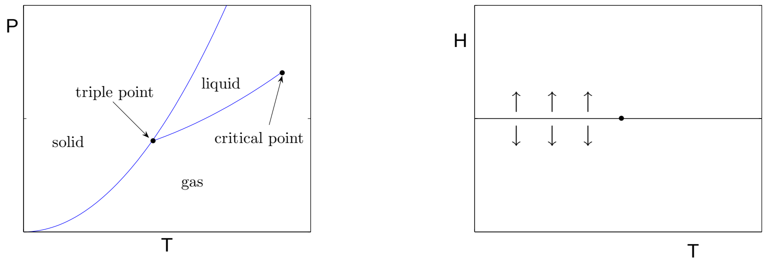
Definition: n-th order phase transition has a discontinuity in the n-th derivative of a free energy. Hence a 1st order transition has a jump in entropy $(-\partial F/\partial T)$ which is the latent heat. A 2nd order transition has a jump in C_v (contains $\partial^2 F/\partial T^2$).

3a. First order transitions

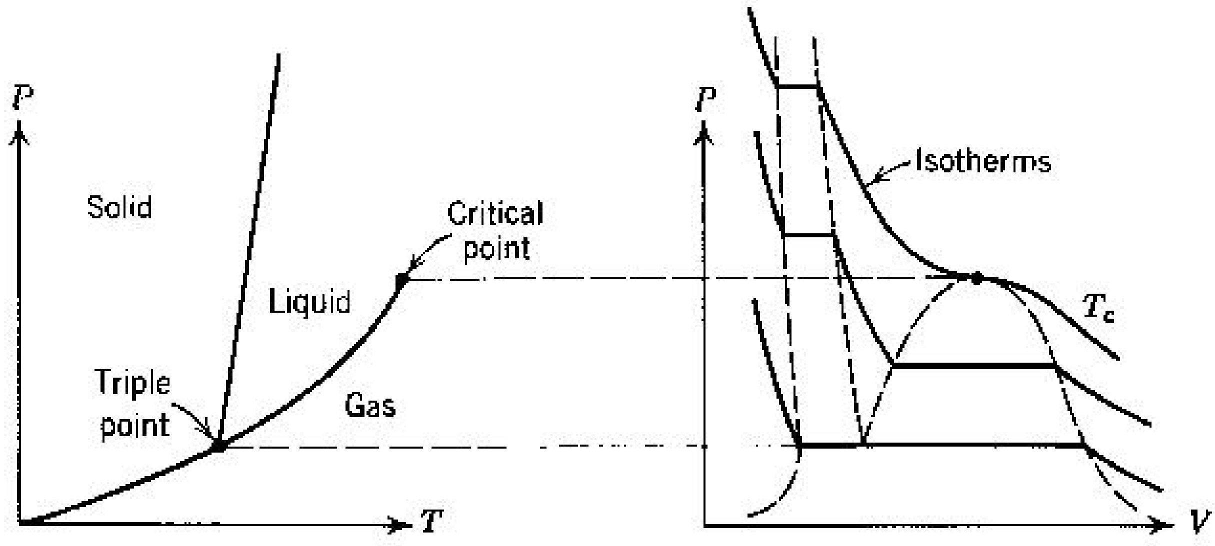




Infinitesimal change in P (liquid-gas on left figures) or in H (magnetic field in a ferromagnet on right figures) leads to a jump in density n (on left) or in magnetization (on right). In $P-T$ plane (left) or $H-T$ plane (right) first order transition ends at a critical point T_c.



Consider the liquid-gas phase transition as a prototype of a 1st order transition

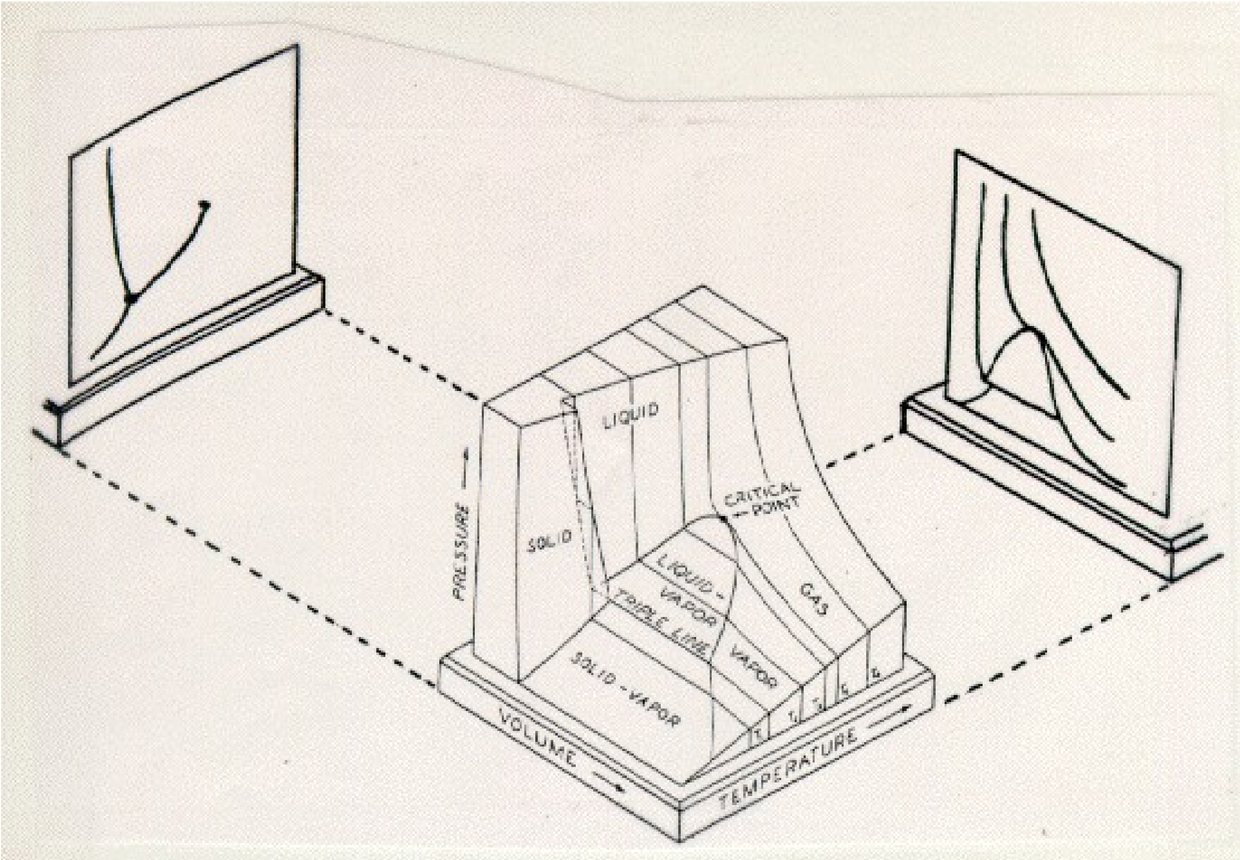


Liquid-gas: 1st transition, no symmetry change.

Solid-liquid: 1st order transition, change in translation symmetry.

Fixing V below T_c leads to liquid/gas coexistence.

Fixing P leads to a jump in V from fully gas phase to fully liquid phase.



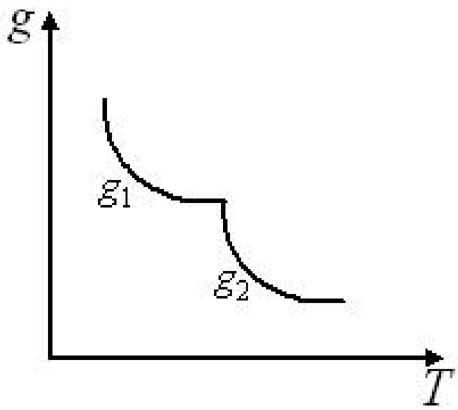
Clapeyron's equation

$$g(P,T) = \frac{1}{N} G(P,T,N)$$

where $G(P,T,N)$ is the Gibbs free energy.

$$\Delta g(P,T) = g_2(P,T) - g_1(P,T)$$

where $g_i(T,P)$ is formally continued across T_c.



Define $s = S/N$, $v = V/N$

$$\Delta s = s_2 - s_1; \qquad \Delta v = v_2 - v_1$$

$$\left(\frac{\partial \Delta g}{\partial T}\right)_P = -\Delta s; \qquad \left(\frac{\partial \Delta g}{\partial P}\right)_T = \Delta v$$

By the chain rule

$$\left(\frac{\partial \Delta g}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_{\Delta g} \left(\frac{\partial P}{\partial \Delta g}\right)_T = -1$$

we get

$$\frac{(\partial \Delta g/\partial T)_P}{(\partial \Delta g/\partial P)_T} = -\left(\frac{\partial P}{\partial T}\right)_{\Delta g} = -\frac{\Delta s}{\Delta v}$$

Along the transition line $P(T)$ we get $\Delta g = 0$ =const.

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{\text{latent heat}}{T\Delta v}.$$

Van-der Waals equation

A rough argument:

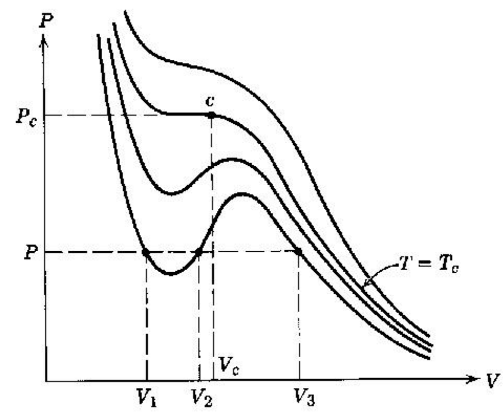
$$V_{eff} = V - b$$
$$P = P_{kin} - \frac{a}{V^2}$$

where $b \sim N$ is the excluded volume and $a \sim N^2$ is a measure of attractive forces among the molecules of the system; $a \sim N^2$ since there are N^2/V^2 pairs. Hence

$$P_{kin}V_{eff} = (V-b)\left(P + \frac{a}{V^2}\right) = NK_BT$$

At $T > T_c$ we get one solution for the equation, and for $T < T_c$ we get three.

The three roots merge to one root at inflection point P_c, V_c, T_c

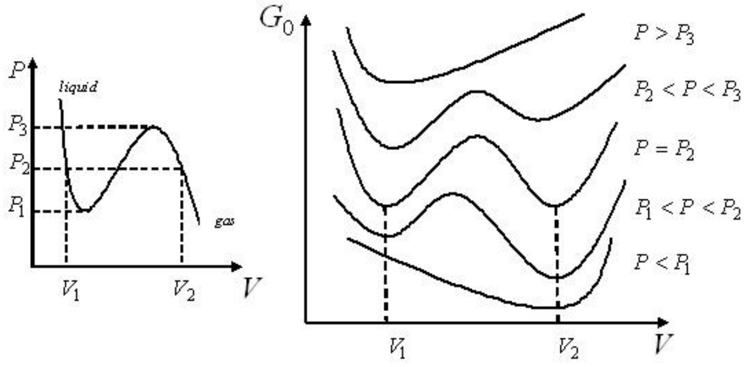


The parameters a, b are sample specific. To identify them in term of P_c, V_c, and T_c rewrite the equation in the form

$$(V - V_c)^3 = 0 = \left[(V-b)\left(P_c + \frac{a}{V^2}\right) - Nk_BT_c\right]\frac{V^2}{P_c}$$

By identifying each power of V in this form we write a, b in terms of P_c, V_c, T_c, and with $\bar{P} = P/P_c$, $\bar{T} = T/T_c$, $\bar{V} = V/V_c$ we obtain

$$\left(\bar{P} + \frac{3}{\bar{V}^2}\right)\left(\bar{V} - \frac{1}{3}\right) = \frac{8}{3}\bar{T}$$



which is the law of corresponding states – all substances have the same equation of state when their P, V, T are measured in units of the critical point.
Note the region with $\frac{\partial P}{\partial V} > 0$ is unstable so that $\left\langle (\Delta N)^2 \right\rangle \to 0$.
<u>Alternative derivation</u> (S.K.Ma p.470)

$$G_0(T,P,N) = E - TS + PV$$

where

$$E = \frac{3}{2} N K_B T - a_1 N \frac{N}{V}$$

attraction from neighboring $\sim N/V$ atoms, and

$$S = k_B \ln \left[\frac{1}{N!} \frac{(V - b_1 N)^N}{\lambda^{3N}} \right]$$

where $b_1 N$ is the excluded volume and λ is the thermal wavelength.

Proper $G(T,P,N)$ is obtained at minimum with respect to V which is a redundant variable for G.

$$G_0(T,P,N;V) = \frac{3}{2} N K_B T - a_1 \frac{N^2}{V} - k_B T \left[N \ln \left(\frac{V - b_1 N}{N \lambda^3} \right) + N \right] + PV$$

If $\frac{\partial G_0}{\partial V} = 0$, we get the Van der Waals equation with $a = a_1 N^2$ and $b = b_1 N$.

G_0 shows (see figure) that with 3 solutions 1 is metastable and 1 is unstable (max of G_0)
For $P_1 < P < P_2$ gas is stable, liquid is metastable.
For $P_2 < P < P_3$ liquid is stable, gas is metastable.

P_2 is when gas and liquid are degenerate $G_0(V_1) = G_0(V_2)$.

