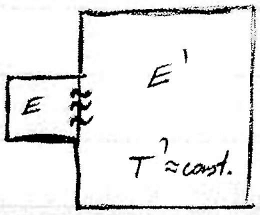
# Canonical ensemble

system in contact with heatbath at temperature $T$




$E$: energy of system of interest
$E'$: energy of heatbath
composite system: $E^{(0)}$

$\mathcal{H}(p,q) = E$ $\qquad \boxed{E + E' = E^{(0)} = \text{const.}}$ $\qquad E \ll E' \lesssim E^{(0)}$

system of interest (not conserved: in touch with heat bath)

system and heatbath are quasi independent.
$s = (p,q)$ etc

$$\rho(p,q) = \frac{\Omega'(E')}{\Omega^{(0)}(E^{(0)})}$$

probability of being in a particular state with $(p,q)$ ($\Rightarrow$ energy $E = E^{(0)} - E'$)

$$\ln \rho = \text{const.} + \ln \Omega'(E^{(0)} - E) = \qquad \text{expand about } E' \lesssim E^{(0)}$$

$$= \text{const.}' - \left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E' \simeq E^{(0)}} E + \ldots = \text{const.} - \frac{E}{kT'}$$

$T'$: temperature of heat bath

we showed that in thermal equilibrium, $T = T'$ (system and heatbath)

$$\rho(p,q) = \frac{1}{Z} e^{-\frac{E}{kT}} = \frac{1}{Z} \underbrace{e^{-\beta \mathcal{H}(p,q)}}_{\text{"Boltzmann" factor}} \qquad \beta = \frac{1}{kT}$$

elaborate microcan

$$\langle f(p,q)\rangle = \int \frac{dp^{3N}dq^{3N}}{N!\,h^{3N}}\,\rho(p,q)\,f(p,q)$$

$$\int \frac{dp^{3N}dq^{3N}}{N!\,h^{3N}}\,\rho(p,q) = 1$$

normalization

$$\boxed{Z = \int \frac{dp^{3N}dq^{3N}}{N!\,h^{3N}}\, e^{-\beta \mathcal{H}(p,q)}}$$

partition function (normalization factor for $\rho$ as well)

one can characterize systems with general "quantum" numbers $s$

$$\rho_s = \frac{e^{-\beta E_s}}{Z} \qquad Z = \sum_s e^{-\beta E_s}$$

discrete

use this def: $\boxed{d\Gamma \equiv \frac{dp^{3N}dq^{3N}}{N!\,h^{3N}}}$ $\boxed{Z = \int d\Gamma\, e^{-\beta\mathcal{H}(p,q)}}$ $\int \rho(p,q)\,d\Gamma = 1$

generating function normalize!

(extensive variable)

$$\langle E\rangle = \langle \mathcal{H}(p,q)\rangle = \int d\Gamma\,\rho(p,q)\,\mathcal{H}(p,q) = \int d\Gamma\,\mathcal{H}(p,q)\frac{e^{-\beta\mathcal{H}(p,q)}}{Z} =$$

$$\frac{1}{Z}\int d\Gamma\,\mathcal{H}(p,q)\,e^{-\beta\mathcal{H}(p,q)} = -\frac{\partial}{\partial\beta}\ln Z \quad \sim O(N) \quad \text{(extensive)}$$

$$-\frac{\partial\langle E\rangle}{\partial\beta} = \left[\frac{\int d\Gamma\,\mathcal{H}^2 e^{-\beta\mathcal{H}}}{Z} - \frac{\left(\int d\Gamma\,\mathcal{H}e^{-\beta\mathcal{H}}\right)^2}{Z^2}\right] = \langle E^2\rangle - \langle E\rangle^2 \quad \sim O(N)$$

extensive

$\frac{\partial\,\text{ext}}{\partial\,\text{int}}$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial\langle E\rangle}{\partial\beta}\right)_V\frac{d\beta}{dT} = -\frac{1}{kT^2}\left(\frac{\partial\langle E\rangle}{\partial\beta}\right)_V$$

$\ln Z \sim$ cumulant generating function

$$C_V = \frac{1}{kT^2}\left(\langle E^2\rangle - \langle E\rangle^2\right)$$

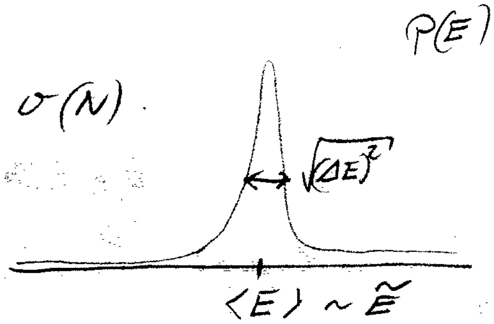
$$\Delta E = E - \langle E\rangle \qquad \boxed{\langle E^2\rangle - \langle E\rangle^2 = kT^2 C_V}$$

(linear response) fluct.-dissip relations

$\langle E \rangle \sim \mathcal{O}(N)$

$\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \sim \mathcal{O}(N)$.

