Canonical Ensemble II

microcanonical ensemble:

every microstate r has the same energy: $E_r = U$

canonical ensemble:

microstate i can have any energy E_r

but average over ensemble is U: $\langle E_r \rangle = U$

How large are fluctuations around the average?

mean-square deviation in energy

$$\sigma_E^2 = \langle (H-U)^2 \rangle = \langle H^2 \rangle - 2U\langle H \rangle + U^2$$

$$= \langle H^2 \rangle - 2U \cdot U + U^2 = \langle H^2 \rangle - U^2$$

average energy: $U = \langle H \rangle$

$$= \frac{1}{Z}\sum_r E_r e^{-\beta E_i} \qquad Z = \sum_r e^{-\beta E_r}$$

differentiate U with respect to β:

$$\frac{\partial U}{\partial \beta} = \frac{1}{Z}\sum E_r e^{-\beta E_r}(-E_r) - \frac{1}{Z^2}\left(\sum_r e^{-\beta E_r}(-E_r)\right)\sum_r E_r e^{-\beta E_r}$$

$$= -\frac{1}{Z}\sum_i E_r^2 e^{-\beta E_r} + \left(\frac{1}{Z}\sum_r E_r e^{-\beta E_r}\right)^2$$

$$= -\langle H^2 \rangle + \langle H \rangle^2 = -\langle H^2 \rangle + U^2$$

standard deviation in energy: σ_E

$$\sigma_E^2 = -\frac{\partial U}{\partial \beta} = +T^2 \frac{\partial U}{\partial T}$$

U is extensive variable: scales like N^1

T intensive " N^0

$\Longrightarrow$ σ_E scales as $N^{1/2}$

relative fluctuation: $\frac{\sigma_E}{U} \sim \frac{1}{\sqrt{N}}$

partition function: $Z = \sum_r e^{-\beta E_r}$ for specified V, N.

$$\Longrightarrow \sigma_E^2 = T^2 \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

thermodynamic relation: $dU = \underbrace{TdS}_{\text{heat flow}} - PdV + \mu dN$

heat capacity at fixed X: $C_X = T\left(\frac{\partial S}{\partial T}\right)_X$

special case: $X = V,N$ $\quad C_V \equiv T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N}$

$$\Longrightarrow \boxed{\sigma_E^2 = T^2 C_V}$$

Partition function: $Z = \sum_r e^{-\beta E_r}$

$\uparrow$ sum over microstates

degeneracy of energy eigenvalues:

$g(E)$ = # of microstates with energy E

express Z as sum over distinct energies

$$Z = \sum_E \left(\sum_{r:E_r=E} e^{-\beta E_r} \right)$$

$$= \sum_E e^{-\beta E} \underbrace{\sum_{r:E_r=E} 1}_{g(E)} = \sum_E g(E)\, e^{-\beta E}$$

If energy eigenvalues are continuous, $Z = \int_{-\infty}^{\infty} dE\, g(E)\, e^{-\beta E}$

density of states: $g(E)\,dE$

Single atom in volume V at temperature $T = 1/\beta$

$$Z_1 = \frac{1}{(2\pi\hbar)^3} \int d^3p \int d^3r\, e^{-\beta p^2/2m}$$

$$\int d^3r = V, \quad \int d^3p = 4\pi \int_0^\infty p^2 dp = 2\pi \int_0^\infty (p^2)^{1/2} dp^2$$
$$= 2\pi \int_0^\infty (2mE)^{1/2} d(2mE) = 2\pi (2m)^{3/2} \int_0^\infty E^{1/2} dE$$

$$Z_1 = 2\pi \left(\frac{m}{2\pi^2\hbar^2} \right)^{3/2} V \int_0^\infty \sqrt{E}\, dE \implies g(E)\,dE = 2\pi \left(\frac{m}{2\pi^2\hbar^2} \right)^{3/2} \sqrt{E}\, dE$$

If energy eigenvalue are continuous,

$$Z(\beta) = \int_{-\infty}^{\infty} dE \, g(E) \, e^{-\beta E}$$

density of states : $g(E)dE$

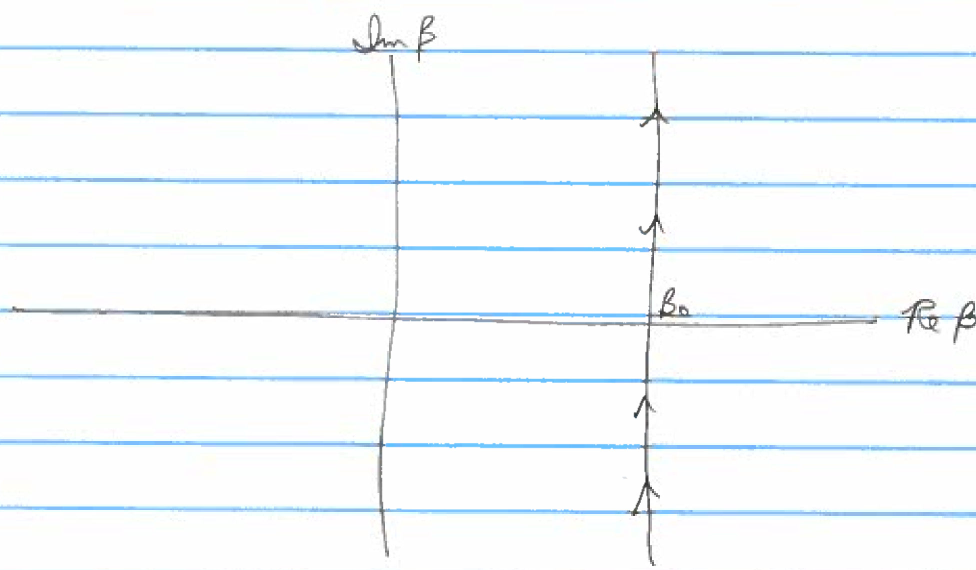
$Z(\beta)$ is Laplace transform of $g(E)$