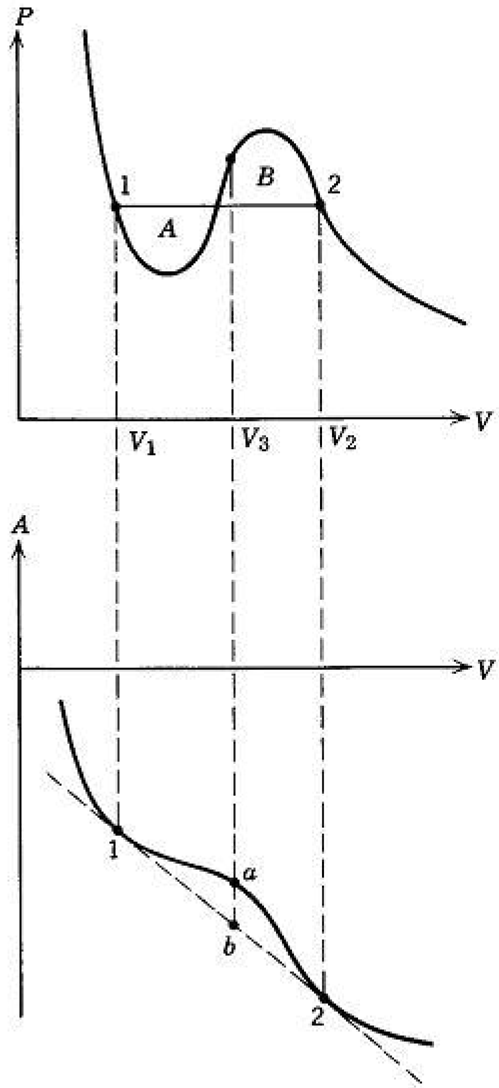
Maxwell's construction

In general $G_0 = F(V, T, N) + PV$ where $P(V) = -\partial F/\partial V$. At P_2:

$$0 = G_0(V_2) - G_0(V_1) = \int_{V_1}^{V_2} [-P(V) + P] dV \, .$$

Hence the area between $P = P_2$ line and the $P(V)$ curve vanishes – this is Maxwell's construction.

An alternative derivation: In terms of $F(V)$ choose V_1 and V_2 such that parallel tangents generate one line with $\frac{\partial F}{\partial V_1} = \frac{\partial F}{\partial V_2}$.



The line is

$$\frac{F_2 - F_1}{V_2 - V_1} = \frac{\partial F}{\partial V_1} \Rightarrow$$

$$P_2(V_2 - V_1) = -(F_2 - F_1) = \int_{V_1}^{V_2} P(V) dV$$

which is the same Maxwell's construction. The line is realized by coexistence of the two phases with fractions x and $1 - x$, respectively $(0 < x < 1)$,

$$V = xV_1 + (1 - x)V_2$$

$$F_{line} = xF_1 + (1-x)F_2 = \frac{(V - V_2)F_1 + (V_1 - V)F_2}{V_1 - V_2} < F$$

$\Rightarrow$ Phase separation at P_2 since $V_1 < V < V_2$ has lower F_{line} then F on the continuous curve.

When V is changed carefully to avoid strong fluctuation, metastable phases can persist until they become unstable; this leads to hysteresis.

3b. Second order phase transitions – Mean Field theory

Consider ferromagnetism as a prototype second order phase transition. Localized independent moments $\pm\mu$ in a magnetic field B lead to magnetization

$$M = N\frac{\mu e^{\beta\mu B} - \mu e^{-\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}} = N\mu \tanh\left(\beta\mu B\right).$$

Mean field theory for interactions: neighbors with magnetization $\sim M/V$ induce an additional field, $B \to B + \alpha\frac{M}{V}$, $\alpha \sim$ interaction strength.

$\Longrightarrow \quad M = N\mu \tanh\left(\beta\mu\left(B + \alpha\frac{M}{V}\right)\right)$ has $M \neq 0$ solutions even if $B = 0$.

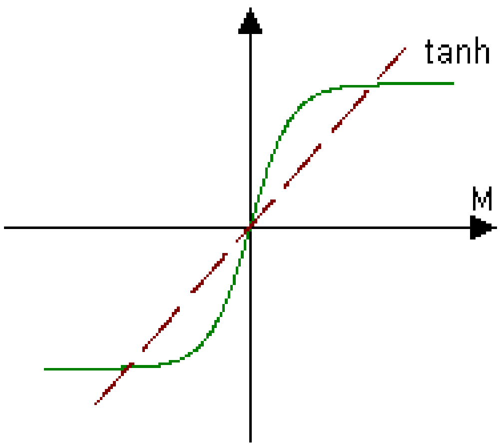
If $T = T_c$, $1 = \frac{N}{V}\mu^2\alpha/k_B T_c$

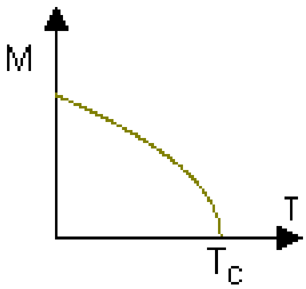
Expand near T_c:

$$M = \frac{T_c}{T}M - \frac{1}{3}\left(\beta\mu\alpha\frac{M}{V}\right)^3 N\mu \implies M \sim \left(T_c - T\right)^{1/2}.$$

Susceptibility at $T > T_c : B \to 0, M \to 0$

$$M = N\mu\beta\mu\left(B + \alpha\frac{M}{V}\right) \implies \chi \equiv \left(\frac{\partial M}{\partial B}\right)_{B=0} = \frac{\beta N\mu^2}{1 - \beta N\mu^2\alpha/V} \sim \frac{1}{T - T_c}.$$





Microscopic Model

Consider two neighbors of spin 1/2, total spin is $S = 0, 1$ with energy difference which defines the "exchange energy" J. The requirement for an antisymmetric wavefunction requires a symmetric orbital for the singlet $S = 0$ and antisymmetric one for the triplet $S = 1$, hence a large energy difference from the difference Coulomb interactions. Hence J is much larger then that of interacting magnetic dipoles. Consider

$$\vec{s}_i \cdot \vec{s}_j = \tfrac{1}{2}\left((\vec{s}_i + \vec{s}_j)^2 - \vec{s}_i^2 - \vec{s}_j^2\right) = \tfrac{1}{2}S(S+1) - \tfrac{1}{2}\cdot\tfrac{3}{2} = \begin{cases} -3/4 & S=0 \\ 1/4 & S=1 \end{cases}.$$

$\Longrightarrow$ Interaction energy $= -J\sum'_{\text{n.n.}} \vec{s}_i \cdot \vec{s}_j$+const (n.n. is summation on γ nearest neighbors). $\sum'$ means that each pair is summed once.

If the crystal has an easy axis for the spin, $\vec{s}_i \to (s_z)_i$, hence two models:

$$H = -J\sum_{\langle i,j\rangle}{}' \vec{s}_i \cdot \vec{s}_j \quad \vec{s}\text{ spin operator: Heisenberg model}$$

$$H = -J\sum_{\langle i,j\rangle}{}' \sigma_i\sigma_j \quad \sigma_i = \pm 1\text{: Ising model.}$$

Solution of the Ising model by mean field:

$$H^{\text{MF}} = -\tfrac{1}{2}J\gamma\langle\sigma\rangle\sum_i \sigma_i \quad \gamma\text{ no. of nearest neighbors.}$$

$\frac{1}{2}$ is needed so that $\langle H^{\text{MF}}\rangle = -\frac{1}{2}NJ\gamma\langle\sigma\rangle^2$, $\frac{1}{2}N\gamma$ no. of bonds. (e.g. $N/2$ "odd" sites each generates γ bonds.)

$$\langle\sigma\rangle = \langle\sigma_i\rangle = \frac{\sum\limits_{\sigma_i=\pm}\sigma_i \mathrm{e}^{\beta\gamma J\langle\sigma\rangle\sigma_i/2}}{\sum\limits_{\sigma_i=\pm}\mathrm{e}^{\beta\gamma J\langle\sigma\rangle\sigma_i/2}} \frac{\sum\limits_{\{\sigma_{j\neq i}\}}\mathrm{e}^{\beta\gamma J\langle\sigma\rangle\sum_{j\neq i}\sigma_j/2}}{\sum\limits_{\{\sigma_{j\neq i}\}}\mathrm{e}^{\beta\gamma J\langle\sigma\rangle\sum_{j\neq i}\sigma_j/2}} = \tanh\left(\beta J\gamma\tfrac{1}{2}\langle\sigma\rangle\right)$$

$\Longrightarrow$ $kT_c = \frac{1}{2}J\gamma$.

3c. Exact results

Mapping between systems

1. Lattice gas model to Ising

N_a atoms occupy sites in lattice with N cells; N_{aa} number of nearest neighbors, each with energy ϵ_0, $g(N_a, N_{aa})$ is the number of configurations with a given N_a, N_{aa} (a non-trivial function). Grand partition

$$\mathcal{L}_G = \sum_{N_a}\zeta^{N_a}\sum_{N_{aa}} g\left(N_a, N_{aa}\right)\mathrm{e}^{\beta\epsilon_0 N_{aa}}.$$

Canonical partition of Ising has the same form:

N_+ no. of + spins, N_{++} no. of ++ neighbors. Draw one line from all + sites to all their neighbors:

Number of lines $= \gamma N_+ = 2N_{++} + N_{+-}$

same for N_{--} $\quad \gamma N_- = 2N_{--} + N_{+-}, \quad N_+ + N_- = N$

$$\Longrightarrow \sum_{\langle i,j\rangle} \sigma_i \sigma_j = N_{++} + N_{--} - N_{+-} = 4N_{++} - 2\gamma N_+ + \tfrac{1}{2}\gamma N$$
$$\sum_i \sigma_i = N_+ - N_- = 2N_+ - N$$
$$E_{\text{Ising}} = -4JN_{++} + 2(J\gamma - \mu B)N_+ - \left(\tfrac{1}{2}\gamma J - \mu B\right) N$$
$$Z = \mathrm{e}^{\beta N\left(\frac{1}{2}\gamma J - \mu B\right)} \sum_{N_+} \mathrm{e}^{-2\beta(J\gamma - \mu B)N_+} \sum_{N_{++}} g\left(N_+, N_{++}\right) \mathrm{e}^{4\beta J N_{++}}$$

Since configuration counting is the same as in lattice gas we get the same function $g(N_a, N_{aa})$, hence the two problems are equivalent as in the following table:

Ising	Lattice gas
N_+	N_a
$4J$	ϵ_0
$\mathrm{e}^{-2\beta(J\gamma-\mu B)}$	ζ
$-\left(\frac{1}{N}F_{\text{Ising}} + \frac{1}{2}\gamma J - \mu B\right)$	P
$M = N_+ - N_-$, $\frac{N_+}{N} = \frac{1}{2}\left(\frac{M}{N} + 1\right)$	$\frac{1}{v} = \frac{\langle N_a\rangle}{N}$ order parameter

2. Binary alloy to lattice gas

N_{11}, N_{22}, N_{12} no. of pairs of each type

$E_A = \epsilon_1 N_{11} + \epsilon_2 N_{22} + \epsilon_{12} N_{12}$

As above

$$\begin{aligned} \gamma N_1 &= 2N_{11} + N_{12} \\ \gamma N_2 &= 2N_{22} + N_{12} \end{aligned}$$

$\Longrightarrow$

$$\begin{aligned} N_{12} &= \gamma N_1 - 2N_{11} \\ N_{22} &= \tfrac{1}{2}\gamma N + N_{11} - \gamma N_1 \end{aligned}$$

$$N_1 + N_2 = N$$

$$E_A = (\epsilon_1 + \epsilon_2 - 2\epsilon_{12}) N_{11} + \left[\gamma (\epsilon_{12} - \epsilon_2) N_1 + \tfrac{1}{2}\gamma\epsilon_2 N\right], \quad Z(N_1, T) = \sum_{N_{11}} g(N_{11})\, \mathrm{e}^{-\beta E_A}$$

Lattice gas	Binary alloy
N_a	N_1
$-\epsilon_0$	$\epsilon_1 + \epsilon_2 - 2\epsilon_{12}$
F	$F + \gamma(\epsilon_{12} - \epsilon_2) N_1 + \frac{1}{2}\gamma\epsilon_2 N$

Ising Model in 1D: Exact Solution

$$Z = \sum_{\sigma_1=\pm}\sum_{\sigma_2=\pm} \dots \sum_{\sigma_N=\pm} \mathrm{e}^{\beta J \sum_{k=1}^{N} \sigma_k\sigma_{k+1} + \frac{1}{2}\beta\mu B \sum_k (\sigma_k + \sigma_{k+1})} \quad ; \quad \sigma_1 = \sigma_{N+1}$$

Consider the bond $(k, k+1)$ with the elements

$$\mathrm{e}^{\,\beta J\sigma_k\sigma_{k+1} + \frac{1}{2}\beta\mu B(\sigma_k + \sigma_{k+1})}$$

This element can have 4 values for $\sigma_k = \pm$ and $\sigma_{k+1} = \pm$. Call these elements $P_{1,1}\,, P_{1,-1}\,, P_{-1.1}\,, P_{-1,-1}$ and define a matrix

$$\hat{P} = \begin{pmatrix} P_{1,1} & P_{1,-1} \\ P_{-1,1} & P_{-1,-1} \end{pmatrix} = \begin{pmatrix} \mathrm{e}^{\beta(J+\mu B)} & \mathrm{e}^{-\beta J} \\ \mathrm{e}^{-\beta J} & \mathrm{e}^{\beta(J-\mu B)} \end{pmatrix}$$