$\dfrac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} \sim \dfrac{1}{\sqrt{N}}$



## The distribution of the energy

$$\rho(p,q) = \frac{e^{-\beta \mathcal{H}(p,q)}}{Z} \qquad Z = \int d\Gamma\, e^{-\beta \mathcal{H}(p,q)}$$

N-particle density of states

$$\rho(p,q)\, d\Gamma = P(E)\, dE \quad \Rightarrow \quad P(E) = \rho(p,q)\frac{d\Gamma}{dE} = \rho(\mathcal{H}(p,q))\, g(E)$$

$$P(E) = \frac{e^{-\beta E}}{Z} g(E)$$

probability density that the macroscopic system has energy between $E$ and $E+dE$

$$P(E) = \frac{1}{Z} e^{\ln(g(E)) - \beta E} = \frac{1}{Z} e^{f(E)}$$

$$f(E) \equiv \ln(g(E)) - \beta E$$

expand about $\tilde{E}$, which maximizes $f$

$$f(E) \simeq f(\tilde{E}) + \frac{1}{2}\frac{\partial^2 f(E)}{\partial E^2}\Big|_{\tilde{E}} (E-\tilde{E})^2 + \dots$$

$$\frac{\partial f(E)}{\partial E}\Big|_{\tilde{E}} = 0$$

$$\frac{\partial \ln(g(E))}{\partial E}\Big|_{\tilde{E}} - \beta = 0$$

$$\Downarrow$$

$$\tilde{E}(\beta) \leftrightarrow \beta(\tilde{E})$$

"equilibrium" energy $\tilde{E}$ for a given $\beta$

$$\frac{\partial^2 f}{\partial E^2}\Big|_{\tilde{E}} = \frac{\partial^2 \ln(g(E))}{\partial E^2}\Big|_{\tilde{E}} = \frac{\partial \beta(\tilde{E})}{\partial \tilde{E}}$$

$$= \frac{\partial}{\partial \tilde{E}}\left(\frac{1}{kT}\right) = -\frac{1}{kT^2}\frac{\partial T}{\partial \tilde{E}} = -\frac{1}{kT^2 C_V}$$

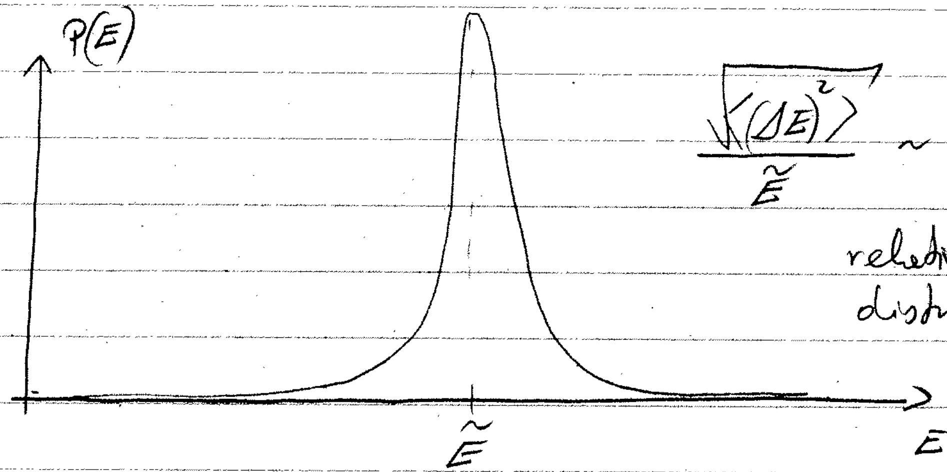
$$P(E) \simeq \frac{e^{\ln(g(\tilde{E})) - \beta \tilde{E}}}{Z}\, e^{-\frac{(E-\tilde{E})^2}{2kT^2 C_V}}$$

$$= \text{Const.}\; e^{-\frac{(E-\tilde{E})^2}{2kT^2 C_V}}$$

Gaussian energy fluctuations

$$\tilde{E} \simeq \langle E \rangle \sim N \quad (\text{extensive quantity})$$

variance $\langle (\Delta E)^2 \rangle = \langle (E - \tilde{E})^2 \rangle = kT^2 C_V \sim N$ also extensive as discussed earlier




$$\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\tilde{E}} \sim \frac{1}{\sqrt{N}}$$

relatively sharp distribution

In the $N \to \infty$ limit, $P(E)$ asymptotically becomes Gaussian

# Connection with thermodynamics

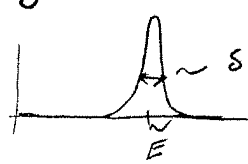
$$P(E) = \frac{g(E)\, e^{-\beta E}}{Z} \qquad g(E) \quad \text{N-particle density of states}$$

$$\int P(E)\, dE = 1 \qquad \boxed{Z = \int g(E)\, e^{-\beta E}\, dE}$$

for macroscopic systems $E$ is sharply distributed about $\tilde{E}$

"Rough" derivation:

$$Z \approx g(\tilde{E})\, e^{-\beta \tilde{E}}\, \delta E$$




$$\ln Z \approx \ln g(\tilde{E}) - \beta \tilde{E} + \ln \delta E \qquad |\ln \delta E| \sim o(\ln \sqrt{N})$$

$$-kT \ln Z \approx -kT \ln g(\tilde{E}) + \tilde{E} \approx E - T \cdot k \ln g(E)$$