If partition function $Z(\beta)$ is known as function of β, density of state $g(E)$ can be determined

by inverse Laplace transform

$$g(E) = \frac{1}{2\pi i} \int_{\beta_0 - i\infty}^{\beta_0 + i\infty} d\beta \; Z(\beta) \, e^{+\beta E}$$

where the integration contour in the complex β plane runs along a vertical line to the right of all singularities of $Z(\beta)$

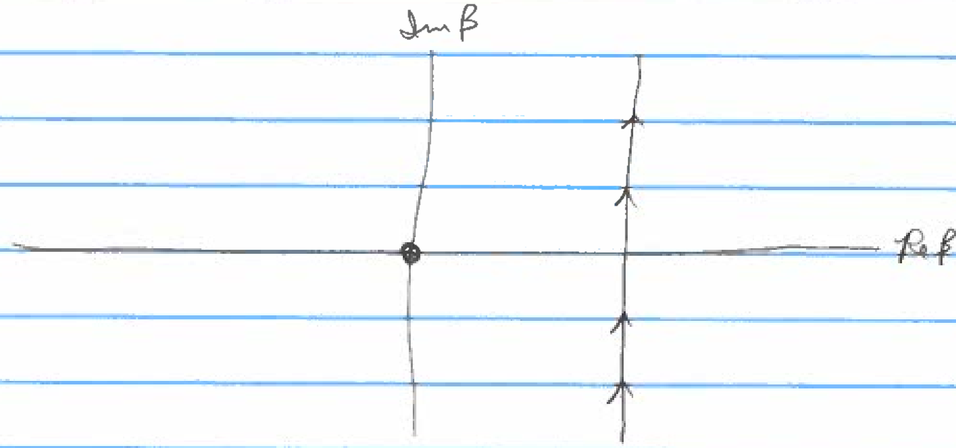


Example: classical monatomic ideal gas

$$Z(\beta) = \frac{1}{N!}\left[V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2}\right]^N$$

has singularity at $\beta = 0$: pole of degree $\frac{3}{2}N$

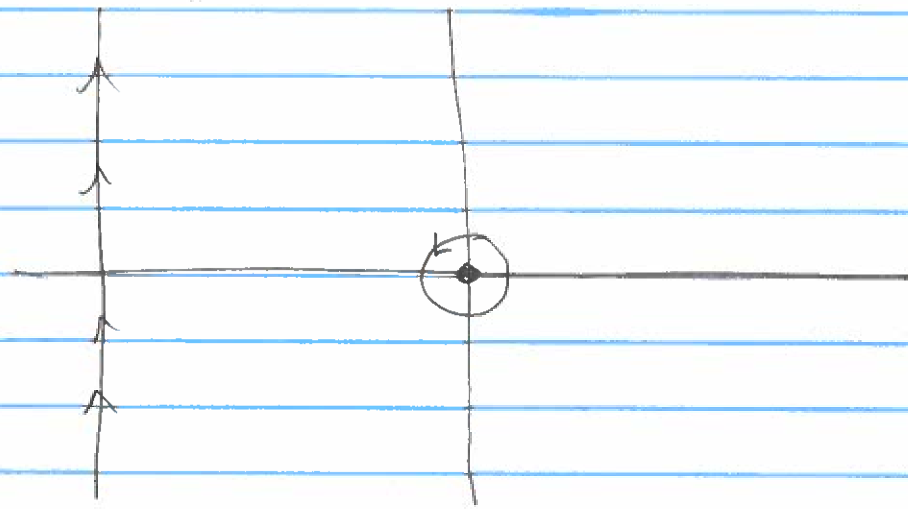
density of states: $g(E) = \frac{1}{2\pi i}\int_{\beta_0 - i\infty}^{\beta_0 + i\infty} d\beta\, Z(\beta) e^{+\beta E}$



If $E<0$, $e^{\beta E}$ decreases to 0 as $\mathrm{Re}\,\beta \to +\infty$
move contour to the right towards $\mathrm{Re}\,\beta = +\infty$
integrand decrease to 0

$$g(E) = 0 \qquad E<0$$

If $E>0$, $e^{\beta E}$ decreases to 0 as $\mathrm{Re}\,\beta \to -\infty$
moving contour to the left toward $\mathrm{Re}\,\beta \to -\infty$
leaves a contour wrapped around singularity at $\beta = 0$



integrand along the vertical contour decreases to 0

$\Longrightarrow$ integral $\to 0$

density of state reduces to contour integral around $\beta = 0$

$$g(E) = \frac{1}{2\pi i} \oint d\beta \; Z(\beta)\, e^{+\beta E}$$

$$= \frac{1}{N!}\left[V\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\right]^N \frac{1}{2\pi i}\oint d\beta \, \frac{1}{\beta^{\frac{3}{2}N}}\, e^{+\beta E}$$

expand $e^{\beta E}$ as power series

$$e^{\beta E} = \sum_{n=0}^{\infty} \frac{1}{n!}(\beta E)^n$$

contour integral formula: $\frac{1}{2\pi i}\oint d\beta\, \beta^p = 1$ if $p = -1$

$= 0$ if p any other integer

$$g(E) = \frac{1}{N!}\left[V\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\right]^N \frac{1}{(\frac{3}{2}N-1)!}\, E^{3/2-1}$$

$$\simeq \frac{1}{N!\,(\frac{3}{2}N)!}\left[V\left(\frac{mE}{2\pi\hbar^2}\right)^{3/2}\right]^N \frac{dE}{E}$$