Note that $\hat{P}$ is symmetric by the choice of $\sigma_k + \sigma_{k+1}$ for the B term in the Hamiltonian.
$\hat{P}$ is defined in a spinor space $|\pm\rangle$, e.g. $\langle +|\hat{P}|-\rangle = P_{1,-1}$.
E.g. for $N = 3$ the partition Z has 2^3 terms, one of them is

$$\uparrow\uparrow\downarrow\uparrow \Longrightarrow P_{1,1}P_{1,-1}P_{-1,1} = \langle +|\hat{P}|+\rangle\langle +|\hat{P}|-\rangle\langle -|\hat{P}|+\rangle$$

In general we need

$$Z = \sum_{\text{all } |i\rangle = |\pm\rangle} \langle 1|\hat{P}|2\rangle \dots \langle k|\hat{P}|k+1\rangle\langle k+1|\hat{P}|k+2\rangle \dots \langle N|\hat{P}|N+1\rangle$$

$$= \sum_{\sigma_1=\sigma_N=\pm} (P^N)_{\sigma_1,\sigma_N} = Tr(P^N) = \lambda_1^N + \lambda_2^N$$

λ_1, λ_2 are the eigenvalues of $\hat{P}$: $\lambda^2 - 2\lambda e^{\beta J}\cosh(\beta\mu B) + 2\sinh(2\beta J) = 0$
$\implies \lambda_{1,2} = e^{\beta J}\cosh(\beta\mu B) \pm [e^{-2\beta J} + e^{2\beta J}\sinh^2(\beta\mu B)]^{\frac{1}{2}}$

$\lambda_2 < \lambda_1$, $\quad N \to \infty$, $\quad \lambda_1$ dominates, hence $\frac{1}{N}\ln Z \to \ln\lambda_1$ and is an analytic function (except at $T = 0$). For the magnetization we have
$M = \frac{1}{\beta}\frac{\partial}{\partial B}\ln Z = N\mu\frac{\sinh(\beta\mu B)}{[e^{-4\beta J} + \sinh^2(\beta\mu J)]^{\frac{1}{2}}}$

$\implies M(B = 0, T > 0) = 0, \quad M(T = 0) = N\mu\mathrm{sign}(B)$, hence an ordered phase is only at $T = 0$. The susceptibilty:
$\chi = \frac{\partial M}{\partial B}|_{B=0} = \frac{N\mu^2}{k_B T}\mathrm{e}^{2J/k_B T}|_{T\to 0} \to \infty$ indicates ordering at $T = 0$.

No phase tradition in 1-dimension – general argument:
Low energy excitations are walls $\uparrow\uparrow\uparrow|\downarrow\downarrow\downarrow$, energy is $2J$ (relative to the ground state), while entropy is $S = k_B\ln N$ since the wall can be positioned at any bond.
$\implies F = E - TS = 2J - k_B T\ln N < 0 \Rightarrow$ no long range order in 1-dimension at any finite temperature.

2D Ising model: Onsager's solution (1944)
$KT_c = 2.269J$
$M \sim (T_c - T)^{1/8}$ near T_c
$C_v \sim -\ln(1 - \frac{T}{T_c})$

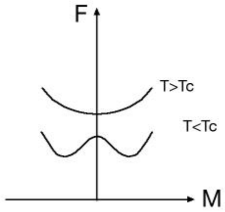
3d. Landau's Theory for second order phase transitions

Partition sum is done first locally to define a "'coarse grained"' order parameter, slowly varying. $F\{M(r)\}$ is determined by symmetry for small $M(r)$, i.e near a 2nd order phase transition. Coarse graining involves a finite cluster $\Rightarrow$ $F\{M(r)\}$ has an analytic expansion. For ferromagnet, $M \to -M$, symmetry+analiticity $\Rightarrow$

$$F\{M(r)\} = \frac{1}{2}a(T)M^2(T) + \frac{1}{4}bM^4(T) + \frac{1}{2}c(\vec{\nabla}M)^2$$

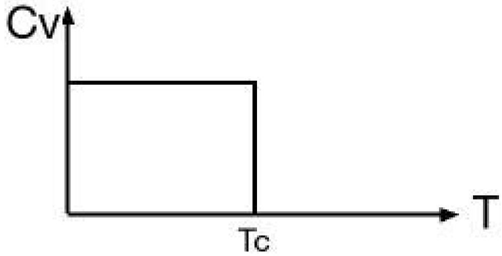
where $a(T) = a'(T - T_c)$ so that in Mean Field the transition occur at T_c.

Mean Field: $M(r) = M$ is homogenous, no fluctuations.
$\frac{\partial F}{\partial M} = 0 \Rightarrow M = \sqrt{\frac{a'}{b}(T_c - T)}$



$$F = \begin{cases} -\frac{1}{4}\frac{a'^2}{b}(T_c - T)^2 & T < T_c \\ 0 & T > T_c \end{cases}$$

$S = -\frac{\partial F}{\partial T}$ continuous ($S < 0$ at $T < T_c$, needs correction by fluctuations, see below.)



$c_V = T\frac{\partial S}{\partial T}$ has a jump, and is $\sim (T_c - T)^0$ at $T < T_c$.

Consider next $B \neq 0$ and add $-M \cdot B$ to F:

$T > T_c, \quad a'(T - T_c)M - B = 0 \Rightarrow \chi = \frac{M}{B}|_0 \sim \frac{1}{T - T_c}$

$T = T_c, \quad bM^3 - B = 0 \Rightarrow M \sim B^{1/3}$

Consider fluctuations at $T > T_c$: neglect M^4, $M(r) = V^{-1/2} \sum_k M_k e^{ik \cdot r}$

$\int F\{M(\vec{r})\} d^3r = \frac{1}{2}\sum_k (a + ck^2)|M_k|^2$ since $\int e^{ik\cdot r + ik' \cdot r} d^3r = V\delta_{-k,k'}$. Note that $M_{-k} = M_k^*$ for a real $M(r)$.
The weight of $\pm k$ modes is $e^{-\beta(a+ck^2)|M_k|^2}$. The correlation function is then

$$< M(r)M(0) >= V^{-1}\sum_k < M_k M_{-k} > e^{ikr} = V^{-1}\sum_k e^{ikr} \prod_{k'} \frac{\int d(ReM_{k'})d(ImM_{k'})|M_k|^2 e^{-\beta(a+ck'^2)|M_k'|^2}}{\int d(ReM_{k'})d(ImM_{k'})e^{-\beta(a+ck'^2)|M_{k'}|^2}}$$

$$= V^{-1}\sum_k e^{ikr} \frac{\int d(|M_k|^2)|M_k|^2 e^{-\beta(a+ck^2)|M_k|^2}}{\int d(|M_k|^2) e^{-\beta(a+ck^2)|M_k|^2}} = V^{-1}\sum_k e^{ikr}\frac{\partial}{\partial(\beta(a + ck^2))} \ln \int_0^\infty dx e^{-\beta(a+ck^2)x}$$

$$< M(r)M(0) >= V^{-1}\sum_k \frac{e^{ik\cdot r}}{\beta(a + ck^2)} = \frac{k_B T}{4\pi rc} \mathrm{e}^{-r/\xi}$$

where $\xi = \sqrt{\frac{c}{a}} \sim (T - T_c)^{-\frac{1}{2}}$ is the correlation length. Consider next the free energy

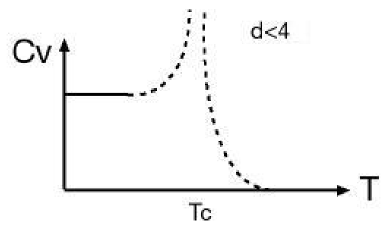
$$Z = \prod_k \int d|M_k|^2 \mathrm{e}^{-\beta(a+ck^2)|M_k|^2} \sim \prod_k [\beta(a + ck^2)]^{-1}$$

$$\Rightarrow F = k_B T[\sum_k \ln \beta(a + ck^2) + const.]$$

Therefore

$$C_V = -T\frac{\partial^2 F}{\partial T^2}$$

$$\sim \int^{1/a_0} \frac{d^d k}{(a + ck^2)^2} + \text{less singular terms.}$$



a_0 is a lattice constant, d=dimensions. Using $k' = \xi k$

$$C_V \sim \frac{1}{a^2}\int^{\frac{\xi}{a_0}} \frac{d^d k'}{(1 + k'^2)^2}\xi^{-d} \sim \xi^{4-d} \sim (T - T_c)^{\frac{d-4}{2}}$$

<u>Validity of mean field:</u>

$\langle M^2(0)\rangle \quad << \quad \langle M\rangle^2$; evaluate at $T > Tc$ (similar result at $T < T_c$) :

$\langle M^2(0)\rangle \sim \int \frac{d^d k}{\beta(a+ck^2)} \sim \int \frac{k^{d-1}dk}{(a+ck^2)} \sim (\sqrt{a})^{d-2} \sim |T - T_c|^{(d-2)/2}$

Comparing with $\langle M\rangle^2 \sim (T_c - T)$ shows that mean field is valid at T $\rightarrow T_c$ if $d > 4$.

At $d < 4$ mean field breaks down at T $\rightarrow T_c$

<u>Critical exponents:</u>

$t = \frac{T-T_c}{T_c}$, $T > Tc$; for exponents $\beta\alpha'\gamma'\nu'$ $t = \frac{T_c-T}{T_c}$, $T < Tc$

Exponent	Definition	Mean Field	Fe
α,α'	Specific heat $c_V \sim t^{-\alpha}$	$2 - d/2$	-0.12
β	Order parameter $\sim t^{\beta}$	1/2	0.34
γ, γ'	Susceptibility $x \sim t^{-\gamma}$	1	1.33
δ	Order parameters at $T_c \sim B^{1/\delta}$	3	4.2 (Ni)
ν, ν'	correlation length $\xi \sim t^{-\nu}$	1/2	
η	at T_c $\langle M(r)M(0)\rangle \sim 1/r^{d-2+\eta}$	0	0.07

Universality: exponents depend only on symmetry of order parameter and dimensionality.

Scaling assumption:

ξ is the single length responsible for singular behavior.

$\Rightarrow$ obtain relations between exponents.

e.g. $\langle M(r)M(0)\rangle \sim \frac{1}{r^{d-2+\eta}}g(r/\xi)$ at T_c need $g \to g(0) \neq 0$

In terms of $\int_M$, integration on all configurations $M(r)$, and the Hamiltonian $\mathcal{H}$ we have for the susceptibility

$$\chi = \frac{\partial\langle M\rangle}{\partial B}|_{B\to 0} = \frac{\partial}{\partial B}\frac{\int_M M(0)\mathrm{e}^{-\beta(\mathcal{H}-\int M(r)Bd^dr)}}{\int_M \mathrm{e}^{-\beta(\mathcal{H}-\int M(r)Bd^dr)}}|_{B=0} = \frac{\int_M \int M(0)M(r)d^dre^{-\beta\mathcal{H}}}{\int_M \mathrm{e}^{-\beta\mathcal{H}}} = \int \langle M(0)M(r)\rangle\, d^dr$$

since at $T > T_c$ the $\langle M\rangle_{B=0} = 0$ term vanishes (from $\partial/\partial B$ of denominator.)

$$\chi \sim \int r^{-d+2-\eta}g(r/\xi)d^dr \sim \xi^{-d+2-\eta}\cdot\xi^d \sim (t^{-\nu})^{2-\eta}$$

$$\Rightarrow \quad \gamma = \nu(2-\eta)$$

Renormalization Group:

Consider the 1-dimensional Ising model $Z = \sum_{\sigma_k=\pm} \mathrm{e}^{\beta J\sum_k \sigma_k\sigma_{k+1}}$

Sum on all even sites to obtain a new form for Z

$$\sum_{\sigma_2} \mathrm{e}^{\beta(J\sigma_1\sigma_2 \,+\, J\sigma_2\sigma_3)} = \mathrm{e}^{\beta(a' \,+\, J'\sigma_1\sigma_3)}$$

Identify a', J' by two cases:

$$\sigma_1\sigma_3 = + \text{ case: } \mathrm{e}^{2J\beta} + e^{-2J\beta} = e^{(a'+J')\beta}$$

$$\sigma_1\sigma_3 = - \text{ case: } \quad 2 = e^{(a'-J')\beta}$$

$$\Rightarrow \quad Z(k) \sim \sum_{\text{odd } i\ \sigma_i=\pm} \mathrm{e}^{J'\sum_{\text{odd } k}\sigma_k\sigma_{k+2}}$$

with the renormalized coupling J' given by $\mathrm{e}^{-2\beta J'} = \frac{2}{\mathrm{e}^{2\beta J}+\mathrm{e}^{-2\beta J}}$

At T_c $\xi \to \infty$ $\mathcal{H}$ is scale invariant, i.e. $J' = J \Rightarrow$ $T_c = 0.$

4. NON- EQUILIBRIUM

4a. Kinetic theory and Boltzmann's equation:

$f(\vec{r}, \vec{v}, t)$ is particle density in phase space d^3rd^3v. In absence of collisions
$\vec{r},\ \vec{v} \quad \rightarrow \vec{r}\ +\ \vec{v}\delta t\ ,\quad \vec{v}\ +\ \frac{\vec{F}}{m}\delta t$
so that volume A moves to an infinitesimally close volume B with f changed only by collisions,
$f(\ \vec{r}+\vec{v}\delta t,\ \vec{v}+\frac{\vec{F}}{m}\delta t\ ,\ t+\delta t)\ -\ f(\ \vec{r}, \vec{v}, t) \quad \equiv\ (\frac{\partial f}{\partial t})_{coll}\delta t$

Effect of collisions: If one initial particle is in A the result is certainly outside A (up to the differential volume of A) – this is a loss term; conversely with one final particle in B,
$R\delta t d^3rd^3v\ =$ no. of collisions with one initial particle in A
$\bar{R}\delta t d^3rd^3v\ =$ no. of collisions with one final particle in B $[= A + O(\delta t)]$
$(\frac{\partial f}{\partial t})_{coll}\delta t\ =\ (\bar{R}\ -\ R)\delta t$

Assume binary collisions (dilute gas) $\vec{v_1}\ ,\ \vec{v_2}\ \rightarrow\ \vec{v_1}'\ ,\ \vec{v_2}'$

$$\vec{v_1} + \vec{v_2}\ =\ \vec{v_1}'\ +\ \vec{v_2}'$$
$$\vec{v_1}^2 + \vec{v_2}^2 = \vec{v_1}'^{\,2}\ +\ \vec{v_2}'^{\,2}$$

Define $\vec{V}\ =\ \frac{1}{2}(\vec{v_1}+\vec{v_2})\ ,\ \vec{u}\ =\ \vec{v_2}-\vec{v_1}\ ;\quad \vec{V}'\ =\ \frac{1}{2}(\vec{v_1}'+\vec{v_2}')\ ,\ \vec{u}'\ =\ \vec{v_2}'-\vec{v_1}'$
$\Rightarrow\quad \vec{V}\ =\ \vec{V}'\ ,\quad |\vec{u}|\ =\ |\vec{u}'|$
A collision is defined by an angle Ω in the center of mass, i.e. between $\vec{u},\ \vec{u}'$. $\vec{V},\ \vec{u}, \Omega$ are independent parameters which determine $\vec{V}',\ \vec{u}'$.
Consider $\vec{u}\ \rightarrow\ \vec{u}\ +\ d\vec{u}$, as Ω is fixed (i.e. $d\Omega$ is independent of d^3u).
For $\vec{u}'\ \rightarrow\ \vec{u}'\ +\ d\vec{u}'$ the triangle ($\vec{u},\ \vec{u}\ +\ d\vec{u}$) is similar to ($\vec{u}',\ \vec{u}'\ +\ d\vec{u}'$), hence $|du'| = |du|$
Choosing an orthogonal basis set $d\vec{u}_1$, $d\vec{u}_2$, $d\vec{u}_3$ it transforms to a rotated orthogonal basis with axes equal in magnitude, hence $d^3u = d^3u'$
Since $d^3V\ =\ d^3V' \quad \Rightarrow \quad d^3v_1d^3v_2 = d^3v_1'd^3v_2'$.

Assumption of molecular chaos: This is the central assumption of the Boltzman equation.
The number of pairs with velocities $(\vec{v_1}, \vec{v_2})$ about to collide is the product

$$f(\vec{r},\vec{v_1},t)d^3rd^3v_1 \cdot f(\vec{r},\vec{v_2},t)d^3rd^3v_2$$

i.e. both particles "do not know" about each other until they collide, hence no correlation before the collision.

The scattered flux of $\vec{v_2}$ hitting $\vec{v_1}$ is

$$I = \int d^3v_2 \int d\Omega\sigma(\Omega)\,|\vec{v_1}-\vec{v_2}|\,f(\vec{r},\vec{v_2},t)$$

where $\sigma(\Omega)$ is the scattering cross section.

$f(r,\vec{v_1},t)d^3v_1$ is the number of target particles, therefore $Rd^3v_1 = f(\vec{r},\vec{v_1},t)d^3v_1 \cdot I$

For $\bar{R}$ define a collision by variables $\vec{v_1'},\vec{v_2'} \to \vec{v_1},\vec{v_2}$ so that $v_1 \in A$.

The scattered flux of $\vec{v_2'}$ on $\vec{v_1'}$ is

$$I' = \int d^3v_2' \int d\Omega\sigma'(\Omega)\left|\vec{v_1'}-\vec{v_2'}\right| f(r,\vec{v_2'},t) = \int d^3v_2' \int d\Omega\sigma(\Omega)\,|\vec{v_1}-\vec{v_2}|\,f(\vec{r},\vec{v_2'},t)$$

using microscopic time reversal $\sigma'(\Omega) = \sigma(\Omega)$ (spin and internal quantum states are neglected).

$f(\vec{r},\vec{v_1'},t)d^3v_1'$ is the number of target particles (no integral since $(\vec{v_1},\vec{v_2'},\Omega)$ determine $\vec{v_1'}$).

Therefore, $\overline{R}d^3v_1 = f(\vec{r},\vec{v_1'},t)d^3v_1' \cdot I'$.

Since $d^3v_1d^3v_2 = d^3v_1'd^3v_2'$ the probability for the reverse collision process is

$$\overline{R} = \int d^3v_2 \int d\Omega\sigma(\Omega)\,|\vec{v_1}-\vec{v_2}|\,f(\vec{r},\vec{v_1'},t)f(\vec{r},\vec{v_2'},t)$$

Hence **Boltzman's transport equation**:

$$\begin{aligned}&(\frac{\partial}{\partial t} + \vec{v_1}\cdot\vec{\nabla}_r + \frac{1}{m}\vec{F}\cdot\vec{\nabla}_{v_1})f(\vec{r},\vec{v_1},t) = \\ &\int \sigma(\Omega)d\Omega \int d^3v_2\,|\vec{v_1}-\vec{v_2}|\,[f(\vec{r},\vec{v_2'},t)f(\vec{r},\vec{v_1'},t) - f(\vec{r},\vec{v_2},t)f(\vec{r},\vec{v_1},t)]\end{aligned}$$

Time reversal would imply that $f(\vec{r},-\vec{v_1},-t)$ also solves this equation. However, changing $t\to -t$, and all $\vec{v}\to-\vec{v}$ in this equation, the left side changes sign (acting on $f(\vec{r},-\vec{v_1},-t)$) while the right hand side does not change sign (acting on $f(\vec{r},-\vec{v},-t)$ with the various v). Hence time reversal, although valid on the microscopic level, is broken on the macrospcopic level. [If $t \rightarrow -t$ and also $\vec{v_i} \rightarrow -\vec{v_i'}$ the equation is invariant, i. e. reversing the order of colliding particles; assumption of "molecular chaos" looses this symmetry.]

Consider the case with no external force $F = 0$ and no $\vec{r}$ dependence (e.g. no density waves). In equilibrium $\frac{\partial f}{\partial t} = 0$, therefore the right side is equal to 0 for all v_1, which requires

$$f(v_2)f(v_1) = f(v_2')f(v_1')$$

hence $\ln f(\vec{v})$ is conserved in all collisions. The conserved quantities are momentum and energy, therefore

$$\ln f(\vec{v}) = A + \vec{B} \cdot \vec{v} + c \cdot (\vec{v})^2 = -b(\vec{v} - \vec{v_0})^2 + \ln a$$
$$\Rightarrow f(\vec{v}) = ae^{-b(\vec{v}-\vec{v_0})^2}$$

which is the Maxwell distribution (up to a center of mass velocity).

Boltzman's H theorem

As a candidate for entropy, Boltzman defined the function H(t):

$$H(t) \equiv \int f(\vec{v}, t) \ln[f(\vec{v}, t)] d^3v$$

where $f(\vec{v}, t)$ is a solution of Boltzmann's equation.

We show now that $\frac{dH(t)}{dt} \leq 0$ so that $H(t)$ decreases with time. Define as a shorthand

$$\begin{aligned} f_1 &= f(\vec{v_1}, t) & f_2 &= f(\vec{v_2}, t) \\ f_1' &= f(\vec{v_1'}, t) & f_2' &= f(\vec{v_2'}, t) \end{aligned} \tag{2}$$

Thus we get:

$$\frac{\partial f_1}{\partial t} = \int d^3v_2 \int d\Omega\sigma(\Omega)\, |\vec{v_1} - \vec{v_2}|\, (f_2' f_1' - f_2 f_1)$$

$$\frac{dH}{dt} = \int d^3v_2 \int d^3v_1 \int d\Omega\sigma(\Omega)\, |\vec{v_1} - \vec{v_2}|\, (f_2' f_1' - f_2 f_1)(1 + \ln f_1)$$

by changing $v_1 \leftrightarrow v_2$, using eq. for $\frac{\partial f_2}{\partial t}$ and taking $\frac{1}{2}$ of both, we get

$$\frac{dH}{dt} = \frac{1}{2} \int d^3v_1 \int d^3v_2 \int d\Omega\sigma(\Omega)\, |\vec{v_2} - \vec{v_1}|\, (f_2' f_1' - f_2 f_1)[2 + \ln(f_1 \cdot f_2)]$$

Now, using equations for $\frac{\partial f_1'}{\partial t}$, $\frac{\partial f_2'}{\partial t}$, i.e. $f_i' \leftrightarrow f_i$ we get

$$\frac{dH}{dt} = \frac{1}{2}\int d^3v_1 \int d^3v_2 \int d\Omega\sigma'(\Omega)\left|\vec{v_2'} - \vec{v_1'}\right|(f_2 f_1 - f_2' f_1')[2 + \ln(f_1' \cdot f_2')]$$

And finally, adding the last two equations

$$\frac{dH}{dt} = \frac{1}{4}\int d^3v_1 \int d^3v_2 \int d\Omega\sigma(\Omega)\left|\vec{v_2} - \vec{v_1}\right|(f_2' f_1' - f_2 f_1)[\ln(f_1 \cdot f_2) - \ln(f_1' \cdot f_2')]$$

Since $(x-y)\ln\frac{x}{y} > 0$ for all x, y we have

$$\frac{dH}{dt} \leq 0 \tag{3}$$

In equilibrium $f_2' f_1' = f_2 f_1$ and $\frac{dH}{dt} = 0$.

Therefore, a candidate for entropy is $(-H)$ which increases with time and is maximal in equilibrium. [Note that $f(r, v, t)$ is coarse grained by the assumption of molecular chaos, therefore initial velocities v_i and final velocities v_i' are distinguished].

4b. Brownian motion

Brown (1828) - the random motion of pollen particles in a solution.

Einstein (1905) - random walk problem.

Consider one dimension: $P_n(m)$ is the probability of arriving at coordinate m after n steps, i.e. one needs $\frac{1}{2}(n+m)$ steps to the right and $\frac{1}{2}(n-m)$ steps to the left,

$$P_n(m) = \left(\tfrac{1}{2}\right)^n \frac{n!}{[\frac{1}{2}(n+m)]![\frac{1}{2}(n-m)]!}$$

where $\frac{1}{2}$ is the equal probability of going right or left. Normalization: $\sum_{m=-n}^{n} P_n(m) = 1$

Averages: $\overline{m} = 0$, $\overline{m^2} = n$. For $m \ll n$ (since $\sqrt{\overline{m^2}} = \sqrt{n} \ll n$)) and using Stirling's limit we get:

$$P_n(m) \approx \frac{2}{\sqrt{2\pi n}} e^{-m^2/2n}$$

Defining $x = ml$ (l is a step size in space) and $t = n\tau$ (τ is the time for each step)), we get

$$\overline{x^2} = \frac{l^2}{\tau} t = 2Dt$$

so that $D = \frac{l^2}{2\tau}$ is the diffusion coefficient.

In this continuoum form

$$P(x) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

In general, D is defined by the linear response:

$$j(\vec{r}, t) = -D\vec{\nabla} n(\vec{r}, t)$$

If there is a gradient, then there is a current which responds to reduce this gradient.

The continuity equation is $\nabla \cdot j + \frac{\partial}{\partial t} n(r, t) = 0$. Taking a gradient yields

$$\nabla^2 n(\vec{r}, t) - \frac{1}{D} \frac{\partial n(\vec{r}, t)}{\partial t} = 0$$

This is the diffusion equation. The solution with an initial value $n(r, t = 0) = N\delta^3(r)$ is

$$n(\vec{r}, t) = \frac{N}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt}$$

with $\int_0^\infty n(\vec{r}, t) 4\pi r^2 dr = N$. This solution shows $< r(\vec{t}) >= 0$ and

$$< (\vec{r}(t))^2 >= \frac{1}{N} 4\pi \int_0^\infty n(\vec{r}, t) r^4 dr = 6Dt$$

Langevin's equation

A particle of mass M is immersed in a medium which produces a random fluctuating force $M\vec{A}(t)$. $\vec{A}(t)$ has time correlation $\left\langle \vec{A}(t+\tau)\vec{A}(t) \right\rangle$ which decays fast with τ.

The correlation time τ_{col} is the time between collisions of medium particles and the particle of mass M. The medium leads also to irreversibility, i.e. friction.

$$\dot{\vec{v}} = -\gamma \vec{v} + \vec{A}(t)$$

$1/\gamma$ is the time scale for approaching equilibrium (see below).

We assume $\tau_{col} << 1/\gamma$ so that the average on the distribution of random forces is $\left\langle \vec{A}(t) \right\rangle = 0$, while $\langle A_i(t+\tau) A_j(t) \rangle = \frac{1}{3} C \cdot \delta(\tau) \delta_{ij}$, i.e. $\langle \vec{A}(t+\tau) \cdot \vec{A}(t) \rangle = C\delta(\tau)$.

