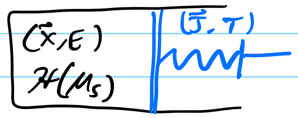
Kardar 4.8

# The Gibbs Canonical Ensemble

Suppose we allow the energy of a system to change by the addition of both heat and work from a reservoir.

Macrostate $M = (T, \vec{J})$

temperature    forces — balanced w/ reservoir




Energy and thermodynamic coordinates are random variables.

Energy of system + reservoir includes

$$\mathcal{H}(\mu_s) - \vec{J} \cdot \vec{x}$$

Energy change of reservoir is opposite the work done on the system.

Probabilities

$$p(\mu_s, \vec{x}) = \frac{\exp\left[-\beta \mathcal{H}(\mu_s) + \beta \vec{J} \cdot \vec{x}\right]}{\mathcal{Z}(T, N, \vec{J})}$$

where

$$\mathcal{Z}(T, N, \vec{J}) = \sum_{\mu_s, \vec{x}} \exp\left[-\beta \mathcal{H}(\mu_s) + \beta \vec{J} \cdot \vec{x}\right]$$

N fixed — no chemical work

$\mathcal{Z}$ = Gibbs partition function.

$$\boxed{\langle \vec{x} \rangle} = \sum_{\mu_s, \vec{x}} \vec{x}\, p(\mu_s, \vec{x})$$

$$\boxed{= k_B T \frac{\partial \ln Z}{\partial \vec{J}}}$$

In terms of the Gibbs Free Energy

$$G(N, T, \vec{J}) = E - TS - \vec{x} \cdot \vec{J},$$

$$dG = -S\,dT - \vec{x} \cdot d\vec{J} + \cancel{\mu\, dN} \quad \text{fixed}$$

$$\vec{x} = -\frac{\partial G}{\partial \vec{J}}$$

Comparing with $\langle \vec{x} \rangle$, we identify

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

Enthalpy

$$H = E - \vec{x} \cdot \vec{J}$$

enthalpy

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

Hamiltonian

Heat Capacities $C_{\vec{J}} = \left.\frac{\partial H}{\partial T}\right|_{\vec{J}}$

Example: Ideal Gas — Isobaric ensemble (fixed pressure)

Macrostate $M = (T, N, P)$

Microstate $\mu = \{\vec{p}_i, \vec{q}_i\}$, volume $V$

random variable

$$p(\{\vec{p}_i, \vec{q}_i\}, V) = \frac{1}{\mathcal{Z}} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta P V\right] \times \begin{cases} 1 & \text{for } \{\vec{q}_i\} \text{ in } V \\ 0 & \text{otherwise.} \end{cases}$$

Gibbs Partition Function:

$$\mathcal{Z}(N,T,P) = \int_0^\infty dV \left( e^{-\beta P V} \int \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3q_i \, d^3p_i}{h^3} \exp\left[-\beta \sum_i \frac{p_i^2}{2m}\right] \right)$$

identical particles

$$= \left( \int_0^\infty V^N e^{-\beta P V} \right) \cdot \frac{1}{N! \, \lambda(T)^{3N}}$$

$$\boxed{\mathcal{Z}(N,T,P) = \frac{1}{(\beta P)^{N+1} \lambda(T)^{3N}}} \overset{N \gg 1}{\approx} \frac{1}{P^N} \left( \frac{2\pi m}{h^2} \right)^{3N/2} (k_B T)^{5N/2}$$

where $\lambda(T) = \dfrac{h}{\sqrt{2\pi m k_B T}}$

Gibbs Free Energy:

$$\boxed{G = -k_B T \ln Z \approx N k_B T \left[\ln P - \frac{5}{2}\ln(k_B T) + \frac{3}{2}\ln\left(\frac{h^2}{2\pi m}\right)\right]}$$

$$dG = -S\,dT + V\,dP + \mu\,dN$$

volume $\quad V = \left.\frac{\partial G}{\partial P}\right|_{T,N} = \frac{N k_B T}{P}$

$$\Rightarrow \boxed{PV = N k_B T}$$

Enthalpy:

$$H = \langle E + PV \rangle = -\left.\frac{\partial \ln Z}{\partial \beta}\right|_{P,N} = \frac{5}{2} N k_B T$$