$N \to \infty \qquad E \approx \langle E \rangle \approx \tilde{E}$

this is the reason why thermodynamics works!

$$\boxed{F \equiv -kT \ln Z}$$ Helmholtz free energy

$$\boxed{S = k \ln g(E)}$$ entropy (as we had)

$$\boxed{F = E - TS}$$

$$E = E(S, V, N)$$

$$dE = T dS - P dV + \mu dN$$

$$\Rightarrow \quad F = F(T, V, N) \qquad dF = -S dT - P dV + \mu dN$$

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

More "rigorous" derivation: (essentially the same approx. used for $P(E)$ – "saddle point method")

$$Z = \int d\Gamma\, e^{-\beta \mathcal{H}(p,q)} = \int \frac{d\Gamma}{dE}\, dE\, e^{-\beta E} = \int dE\, g(E)\, e^{-\beta E}$$

$$= \int dE\, e^{\ln(g(E)) - \beta E} \simeq \int_{-\infty}^{+\infty} dE\, e^{\ln g(\tilde{E}) - \beta\tilde{E} - \frac{(E-\tilde{E})^2}{2kT^2 C_V}}$$

$$= e^{\ln g(\tilde{E}) - \beta\tilde{E}} \int_{-\infty}^{+\infty} dE\, e^{\frac{-(E-\tilde{E})^2}{2kT^2 C_V}} = e^{\ln g(\tilde{E}) - \beta\tilde{E}} \sqrt{2\pi k T^2 C_V}$$

$$-kT \ln Z \simeq -kT\left(\ln g(\tilde{E}) - \frac{1}{kT}\tilde{E}\right) - kT \ln\sqrt{2\pi k T^2 C_V}$$

$\tilde{E}$ is the equilibrium energy, extensive $\sim N$

$k \ln g(\tilde{E})$ is the entropy $S$, extensive $\sim N$

$C_V$ is the spec. heat, extensive $\sim N$

thus $\ln C_V \sim \ln N$ can be dropped in the $N \to \infty$ limit compared to $N$

$$\underbrace{-kT \ln Z}_{\text{Helmholtz free energy}} \simeq \tilde{E} - T \underbrace{k \ln g(\tilde{E})}_{S \text{ entropy}}$$

$$F = E - TS$$

where used $E = \tilde{E}$ thermodyn. notation

Example:

Ideal Gas $\quad \mathcal{H}(p,q) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \quad$ 3-dim, N particles

$$Z_N = \int d\Gamma \, e^{-\beta \mathcal{H}(p,q)} = \int \frac{dp^{3N} dq^{3N}}{h^{3N} N!} e^{-\beta \sum_{i=1}^{3N} p_i^2/2m} = \frac{1}{N!} Z_1^N$$

where $\quad Z_1 = \int \frac{dp^3 dq^3}{h^3} e^{-\beta \frac{p_x^2+p_y^2+p_z^2}{2m}} = \frac{V}{h^3} \left[ \int_{-\infty}^{+\infty} dp_x \, e^{-\frac{p_x^2}{2mkT}} \right]^3$

$$= \frac{V}{h^3} \left( \sqrt{2m\pi kT} \right)^3 = \frac{V}{h^3} (2m\pi kT)^{3/2} = \frac{V}{\lambda^3}$$

$$Z_N = \frac{Z_1^N}{N!} = \frac{V^N}{h^{3N} N!} (2m\pi kT)^{\frac{3N}{2}} = \boxed{\frac{V^N}{N!} \left( \frac{2m\pi kT}{h^2} \right)^{\frac{3N}{2}}}$$

partition function of the ideal gas in the canonical ensemble

$\left[ \text{remember } \lambda = \sqrt{\frac{h^2}{2\pi m kT}} \right]$

Thermodynamics of the ideal gas from the canonical ensemble:

$$F(T,V,N) = -kT \ln Z_N = -NkT \ln\left(V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) + kT \ln N!$$

$$\approx NkT \ln\left[\frac{1}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right] + kT\left(N\ln N - N\right) =$$

$$= NkT\left[\ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right) - 1\right]$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = kT \ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right] = \boxed{kT \ln\left(\frac{\lambda^3}{V/N}\right)}$$

$$\lambda = \sqrt{\frac{h^2}{2\pi mkT}}$$ thermal wavelength

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V} \Rightarrow \boxed{PV = NkT}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -Nk\left[\ln \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} - 1\right] + \frac{3}{2}Nk =$$

$$= Nk\left[\ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

$$F = E - TS \Rightarrow$$

$$E = F + TS = \frac{3}{2}NkT$$

$$kT = \frac{2E}{3N}$$

$$\boxed{S(E,V,N) = Nk\ln\left(\frac{V}{N}\right) + \frac{3}{2}Nk\ln\left(\frac{E}{N}\right) + \frac{5}{2}Nk + \frac{3}{2}Nk\ln\left(\frac{4m\pi}{3h^2}\right)}$$