Note that $\left\langle \vec{A} \cdot \vec{r} \right\rangle = 0$, while $\left\langle \vec{A} \cdot \vec{v} \right\rangle \neq 0$ (exercise).

Evaluate now $\langle r^2 \rangle$ assuming that the particle is in equilibrium at temperature T, $\frac{1}{2} M \langle v^2 \rangle = \frac{3}{2} kT$:

$$\vec{r}\cdot\vec{v} = \frac{1}{2}\frac{d}{dt}r^2$$

$$\vec{r}\cdot\dot{\vec{v}} = \frac{1}{2}\frac{d^2}{dt^2}r^2 - v^2 = \vec{r}\cdot(-\gamma\vec{v}+\vec{A})$$

$$\Rightarrow \text{average :} \qquad \frac{d^2}{dt^2}\left\langle r^2\right\rangle + \gamma\frac{d}{dt}\left\langle r^2\right\rangle = 2\left\langle v^2\right\rangle = 6kT/M$$

$$\Rightarrow \left\langle r^2\right\rangle = \frac{6kT}{\gamma M}t + c_1 + c_2 e^{-\gamma t}$$

Initial value $\vec{r}(t=0)=0 \Rightarrow \frac{d}{dt}r^2 = 2\vec{r}\cdot\vec{v} = 0$ at $t=0$.

$$\Rightarrow \left\langle r^2\right\rangle = \frac{6kT}{\gamma M}[t - \frac{1}{\gamma}(1-e^{-\gamma t})]$$

$$t << 1/\gamma \qquad \left\langle r^2\right\rangle = \left\langle v^2\right\rangle t^2 \ \text{ ballistic}$$

$$t >> 1/\gamma \qquad \left\langle r^2\right\rangle \to \frac{6kT}{\gamma M}t \quad \text{diffusive}$$

Friction γ is related to diffusion D, $D=\frac{kT}{\gamma M}$. γ is also related to mobility μ - responce to constant force , e.g electric field E for particle with charge e.

$$\dot{\vec{v}} = -\gamma\vec{v} + \vec{A}(t) + \frac{e\vec{E}}{M}$$

In steady state $\dot{\vec{v}}=0 \quad \Rightarrow \quad \langle v\rangle = eE/\gamma M \equiv \mu E$

$$D = kT\mu/e \quad \text{Einstein's relation}$$

So far the random force $\vec{A}$ was not explicit. Consider next the velocity fluctuations. We assume now $E=0$; if $E\neq 0$ one needs just to shift $\vec{v}\to\vec{v}+e\vec{E}/M\gamma$.

$$\vec{v}(t) = \vec{v}(0)e^{-\gamma t} + e^{-\gamma t}\int_0^t e^{\gamma u}\vec{A}(u)du$$

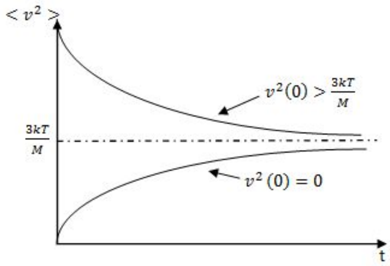
$$\Rightarrow \qquad \langle\vec{v}(t)\rangle = \vec{v}(0)e^{-\gamma t}$$

$$\left\langle v^2(t)\right\rangle = v^2(0)e^{-2\gamma t} + e^{-2\gamma t}\int_0^t\int_0^t e^{\gamma(u_1+u_2)}\left\langle A(u_1)A(u_2)\right\rangle du_1 du_2 = v^2(0)e^{-2\gamma t} + \frac{C}{2\gamma}(1-e^{-2\gamma t})$$

$t\to\infty$ should have equilibrium $\frac{1}{2}M\left\langle v^2\right\rangle = \frac{3}{2}kT \quad \Rightarrow \quad C = 6kT\gamma/M$.

Strength of fluctuating force $\sim\gamma$, both fluctuations and friction are due to the medium.

$$\left\langle v^2(t) \right\rangle = v^2(0) + (\frac{3k_BT}{M} - v^2(0))(1 - e^{-2\gamma t})$$



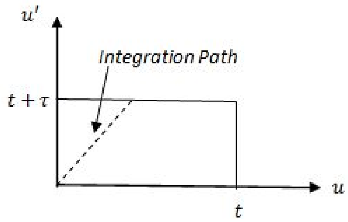
General solution for $\langle r^2 \rangle$ $(v^2(0) \neq 3k_BT/M)$

:

$$\frac{d}{dt^2} \left\langle r^2 \right\rangle + \gamma \frac{d}{dt} \left\langle r^2 \right\rangle = 2 \left\langle v^2 \right\rangle$$

$$\Rightarrow \left\langle r^2 \right\rangle = \frac{1}{\gamma^2} v^2(0)(1 - e^{-\gamma t})^2 - \frac{3k_BT}{M\gamma^2}(1 - e^{-\gamma t})(3 - e^{-\gamma t}) + \frac{6k_BT}{M\gamma} t =$$

$$= \begin{cases} v^2(0)t^2 + O(t^3) & t << 1/\gamma \\ \frac{6k_BT}{M\gamma} t & t >> 1/\gamma \end{cases}$$



Velocity correlations: $K_v(\tau) \equiv \langle v(t)v(t+\tau) \rangle$

$$= v^2(0)e^{-\gamma(2t+\tau)} + e^{-\gamma(2t+\tau)} \int_0^t \int_0^{t+\tau} e^{\gamma(u+u')} C\delta(u-u')dudu' =$$

$$= \begin{cases} v^2(0)\mathrm{e}^{-\gamma(2t+\tau)} + \frac{C}{2\gamma}e^{-\gamma(2t+\tau)}(e^{2\gamma t} - 1) & \tau > 0 \\ v^2(0)\mathrm{e}^{-\gamma(2t+\tau)} + \frac{C}{2\gamma}e^{-\gamma(2t+\tau)}(e^{2\gamma(t+\tau)} - 1) & \tau < 0 \end{cases}$$

$$\Rightarrow K_v(\tau) = v^2(0)\mathrm{e}^{-\gamma|\tau|} + (\frac{3kT}{M} - v^2(0))(\mathrm{e}^{-\gamma|\tau|} - e^{-\gamma(2t+\tau)})$$

$$= \frac{3k_BT}{M}\mathrm{e}^{-\gamma|\tau|} \qquad \text{at long times} \qquad t+\tau, t >> 1/\gamma\,.$$

Note that replacing $v^2(0)$ by its equilibrium average yields $K_v(\tau) = (3k_BT/M)\mathrm{e}^{-\gamma|\tau|}$ at all times t.

Reaching equilibrium at large times $K_v(\tau)$ becomes t independent $\Rightarrow$ **stationary medium**.

Note that for correlations of just one component, e.g. v_x, we have

$K_{v_x}(\tau) = \langle v_x(0)v_x(\tau) \rangle = \frac{k_BT}{M}\mathrm{e}^{-\gamma|\tau|}$.

Below the Fourier transform is needed:

$$\Phi_{v_x}(\omega) = \int_{-\infty}^{\infty} K_{v_x}(\tau)e^{i\omega\tau}d\tau = \frac{2k_BT}{M}\frac{\gamma}{\omega^2+\gamma^2}$$

4c. Fluctuation Dissipation Theorems (FDT)

General properties of averages of stationary medium

Consider a variable x(t) such that $K_x(\tau) = \langle x(t) \cdot x(t+\tau)\rangle$ is independent of the time t.

$$K_x(0) > 0; \quad \langle [x(t) \pm x(t+\tau)]^2 \rangle = 2[K_x(0) \pm K_x(\tau)] \geq 0$$

it follows that $|K_x(\tau)| \leq K_x(0)$ is a decreasing function, and usually $K_x(\tau) \overset{\tau\to\infty}{\to} 0$. Also $K_x(\tau) = \langle x(t-\tau)x(t)\rangle = K_x(-\tau)$, with shift $t \to t-\tau$.

Consider now the Fourier transform $x(\omega)$:

$$x(t) = \int_{-\infty}^{\infty} x(\omega) \mathrm{e}^{-i\omega t} \frac{d\omega}{2\pi}$$

For a precise derivation one needs $x(t)$ to be finite only in the interval $[-\frac{T}{2}, \frac{T}{2}]$. The spacing $\Delta\omega$ between distinct ω values with $\cos(\omega \frac{T}{2}) = 0$ or $\sin(\omega \frac{T}{2}) = 0$ is $\Delta\omega = \frac{2\pi}{T}$. (See Wannier p. 481). For $T \to \infty$ consider

$K_x(\tau) = \int d\omega \int d\omega' \mathrm{e}^{-i\omega t - i\omega'(t+\tau)} \langle x(\omega)x(\omega')\rangle /(2\pi)^2$

Since this is t independent, perform the integral $\int ... \frac{dt}{T}$

$$K_x(\tau) = \int d\omega \int d\omega' \frac{2\pi}{T} \delta(\omega + \omega') \mathrm{e}^{-i\omega'\tau} \frac{\langle x(\omega)x(\omega')\rangle}{(2\pi)^2} = \Delta\omega \int d\omega \langle |x(\omega)|^2 \rangle \mathrm{e}^{i\omega\tau}/(2\pi)^2$$

This is the Wiener-Khinchin theorem:

$$\boxed{\Phi_x(\omega) = \int \langle x(t)x(t+\tau)\rangle \, \mathrm{e}^{-i\omega\tau} d\tau = \frac{\Delta\omega}{2\pi} \left\langle |x(\omega)|^2 \right\rangle}$$

$\left\langle |x(\omega)|^2 \right\rangle$ is called the intensity, or the power spectrum of x.

As an example, consider Langevin's equation:

$$(-i\omega + \gamma)v(\omega) = A(\omega) \qquad \Rightarrow |v(\omega)|^2 = \frac{|A(\omega)|^2}{(\omega^2 + \gamma^2)}$$

from the theorem above $\Phi_v(\omega) = \frac{\Phi_A(\omega)}{\gamma^2 + \omega^2}$ which is consistent with previous result: $\Phi_v(\omega) = \frac{2k_B T}{M} \frac{\gamma}{\gamma^2 + \omega^2}$ and $\Phi_A(\omega) = \frac{2k_B T \gamma}{M}$, the latter corresponds to white noise.

Note also that $-i\omega x(\omega) = v(\omega)$, hence

$$|x(\omega)|^2 = \frac{|v(\omega)|^2}{\omega^2} \qquad \Rightarrow \Phi_x(\omega) = \frac{2k_B T}{M} \frac{\gamma}{(\gamma^2 + \omega^2)\omega^2}$$

Dissipation and Response functions

An external force adds the Hamiltonian term $-F(t)x$. The Hamiltonian becomes:

$$H = \frac{p^2}{2m} + V(x;\mathrm{env}) - F(t)x$$

where "env" stands for the coordinates and momenta of the environment. For an explicit system + environment see the Appendix.

The equations of motion are:

$$\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}, \quad \dot{p} = -\frac{\partial H}{\partial x} = -\frac{\partial V}{\partial x} + F = m\ddot{x}$$

hence $F(t)$ is indeed an external force.

The rate at which the system's energy changes is

$$\frac{dH}{dt} = \overbrace{\frac{\partial H}{\partial p}\dot{p} + \frac{\partial H}{\partial x}\dot{x}}^{=0} + ... + \frac{\partial H}{\partial t} = -x\frac{dF}{dt}$$

where the sum of the first two terms on the right hand side vanishes by Hamilton's equations for x, p; the ... terms are similar derivatives with respect to the coordinates and momenta of the environment which also vanish due to their corresponding Hamilton's equations.