Specific heat at constant pressure:

$$\boxed{C_P = \frac{dH}{dT} = \frac{5}{2} N k_B}$$

Chemical potential:

$$\boxed{\mu = \left.\frac{\partial G}{\partial N}\right|_{P,T} = k_B T \ln\left(\frac{P \lambda(T)^3}{k_B T}\right)}$$

Example: Spins in an external magnetic field

Work done against the magnetic field: $-\vec{B}\cdot\vec{M}$

magnetic field

magnetization

Macrostate $M = (N, T, \vec{M})$

Microstate $\mu = \{\text{spins about } \hat{B}: \ \sigma_i = \pm 1\}$

Magnetization along $\hat{B}$: $M = \mu_0 \sum_{i=1}^{N} \sigma_i$

microscopic magnetic moment.

$$Z(N,T,\vec{B}) = \sum_{\{\sigma_i = \pm 1\}} \exp\left(\beta \vec{B}\cdot\vec{M}\right)$$

$$= \sum_{\{\sigma_i = \pm 1\}} \exp\left(\beta B \mu_0 \sum_{i=1}^{N} \sigma_i\right)$$

$$\boxed{Z = \left(2\cosh\left(\beta \mu_0 B\right)\right)^N}$$

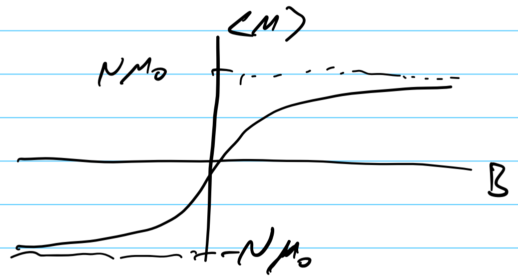
probability $p(\{\sigma_i\}) = \dfrac{\exp\left[\beta B \mu_0 \sum_{i=1}^{N} \sigma_i\right]}{Z}$

Gibbs Free Energy:

$$G = -k_B T \ln Z = -N k_B T \ln\left[2\cosh(\beta B \mu_0)\right]$$

Magnetization: $dG = -S\,dT - M\,dB + \mu\,dN$

$$\langle M \rangle = -\left.\frac{\partial G}{\partial B}\right|_{T,N} = N\mu_0 \tanh(\beta \mu_0 B)$$




Magnetic Susceptibility:

$$\chi(T) = \left.\frac{\partial M}{\partial B}\right|_{\substack{T,N \\ B=0}} = N\beta\mu_0^2 \left(\operatorname{sech}(\beta\mu_0 B)\right)^2\Big|_{B=0}$$

$$\Rightarrow \boxed{\chi(T) = \frac{N\mu_0^2}{k_B T}}$$ Curie's Law

Enthalpy $H = \langle \mathcal{H} - BM \rangle = -BM$

Heat capacity at const. B:

$$C_B = \frac{dH}{dT} = -B \frac{\partial M}{\partial T}$$

$$= \frac{N\mu_0^2 B}{k_B T^2} \left(\operatorname{sech}(\beta \mu_0 B)\right)^2$$

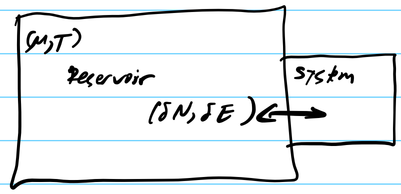
# Grand Canonical Ensemble

If we allow chemical work instead of mechanical work, and heat transfer from the reservoir, then:

Macrostate $M = (T, \mu, \vec{x})$

← chemical potential

Number of particles $N$ is a random variable




Prob of system microstate $\mu_s$:

$$p(\mu_s) = \frac{\exp\left[\beta \mu N(\mu_s) - \beta \mathcal{H}(\mu_s)\right]}{\mathcal{Q}(T, \mu, \vec{x})}$$