The dissipation rate is the rate of energy absorption from the external source, averaged on time. This includes an average on the enviorment $\langle x(t)\rangle$ (e.g. on the random force in Langevin's equation) and on the explicit time dependence in $F(t)$, hence

$$\overline{\frac{dE}{dt}} = -\overline{\langle x\rangle\frac{dF}{dt}}$$

The dissipation rate can be expressed in terms of a response function $\alpha_x(\omega)$ where the linear response at small forces F is defined by

$$\langle x(\omega)\rangle = \alpha_x(\omega)F(\omega)$$

It is more compact to consider a single frequency $F(t) = \frac{1}{2}f_0\mathrm{e}^{-i\omega t} + \frac{1}{2}f_0^*\mathrm{e}^{i\omega t}$ (although a Fourier sum can be added)

$\langle x(t)\rangle = \frac{1}{2}\alpha_x(\omega)f_0\mathrm{e}^{-i\omega t} + \frac{1}{2}\alpha_x^*(\omega)f_0\mathrm{e}^{i\omega t}$ with $\alpha_x^*(\omega) = \alpha_x(-\omega)$

The dissipation is then:

$$\overline{\frac{dE}{dt}} = -\left\langle x\overline{\frac{\partial F}{\partial t}}\right\rangle = \frac{i\omega}{4}\overline{[\alpha_x(\omega)f_0\mathrm{e}^{-i\omega t} + \alpha_x^*(\omega)f_0^*\mathrm{e}^{i\omega t}][f_0\mathrm{e}^{-i\omega t} - f_0^*\mathrm{e}^{i\omega t}]} = -\frac{i\omega}{4}|f_0|^2[\alpha_x(\omega) - \alpha_x^*(\omega)]$$

$$\Rightarrow \qquad \overline{\frac{dE}{dt}} = \frac{1}{2}\omega|f_0|^2\mathrm{Im}\alpha_x(\omega)$$

Consider now the specific case of Langevin's equation, where the environment leads to friction and random force terms. Averaging on the random force, $M(-\omega^2 - i\omega\gamma)\langle x(\omega)\rangle = F(\omega)$, hence the response has the same frequency as the source and the response function is

$$\Rightarrow \qquad \alpha_x(\omega) = \frac{\langle x(\omega)\rangle}{F(\omega)} = \frac{-1}{M(\omega^2 + i\omega\gamma)}$$

The dissipation rate is therefore proportional to $\mathrm{Im}\alpha_x(\omega) = \frac{\gamma\omega}{M(\omega^2+\gamma^2)\omega^2}$
Comparing with $\Phi_x(\omega)$ we get the "Fluctuation - Dissipation theorem":

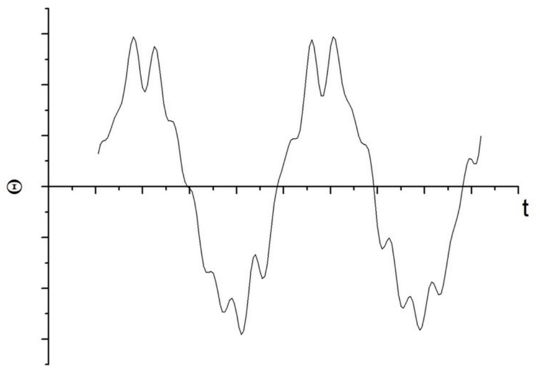
$$\boxed{\Phi_x(\omega) = \tfrac{2k_BT}{\omega}\mathrm{Im}\alpha_x(\omega)}$$

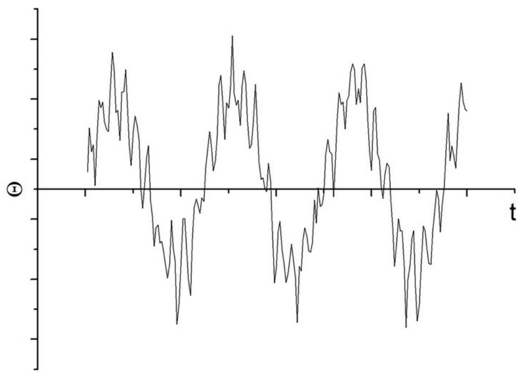
Note: same result holds for $\Phi_v(\omega)$, $\alpha_v(\omega)$ with an external source term in the Hamiltonian $-F(t)p/M$ (exercise).

In conclusion, $\Phi_x(\omega) \rightarrow$ are fluctuations in absence(!) of external force.
$\alpha_x(\omega) \rightarrow$ linear response and energy dissipation due to external force.

Applications

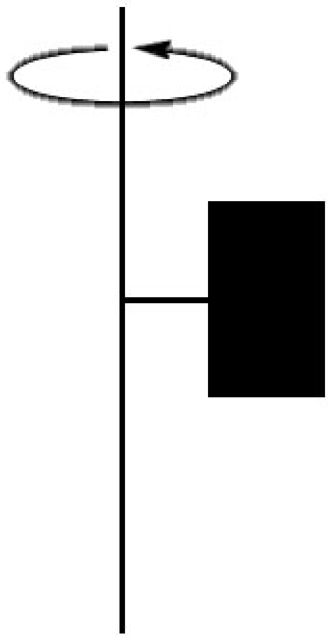
1. Kapplers experiment (1931) : fluctuations in angle θ of a mirror suspended on a fine wire with a restoring force $\left\langle \frac{1}{2}C\theta^2\right\rangle = \frac{1}{2}k_BT \rightarrow$ determine k_B. Note : Variance is independent of gas density. Equilibrium is achieved after time $\gg \tau_{col}, 1/\gamma$.





Low density: rare strong deflections High density: frequent weak deflections

2. A square vane of area $1cm^2$, painted white on one side and black on the other, is attached to a vertical axis and can rotate freely about it as shown. Assume that the vane can support a temperature difference between its black and white sides. Suppose the arrangements is placed in He gas at room temperature and sunlight is allowed to shine on the vane. Explain qualitatively why : (a) At extremely small densities the vane rotates. (b) At some intermediate (very low) density the vane rotates in a sense opposite to that in (a); estimate this intermediate density and the corresponding pressure. (c) At a higher (but still low) density the vane stops.



Answers :

(a) Radiation pressure on white > black.

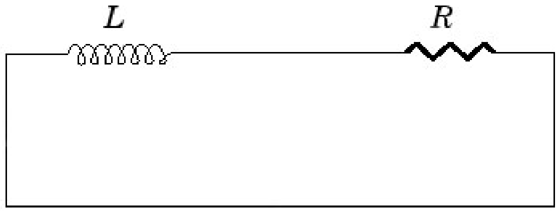
(b) Black heats up and nearby hotter atoms exert higher pressure. Gas is in local equilibrium with density $n \gg 1\text{cm}^{-3}$.

(c) Viscosity is effective at $\tau_{col} << 1/\gamma$ and global equilibrium is achieved.

3. Electrical circuit:

$L\frac{dI}{dt} = -RI + V(t)$

$V(t)$ - voltage fluctuations



Johnson noise (1927)
Nyquist theorem

Langevin analogy: $\frac{dv_x}{dt} = -\gamma v_x + A_x\left(t\right) => \gamma \to R/L$

Correlation of A is determined by $\frac{1}{2}M\left\langle v_x^2\right\rangle = \frac{1}{2}k_BT \overset{M\to L}{=} \frac{1}{2}L\left\langle I^2\right\rangle$

$$\Phi_{v_x(w)} = \frac{2k_BT}{M}\cdot\frac{\gamma}{\omega^2+\gamma^2} \to \Phi_I\left(\omega\right) = \frac{2k_BT}{L}\cdot\frac{R/L}{\omega^2+(R/L)^2} \overset{\omega<<R/L}{=} \frac{2k_BT}{R}$$

$$\Phi_{A_x(\omega)} = \frac{2k_BT\gamma}{M} \to \Phi_{V/L}\left(\omega\right) = \frac{2k_BTR}{L^2} => \Phi_V\left(\omega\right) = 2k_BTR$$

$$K_I\left(\tau=0\right) = \left\langle I^2\left(t\right)\right\rangle = \int\Phi_I\left(\omega\right)\frac{d\omega}{2\pi}$$

Fluctuations measured in interval $\omega_1 < |\omega| < \omega_2$: $\left\langle\Delta I^2\right\rangle_{\omega_1\leftrightarrow\omega_2} = 2\cdot\int\limits_{\omega_1}^{\omega_2}\Phi_I\left(\omega\right)\frac{d\omega}{2\pi}$. The factor 2 accounts for $\omega < 0$.

$$\left\langle\Delta I^2\right\rangle_{\omega_1\leftrightarrow\omega_2} \simeq \frac{2k_BT}{\pi R}\left(\omega_2-\omega_1\right) \qquad [\omega_{1,2} << R/L]$$
$$\left\langle\delta V^2\right\rangle_{\omega_1\leftrightarrow\omega_2} = \frac{2}{\pi}k_BTR\left(\omega_2-\omega_1\right)$$

4. Brownian particle : τ_0 response time of eye, i.e. only frequencies $|\omega| < \frac{2\pi}{\tau_0}$ are observed.

$$\left\langle v_x^2\right\rangle_{obs} = \left[K_v\left(\tau=0\right)\right]_{obs} = 2\int\limits_0^{2\pi/\tau_0}\Phi_v\left(\omega\right)\frac{d\omega}{2\pi} = \frac{2k_BT}{\pi M}\tan^{-1}\left(\frac{2\pi}{\tau_0\gamma}\right)$$
$$\frac{1}{\tau_0\gamma} \simeq 10^{-6} \Rightarrow \left\langle v_x^2\right\rangle_{obs} \simeq \frac{4k_BT}{M}\cdot\frac{1}{\tau_0\gamma} << \frac{k_BT}{M}$$

i.e instead of $\sqrt{k_BT/M} \simeq 10^{-1}cm/\sec$ a small fraction of the fluctuations is observed $\sqrt{\left\langle v_x^2\right\rangle_{obs}} \simeq 10^{-4}cm/\sec$.

Fluctuation Dissipation Theorem (FDT): quantum version

Fluctuations

Consider a system in equilibrium, no external force. For $\hat{x}(t)$ (Heisenberg representation) define a symmetrized correlation

$$K(\tau) = \frac{1}{2}\langle \hat{x}(t)\,\hat{x}(t+\tau) + \hat{x}(t+\tau)\,\hat{x}(t)\rangle\,.$$

where a subscript x is omitted here, for convenience. The symmetrized correlation involves a hermitian operator and has an obvious classical limit. note, however, that there are FDT's for non-symmetrized correlations.

Note that $K(\tau) = K(-\tau)$ and $K(\tau)$ is real. The average is defined by

$$\langle ...\rangle = \sum_n \langle n|\,...\,|n\rangle\, e^{-\beta E_n}/Z.$$

where $Z = \sum_n \mathrm{e}^{-\beta E_n}$ is the partition sum.

Introduce a unit operator $\sum\limits_m |m\rangle\langle m| = 1$ and define (time independent) matrix elements x_{mn} by

$$\langle n|\,\hat{x}(t)\,|m\rangle = \mathrm{e}^{i(E_n - E_m)t/\hbar} x_{nm}.$$

Therefore

$K(\tau) = \frac{1}{2Z}\sum_{n,m} \mathrm{e}^{i(E_n-E_m)t/\hbar} x_{nm} x_{mn} \mathrm{e}^{i(E_m-E_n)(t+\tau)/\hbar} \mathrm{e}^{-\beta E_n} + (t \leftrightarrow t+\tau) =$

$= \frac{1}{2Z}\sum_{n,m} \mathrm{e}^{-i\omega_{nm}\tau} |x_{nm}|^2 \mathrm{e}^{-\beta E_n} + c.c.$ where $\omega_{nm} = \frac{E_n - E_m}{\hbar}$

$\Phi(\omega) = \int K(\tau)\,\mathrm{e}^{i\omega\tau} d\tau = \frac{\pi}{Z}\sum\limits_{n,m} \mathrm{e}^{-\beta E_n}\,|x_{nm}|^2\,[\delta(\omega - \omega_{nm}) + \delta(\omega + \omega_{nm})]$

Interchange $n \leftrightarrow m$ in the first $\delta(\omega - \omega_{nm})$,

$$\begin{aligned}
\Phi(\omega) &= \frac{\pi}{Z}\sum_{n,m}\left(\mathrm{e}^{-\beta E_m} + \mathrm{e}^{-\beta E_n}\right)|x_{nm}|^2 \delta(\omega + \omega_{nm}) = \\
&= \frac{\pi}{Z}\sum_{n,m} \mathrm{e}^{-\beta E_n}\left(\mathrm{e}^{-\beta(E_m - E_n)} + 1\right)|x_{nm}|^2 \delta(\omega + \omega_{nm}) = \\
&= \frac{\pi}{Z}\left(1 + \mathrm{e}^{-\beta\hbar\omega}\right)\sum_{n,m} \mathrm{e}^{-\beta E_n}\,|x_{nm}|^2 \delta(\omega + \omega_{nm})
\end{aligned}$$

Dissipation

Add coupling to an external force, $F(t)$:

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \qquad \text{where} \qquad \hat{V}(t) = -F(t)\hat{x}\,.$$

We use here Shrdinger's representation to avoid the form $H_H(t) \neq H(t)$. The response function $\alpha(\tau)$ gives $\langle \hat{x}(t) \rangle$ in terms of $F(t-\tau)$ at all previous times, i.e. $\tau > 0$:

$$\langle \hat{x}(t) \rangle = \int_0^\infty \alpha(\tau) F(t-\tau) d\tau.$$

Assume, without loss of generality,

$$F(t) = \frac{1}{2} f_0 \mathrm{e}^{-i\omega t} + \frac{1}{2} f_0^* \mathrm{e}^{i\omega t}.$$

Therefore

$$\langle \hat{x}(t) \rangle = \frac{1}{2} \int_0^\infty \alpha(\tau) \left[f_0 \mathrm{e}^{-i\omega(t-\tau)} + f_0^* \mathrm{e}^{i\omega(t-\tau)} \right] d\tau.$$

The Fourier transform is

$$\alpha(\omega) = \int_0^\infty \alpha(\tau) \mathrm{e}^{i\omega\tau} d\tau \quad (\alpha(\tau) = 0 \text{ for } \tau < 0),$$

therefore

$$\langle \hat{x}(t) \rangle = \frac{1}{2} \alpha(\omega) f_0 \mathrm{e}^{-i\omega t} + \frac{1}{2} \alpha(-\omega) f_0^* \mathrm{e}^{i\omega t},$$

since $\alpha(-\omega) = \alpha^*(\omega)$ [$\alpha(\tau)$ is real]. In terms of the density matrix $\hat{\rho}(t)$ corresponding to the full Hamiltonian $\mathcal{H}$, the dissipation rate is

$$\begin{aligned} \frac{dE}{dt} &= \mathrm{Tr}\{\frac{d}{dt}(\hat{\rho}\mathcal{H})\} = \frac{i}{\hbar}\mathrm{Tr}\{[\hat{\rho}, \mathcal{H}]\mathcal{H}\} + \mathrm{Tr}\{\hat{\rho}\frac{\partial \mathcal{H}}{\partial t}\} && (4) \\ &= -\mathrm{Tr}\{\hat{\rho}\hat{x}\frac{\partial F}{\partial t}\} = -\langle \hat{x} \rangle \frac{\partial F}{\partial t} && (5) \end{aligned}$$

where the equation of motion of $\hat{\rho}$ is used, as well as the cyclic property of the trace. The result is formally the same as in the classical case, except that $\langle \hat{x} \rangle$ is a quantum expectation value.

Using the response function and averaging on time,

$$\overline{\frac{dE}{dt}} = \overline{\frac{1}{2} \left(\alpha(\omega) f_0 \mathrm{e}^{-i\omega t} + \alpha(-\omega) f_0^* \mathrm{e}^{i\omega t} \right) \frac{i\omega}{2} \left(f_0 \mathrm{e}^{-i\omega t} - f_0^* \mathrm{e}^{i\omega t} \right)},$$

$$\Rightarrow \overline{\frac{dE}{dt}} = \frac{i\omega}{4} |f_0|^2 [-\alpha(\omega) + \alpha^*(\omega)] = \frac{\omega}{2} |f_0|^2 \mathrm{Im}[\alpha(\omega)].$$

Therefore $\omega \mathrm{Im}[\alpha(\omega)]$ measures the dissipation rate. Since this is positive $\mathrm{Im}[\alpha(\omega)] > 0$ for $\omega > 0$.

Golden Rule for the Dissipation

The rate of transition between states at time T is

$$W_{n\to m} = \frac{1}{\hbar^2}\left|\int \langle m|\hat{V}|n\rangle dt\right|^2 \frac{1}{T} =$$

$$= \frac{1}{\hbar^2}\left|\frac{1}{2}\int dt\left[\mathrm{e}^{i(E_m-E_n)t/\hbar}x_{mn}(f_0\mathrm{e}^{-i\omega t} + f_0^*\mathrm{e}^{i\omega t})\right]\right|^2 \frac{1}{T}$$

We note that

$$\frac{1}{T}\left|\int \mathrm{e}^{i(\omega_{mn}-\omega)t}dt\right|^2 = \frac{1}{T}\int_{-T/2}^{T/2}\mathrm{e}^{-i(\omega_{mn}-\omega)t}dt\int_{-T/2}^{T/2}\mathrm{e}^{i(\omega_{mn}-\omega)t'}dt' =$$

$$= \frac{1}{T}\int_{-T/2}^{T/2}\mathrm{e}^{-i(\omega_{mn}-\omega)t}[2\pi\delta(\omega_{mn}-\omega)]dt = 2\pi\delta(\omega_{mn}-\omega).$$

$$\Rightarrow W_{n\to m} = \frac{\pi}{2\hbar^2}|f_0|^2|x_{mn}|^2[\delta(\omega_{nm}-\omega) + \delta(\omega_{nm}+\omega)].$$

The energy dissipation rate can now be calculated

$$Q = \frac{1}{Z}\sum_{n,m}(E_m - E_n)W_{n\to m}\mathrm{e}^{-\beta E_n} =$$

$$= \frac{\pi}{2\hbar^2}\omega|f_0|^2\frac{1}{Z}\sum_{n,m}\mathrm{e}^{-\beta E_n}|x_{nm}|^2[\delta(\omega+\omega_{nm}) - \delta(\omega-\omega_{nm})] =$$

$$= \frac{\pi}{2\hbar^2}\omega|f_0|^2\frac{1}{Z}\sum_{n,m}(\mathrm{e}^{-\beta E_n} - \mathrm{e}^{-\beta E_m})|x_{nm}|^2\delta(\omega+\omega_{nm}).$$

Noting that

$$\mathrm{e}^{-\beta E_n} - \mathrm{e}^{-\beta E_m} = \mathrm{e}^{-\beta E_n}\left(1 - \mathrm{e}^{-\beta(E_m-E_n)}\right) = \mathrm{e}^{-\beta E_n}\left(1 - \mathrm{e}^{-\beta\omega_{mn}}\right),$$

and using the δ function with $\omega_{mn} = \omega$, we get

$$Q = \frac{\pi}{2\hbar}\omega|f_0|^2(1 - \mathrm{e}^{-\beta\hbar\omega})\frac{1}{Z}\sum_{n,m}\mathrm{e}^{-\beta E_n}|x_{nm}|^2\delta(\omega_{nm}+\omega)$$

$$\Rightarrow \mathrm{Im}[\alpha(\omega)] = \frac{\pi}{\hbar}(1-\mathrm{e}^{-\beta\hbar\omega})\sum_{n,m}\frac{1}{Z}\mathrm{e}^{-\beta E_n}|x_{nm}|^2\delta(\omega_{nm}+\omega).$$

$$\Rightarrow \boxed{\Phi(\omega) = \hbar\coth\left(\tfrac{1}{2}\beta\hbar\omega\right)\mathrm{Im}[\alpha(\omega)]}$$

The $\coth\left(\frac{1}{2}\beta\hbar\omega\right)$ can be interpreted as the mean fluctuation of an oscillator coordinate:

$$\left\langle x_{osc}^2\right\rangle = \frac{\hbar}{2m\omega}\left\langle (a+a^\dagger)^2\right\rangle \sim \frac{2}{\mathrm{e}^{\beta\hbar\omega}-1}+1 = \coth\left(\frac{1}{2}\beta\hbar\omega\right).$$

Note that in the limit $\hbar \to 0$ (i.e. for $k_BT >> \hbar\omega$) the quantum FDT becomes

$$\Phi(\omega) \to \frac{2k_BT}{\omega}\mathrm{Im}[\alpha(\omega)].$$

which is our previous classical FDT.

4d. Onsager's Relations

Onsager's relations (1931) consider the response to deviations from equilibrium. The responses are measured by a flow processes $\dot{x}_i$ in coordinates x_i (e.g heat flow, electric current, mass transfer, etc.), while the deviation from equilibrium corresponds to "forces" f_i, e.g gradients in temperature, potential, pressure, etc. The forces f_i can be external ones, or they can form spontaneously as a fluctuation.

If the system is close to equilibrium, we assume a linear relation between the forces and the responding currents:

$$\dot{x}_i = \gamma_{ij}f_j,$$

where summation convention is used (i.e. repeated indices are summed). γ_{ij} are known as kinetic coefficients. [In general, however, the relation is non-local in time and can be written as $\dot{x}_i(t) \sim \int_{-\infty}^t \gamma_{ij}(t-t')f_j(t')dt'$.]

We consider x_i as coordinates of the entropy S so that the forces are $f_i = \partial S/\partial x_i$. For small deviations from equilibrium values $\bar{x}_i$ we expand near the entropy maximum

$$S = S(\bar{x}_i) - \frac{1}{2}\beta_{ij}(x_i-\bar{x}_i)(x_j-\bar{x}_j)$$

$$\Rightarrow f_i = \frac{\partial S}{\partial x_i} = -\beta_{ij}(x_j-\bar{x}_j)$$

$$\dot{x}_i = -\gamma_{ij}\beta_{jk}(x_k - \bar{x}_k)\,.$$

Consider

$$\langle x_i f_j \rangle = k_B \frac{\int_{-\infty}^{\infty} x_i \frac{\partial}{\partial x_j} \mathrm{e}^{-\beta_{ij}(x_i-\bar{x}_i)(x_j-\bar{x}_j)/2k_B}}{\int_{-\infty}^{\infty} \mathrm{e}^{-\beta_{ij}(x_i-\bar{x}_i)(x_j-\bar{x}_j)/2k_B}}$$

where the $\pm\infty$ limits are allowed due to fast convergence.

By partial integration $\langle x_i f_j \rangle = -k_B \delta_{ij}$

$$\Rightarrow \langle \dot{x}_i x_j \rangle = \gamma_{ik} \langle f_k x_j \rangle = -k_B \gamma_{ij}.$$

This is a type of FDT – the fluctuations $\langle \dot{x}_i x_j \rangle$ are related to the dissipation $\sim \gamma_{ij}$.

Consider $\langle x_i(\tau) x_j(0) \rangle$ with microscopic time reversal (dissipation $\sim \gamma_{ij}$ and irreversibility arise after average on the environment, or on the ensemble.)

$$\langle x_i(\tau) x_j(0) \rangle = \langle x_i(-\tau) x_j(0) \rangle = \langle x_i(0) x_j(\tau) \rangle$$

where in the second form both times are shifted by τ, allowed in equilibrium.

$$\frac{\partial}{\partial \tau}|_0 \Rightarrow \langle \dot{x}_i(0) x_j(0) \rangle = \langle x_i(0) \dot{x}_j(0) \rangle \Rightarrow \qquad \boxed{\gamma_{ij} = \gamma_{ji}}$$

These are Onsager's relations.

Define

$$\tilde{F} = \tfrac{1}{2}\gamma_{ij} f_i f_j \qquad \Rightarrow \qquad \dot{x}_i = \frac{\partial \tilde{F}}{\partial f_i}$$

$$\dot{S} = \frac{\partial S}{\partial x_i}\dot{x}_i = f_i \dot{x}_i = f_i \frac{\partial \tilde{F}}{\partial f_i} = 2\tilde{F}$$

$\dot{S} > 0$, hence $\tilde{F} > 0$ for all choices of f_i, therefore the matrix γ_{ij} is positive definite.

A few more properties of γ_{ij}:

In presence of a magnetic field B time reversal involves $B \to -B$, hence $\gamma_{ij}(B) = \gamma_{ji}(-B)$; e.g. for the Hall conductance $\sigma_{xy}(-B) = \sigma_{yx}(B)$.

In presence of angular velocity Ω, similarly, $\gamma_{ij}(\Omega) = \gamma_{ji}(-\Omega)$.

Furthermore, if for some coordinate $x_i \to -x_i$, $x_j \to +x_j$ under time-reversal, then

$\gamma_{ij} = -\gamma_{ji}$

Alternative derivation:

Consider f_i as external forces with a Legendre transformed entropy $S \to \tilde{S} = S - (x_i - \bar{x}_i) f_i$.

Since $f_i = \frac{\partial S}{\partial x_i} \Rightarrow \qquad d\tilde{S} = -(x_i - \bar{x}_i) df_i$, i.e. $\tilde{S} = \tilde{S}(f_i)$.

Weight of a configuration is now

$$\mathrm{e}^{\tilde{S}/k_B} = \mathrm{e}^{S/k_B - (x_i - \bar{x}_i) f_i / k_B}$$

here $S = S\{x_i\}$ has all orders of x_i.

$\langle \dot{x}_i \rangle_{f=0} = 0$, i.e. flow is only in response to $f_j \neq 0$.

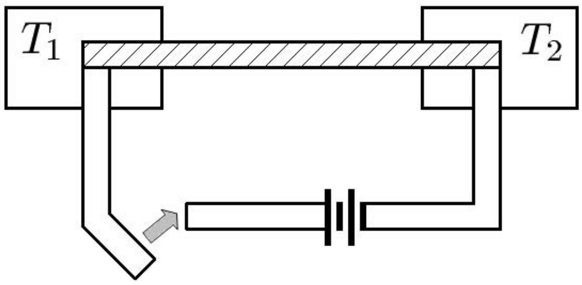
$$\langle \dot{x}_i \rangle = \frac{\int \dot{x}_i \mathrm{e}^{S/k_B - (x_j - \bar{x}_j) f_j / k_B}}{\int \mathrm{e}^{S/k_B - (x_j - \bar{x}_j) f_j / k_B}} = \frac{\int \dot{x}_i \mathrm{e}^{S/k_B} [1 - (x_j - \bar{x}_j) f_j / k_B]}{\int \mathrm{e}^{S/k_B} [1 - (x_j - \bar{x}_j) f_j / k_B]} + \cdots = - \langle \dot{x}_i x_j \rangle_0 f_j / k_B + O(f^2)$$

Here linear response is explicit $\Rightarrow \gamma_{ij} = - \langle \dot{x}_i x_j \rangle_0 / k_B$ as above.

$\langle \dot{x}_i x_j \rangle_0$ is evaluated with $f_i = 0$ and microscopic time reversal can be used as above

$\Rightarrow \qquad \gamma_{ij} = \gamma_{ji}$

<u>Application: Bi-metal junctions</u>



Using $E_1 + E_2$ =const, and $Q_1 + Q_2$ =const we have

$$dE_{1\to 2} = -dE_1 = dE_2, \;\; dQ_{1\to 2} = -dQ_1 = dQ_2$$

and since $dE = TdS + VdQ$ we obtain

$$dS = \frac{dE_1}{T_1} + \frac{dE_2}{T_2} - \frac{V_1}{T_1} dQ_1 - \frac{V_2}{T_2} dQ_2 = \underbrace{dE_{1\to 2}}_{x_1} \underbrace{\left(-\frac{1}{T_1} + \frac{1}{T_2} \right)}_{f_1} + \underbrace{dQ_{1\to 2}}_{x_2} \underbrace{\left(\frac{V_1}{T_1} - \frac{V_2}{T_2} \right)}_{f_2}$$

$$\dot{E}_{1\to 2} = \gamma_{11} \left(-\frac{1}{T_1} + \frac{1}{T_2} \right) + \gamma_{12} \left(\frac{V_1}{T_1} - \frac{V_2}{T_2} \right)$$

$$\dot{Q}_{1\to 2} = \gamma_{21} \left(-\frac{1}{T_1} + \frac{1}{T_2} \right) + \gamma_{22} \left(\frac{V_1}{T_1} - \frac{V_2}{T_2} \right)$$

Seebeck coefficient Ψ is defined by $\Delta V = \Psi \Delta T$ in an open circuit, i.e. $\dot{Q}_{1\to 2} = 0$:

$$V_1 - V_2 = \frac{\gamma_{21}}{\gamma_{22}} \frac{T_2 - T_1}{T} \Rightarrow \qquad \Psi = -\frac{\gamma_{21}}{\gamma_{22} T} \quad \text{(to lowest order in gradients)}$$

Peltier coefficient Π, corresponds to $T_1 = T_2$ and is defined by

$$\dot{E} = \Pi \dot{Q} \Rightarrow \qquad \Pi = \frac{\gamma_{12}}{\gamma_{22}}$$

$$\gamma_{12} = \gamma_{21} \Rightarrow \qquad \Pi = -T\Psi \quad \text{This is Kelvin's relation.}$$

Appendix: Langevin's equation from a Hamiltonian

This appendix considers a microscopic model for an environment that produces the dissipation γ and the random forces $\xi(t)$ in Langevin's equation

$$m\ddot{q} + \gamma\dot{q} + \frac{\partial V}{\partial q} = \xi(t)\,.$$

The derivation is based on Caldeira and Legget, Ann. Phys. **149**, 374(1983) and provides a basis for Brownian motion.