Grand Partition Function $\mathcal{Q}(T,\mu,\vec{x}) = \sum_{\mu_s} \exp\left[\beta \mu N(\mu_s) - \beta \mathcal{H}(\mu_s)\right]$

$$= \sum_{N=0}^{\infty} \left( e^{\beta \mu N} \sum_{\mu_s | N} e^{-\beta \mathcal{H}_N(\mu_s)} \right)$$

↑ sum over $N$. ← sum over microstates w/ fixed $N$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T, N, \vec{x})$$

prob. $p(N) = \dfrac{e^{\beta \mu N} Z(T, N, \vec{x})}{\mathcal{Q}(T, \mu, \vec{x})}$

Average number of particles:

$$\boxed{\langle N \rangle} = \sum N\, p(N)$$

$$= \frac{1}{Q}\frac{\partial}{\partial(\beta\mu)} Q \boxed{= \frac{\partial}{\partial(\beta\mu)} \ln Q}$$

Number fluctuations:

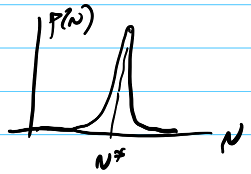
$$\langle N^2 \rangle_c = \langle N^2 \rangle - \langle N \rangle^2$$

$$= \frac{1}{Q}\frac{\partial^2}{\partial(\beta\mu)^2} Q - \left(\frac{\partial}{\partial(\beta\mu)} \ln Q\right)^2$$

$$= \frac{\partial^2}{\partial(\beta\mu)^2} \ln Q$$

$$= \frac{\partial \langle N \rangle}{\partial(\beta\mu)} \propto N$$

$$\frac{\sqrt{\langle N^2 \rangle_c}}{\langle N \rangle_c} \to 0 \text{ as } N \to \infty$$




$$N = N^* \approx \langle N \rangle$$

Then,

$$Q(T,\mu,\vec{x}) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,N,\vec{x})$$

$$\approx e^{\beta\mu N^*} Z(T,N^*,\vec{x})$$

$$= e^{\beta\mu N^* - \beta F} = e^{-\beta(-\mu N^* + E - TS)}$$

$$= e^{-\beta \mathcal{G}}$$

Grand potential

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

$$d\mathcal{G} = -S\,dT + \vec{J}\cdot d\vec{x} - N\,d\mu$$

$$\Rightarrow \quad S = -\frac{\partial \mathcal{G}}{\partial T}\bigg|_{\vec{x},\mu}, \quad N = -\frac{\partial \mathcal{G}}{\partial \mu}\bigg|_{\vec{x},T}, \quad J_i = \frac{\partial \mathcal{G}}{\partial x_i}\bigg|_{\mu,T,x_{j\neq i}}$$

Example: <u>Ideal Gas</u>

Macrostate $M = (T,\mu,V)$

Microstate $\mu = \{\vec{p}_i, \vec{q}_i\}$, with indefinite particle number

$$\mathcal{Q}(T,\mu,V) = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3p_i\, d^3q_i}{h^3} \exp\left[-\beta \frac{p_i^2}{2m}\right]$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} \cdot \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N, \quad \text{with } \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$= \exp\left[e^{\beta\mu}\frac{V}{\lambda^3}\right]$$

$$\mathcal{G}(T,\mu,V) = -k_B T \ln \mathcal{Q} = -k_B T\, e^{\beta\mu}\frac{V}{\lambda^3}$$

$$\mathcal{G} = E - TS - \mu N = -PV$$

$$\Rightarrow \boxed{P = -\frac{\mathcal{G}}{V} = k_B T \frac{e^{\beta\mu}}{\lambda^3}}$$

$\boxed{PV = N k_B T}$

Particle Number:

$$\boxed{N = -\frac{\partial \mathcal{G}}{\partial \mu}\bigg|_{T,V} = e^{\beta\mu}\frac{V}{\lambda^3}}$$

solve for $\mu$

Chemical potential

$$\boxed{\mu = k_B T \ln\left(\lambda^3 \frac{N}{V}\right) = k_B T \ln\left(\frac{P\lambda^3}{k_B T}\right)}$$