Consider a linear coupling of the particle coordinate q to a set of Harmonic oscillators, with coordinates Q_i and momenta P_i; the linearity is valid when the particle's trajectories are sufficiently confined.

$$H = \frac{P^2}{2m} + V(q) + \underbrace{\sum_{i=1}^{N} \lambda_i q Q_i}_{Coupling\ of\ oscillators\ to\ a\ heat\ bath} + \underbrace{\sum_i \left(\frac{P_i^2}{2M_i} + \frac{1}{2}M_i\Omega_i^2 Q_i^2\right)}_{Bath's\ Energy} + \Delta V(q)$$

Where $\Delta V(q)$ is chosen to retain the original minimum of $V(q)$. Minimizing H with respect to Q_i gives $Q_i = \frac{-\lambda_i}{M_i\Omega_i^2}q$, hence q dependent potential terms appear $\sum_i \frac{\lambda_i^2}{M_i\Omega_i}q^2(-1+\frac{1}{2})$ which we wish to cancel by

$$\Delta V(q) = \sum_i \frac{\lambda_i^2}{2M_i\Omega_i^2}q^2\,.$$

The equations of motion for Q_i are

$$\ddot{Q}_i + \Omega_i^2 Q = -\frac{\lambda_i}{M_i}q(t)e^{\eta t}$$

where retarded response is defined by $\eta \to 0^+$, i.e. at $t \to -\infty$ the coupling to the environment vanishes. The solution is

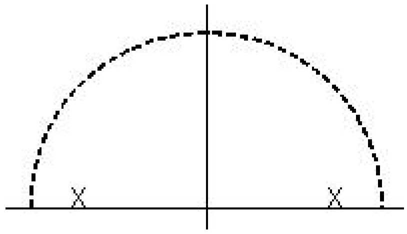
$$Q_i(t) = Q_i^0(t) + \frac{\lambda_i}{M_i}\int dt' q(t') \int \frac{d\omega}{2\pi}\frac{e^{i\omega(t-t')+\eta t'}}{\omega^2 - \Omega_i^2}$$

where Q_i^0 is the solution of $\ddot{Q}_i + \Omega_i^2 Q = 0$. Let us shift $\omega \to \omega - i\eta$ and rewrite

$$Q_i(t) = Q_i^0(t) + \frac{\lambda_i}{M_i}\int dt' q(t') \int \frac{d\omega}{2\pi}\frac{\mathrm{e}^{i\omega(t-t')}}{(\omega - \Omega_i - i\eta)(\omega + \Omega_i - i\eta)}\mathrm{e}^{\eta t}$$

To solve this integral we need to take the upper contour for $t > t'$ (see figure, so that $\mathrm{e}^{i\omega(t-t')}$ vanishes on the upper half circle). The closed contour integration has two poles (see figure) and therefore

$$Q_i(t) = Q_i^0(t) + \frac{\lambda_i}{M_i}\int_{-\infty}^{t} dt' q(t') i \left[\frac{e^{i\Omega_i(t-t')}}{2\Omega_i} - \frac{\mathrm{e}^{-i\Omega_i(t-t')}}{2\Omega_i}\right]\mathrm{e}^{\eta t'}$$



Hence,

$$\begin{aligned} Q_i(t) &= Q_i^0(t) - \frac{\lambda_i}{M_i\Omega_i}\int_{-\infty}^t dt' q(t')\sin\Omega_i(t-t')\mathrm{e}^{\eta t'} \\ &= Q_i^0(t) - \frac{\lambda_i}{M_i\Omega_i^2}q(t) + \frac{\lambda_i}{M_i\Omega_i^2}\int_{-\infty}^t dt'\dot{q}(t')\cos\Omega_i(t-t') \qquad (*) \end{aligned}$$

where partial integration is done, and at $t' \to -\infty$ we use $\mathrm{e}^{\eta t'} \to 0$; in the final form we set $\eta = 0$.

Equation of motion for $q(t)$:

$$\begin{aligned} & m\ddot{q} + \frac{\partial V}{\partial q} + \frac{\partial \Delta V}{\partial q} = -\sum_i \lambda_i Q_i \\ & = -\sum \lambda_i Q_i^0 + \sum_i \frac{\lambda_i^2}{M_i\Omega_i^2}q(t) - \sum_i \frac{\lambda_i^2}{M_i\Omega_i^2}\int_{-\infty}^t dt'\dot{q}(t')cos\Omega_i(t-t') \end{aligned}$$

Note the cancelation of $\frac{\partial\Delta V}{\partial q}$. Define the spectral density as

$$J(\omega) = \frac{\pi}{2}\sum_i \frac{\lambda_i^2}{M_i\Omega_i}\delta(\omega - \Omega_i)$$

so that

$$m\ddot{q} + \frac{\partial V}{\partial q} + \frac{2}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega}\int^t dt'\dot{q}(t')\cos\omega(t-t') = -\sum_i \lambda_i Q_i^0 \,.$$

To obtain linear dissipation, as in Langevin's equation, we assume an "ohmic" bath $J(\omega) = \gamma\omega$. Using

$$\int_0^\infty d\omega\cos\omega(t-t') = \tfrac{1}{2}\mathrm{Re}\int_{-\infty}^\infty \mathrm{e}^{i\omega(t-t')}d\omega = \pi\delta(t-t')$$

we get

$$m\ddot{q} + \gamma\dot{q} + \frac{\partial V}{\partial q} = -\sum_i \lambda_i Q_i^0$$

We identify now the random force $\xi(t) = -\sum_i \lambda_i Q_i^0(t)$. Free oscillators evolve as

$$Q_i^0(t) = \frac{1}{\Omega_i}\dot{Q}_i^0(0)\sin\Omega_i t + Q_i^0(0)\cos\Omega_i t$$

With random initial conditions we have $\langle Q_i^0(0)\rangle = \langle \dot{Q}_i^0(0)\rangle = 0$ so that $\langle Q_i^0(t)\rangle = 0$.
For a thermal distribution (classical oscillators)

$$\left\langle Q_i^0(t)Q_i^0(0)\right\rangle = \left\langle (Q_i^0(0))^2\right\rangle \cos\Omega_i t = \frac{k_B T}{M_i\Omega_i^2}\cos\Omega_i t$$

$$\Rightarrow \qquad \langle \xi(t)\xi(0)\rangle = k_B T\sum_i \frac{\lambda_i^2}{M_i\Omega_i^2}\cos\Omega_i t = \frac{2}{\pi}k_B T\int_0^\infty d\omega\frac{J(\omega)}{\omega}\cos\omega t\,.$$

With $J(\omega) = \gamma\omega$ we obtain

$$\langle \xi(t)\xi(0)\rangle = 2\gamma k_B T\delta(t) \qquad\qquad (**)$$

i.e. the noise correlation relates to the dissipation γ.
To check FDT, we need to evaluate the response of $\xi(t)$ to a source external to the oscillators $q_{ex}(t)$; this source may or may not be the particle's position $q(t)$. Adding a term $-q_{ex}(t)\xi(t)$ to the Hamiltonian, where $q_{ex}(t) = q_{ex}(\omega)\mathrm{e}^{-i\omega t+\eta t}$, the response is then defined by $\xi(\omega) = \alpha(\omega)q_{ex}(\omega)$. Since $q_{ex}(t)$ affects the equation of motion for $Q_i(t)$ in the same way as $q(t)$ in Eq. (*) above,

$$\begin{aligned}
\xi(t) &= \sum_i\frac{\lambda_i^2}{M_i\Omega_i^2}q_{ex}(t) - \sum_i\frac{\lambda_i^2}{M_i\Omega_i^2}\int_{-\infty}^t dt'\dot{q}_{ex}(t')cos\Omega_i(t-t') \\
&= \frac{2}{\pi}\int_0^\infty d\omega'\frac{J(\omega')}{\omega'}q_{ex}(\omega)\mathrm{e}^{-i\omega t+\eta t} + \frac{2}{\pi}\int_0^\infty d\omega'\frac{J(\omega')}{\omega'}\int_{-\infty}^t dt'\mathrm{e}^{-i\omega t'+\eta t'}\cos[\omega'(t-t')]i\omega q_{ex}(\omega) \\
&= \frac{2}{\pi}\left[\int_0^\infty d\omega'\frac{J(\omega')}{\omega'} - \frac{\omega}{2}\int_0^\infty d\omega'\frac{J(\omega')}{\omega'}(\frac{1}{\omega+\omega'+i\eta}+\frac{1}{\omega-\omega'+i\eta})\right]q_{ex}(\omega)\mathrm{e}^{-i\omega t+\eta t}\,.
\end{aligned}$$

Therefore, for a general bath (not necessarily an ohmic one)

$$\mathrm{Im}\alpha(\omega) = J(\omega)$$

For an Ohmic bath $J(\omega) = \gamma\omega$ with Eq. (**) we recover the classical FDT. This relates the fluctuations of the bath to the response $\alpha(\omega)$ of the bath to an external force.
Note that there is a separate FDT relating the fluctuations of the particle $\langle q(t)q(0)\rangle$ and its response $\alpha_q(\omega)$ to an external force, i.e. adding to the Hamiltonian a term $-q(t)\xi_{ex}(t)$. For $V(q) = 0$ this was checked in a previous section on Langevin's equation. For $V(q) \neq 0$ it is nontrivial to find either the fluctuations or the response, yet FDT is guaranteed.
We proceed to check the quantum FDT, allowing for a general $J(\omega)$. Consider the harmonic oscillator's creation $a_i^\dagger$ and annihilation a_i operators,

$$\hat{Q}_i^0(t) = \sqrt{\frac{\hbar}{2M_i\Omega_i}} e^{i\hat{H}_0 t}\left(a_i + a_i^\dagger\right) e^{-i\hat{H}_0 t} = \sqrt{\frac{\hbar}{2M_i\Omega_i}}\left(\mathrm{e}^{-i\Omega_i t} a_i + \mathrm{e}^{i\Omega_i t} a_i^\dagger\right)$$

where $\hat{H}_0 = \sum_i \Omega_i(a_i^\dagger a_i + \frac{1}{2})$ is the free Hamiltonian for the oscillators. Hence the correlations become

$$\frac{1}{2}\left\langle \hat{Q}_i^0(t)\hat{Q}_i^0(0) + \hat{Q}_i^0(0)\hat{Q}_i^0(t)\right\rangle =$$

$$= \frac{\hbar}{4M_i\Omega_i}\left\langle\left(\mathrm{e}^{-i\Omega_i t} a_i + \mathrm{e}^{i\Omega_i t} a_i^\dagger\right)\left(a_i + a_i^\dagger\right) + \left(a_i + a_i^\dagger\right)\left(e^{-i\Omega_i t} a_i + e^{i\Omega_i t} a_i^\dagger\right)\right\rangle =$$

$$= \frac{\hbar}{2M_i\Omega_i}\left(2n_i + 1\right)\cos\Omega_i t$$

Boson occupation $n_i = \left\langle a_i^\dagger a_i\right\rangle = \frac{1}{e^{\beta\hbar\Omega_i}-1}$, hence

$$K_\xi(t) = \frac{1}{2}\left\langle \xi(t)\xi(0) + \xi(0)\xi(t)\right\rangle =$$

$$= \sum_i \frac{\hbar\lambda_i^2}{2M_i\Omega_i^2}\coth\left(\frac{1}{2}\beta\hbar\Omega_i\right) cos\Omega_i t = \frac{\hbar}{\pi}\int_0^\infty d\omega J(\omega)\coth\left(\frac{1}{2}\beta\hbar\omega\right) cos\omega t$$

Using $J(-\omega) = -J(\omega)$ we identify the Fourier transform

$$\Phi_\xi(\omega) = \hbar J(\omega)\coth\left(\tfrac{1}{2}\beta\hbar\omega\right) .$$

Since the response was found as $\mathrm{Im}\alpha(\omega) = J(\omega)$, we obtain the full quantum FDT

$$\Phi_\xi(\omega) = \hbar\coth(\tfrac{1}{2}\beta\hbar\omega)\mathrm{Im}\alpha(\omega) .$$