

Back to the canonical ensemble

Lemma 3

$$\frac{\partial^2}{\partial \beta^2} \Psi = - \{ \overset{\text{expectation}}{\langle E_i^2 \rangle} - \langle E_i \rangle^2 \}$$

variance of fluctuating energies E_i of microstates described by 2nd derivative

Proof

$$\Psi(\beta) = -\log \sum_i e^{-\beta E_i}$$

$$\frac{\partial}{\partial \beta} \Psi(\beta) = U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$\frac{\partial^2}{\partial \beta^2} \Psi(\beta) = \frac{-\sum_i E_i^2 e^{-\beta E_i} \cdot \sum_i e^{-\beta E_i} + (\sum_i E_i e^{-\beta E_i})^2}{(\sum_i e^{-\beta E_i})^2} \quad (\text{Lemma 1})$$

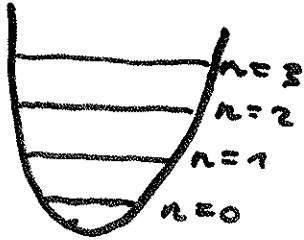
$$= -\sum_i E_i^2 p_i + \sum_i p_i E_i \sum_i p_i E_i$$

$$= -(\langle E_i^2 \rangle - \langle E_i \rangle^2)$$

of course $\langle E_i \rangle = U$ and $p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$

Various example systems

Quantum mechanical harmonic oscillator



in contact with
a heat bath

$$kT = \frac{2}{\beta}$$

$$E_n = \frac{1}{2} \hbar \omega + n \hbar \omega = (n + \frac{1}{2}) \hbar \omega$$

$$\hbar = \frac{h}{2\pi} \leftarrow \text{Planck's constant}$$

$$\omega = 2\pi \nu \leftarrow \text{frequency}$$

$$Z(\beta) = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta (\frac{1}{2} \hbar \omega + n \hbar \omega)}$$

$$= e^{-\frac{1}{2} \beta \hbar \omega} \sum_{n=0}^{\infty} \underbrace{e^{-\beta \hbar \omega \cdot n}}_1$$

$$\sum_{n=0}^{\infty} \lambda^n = \frac{1}{1-\lambda}$$

$$= e^{-\frac{1}{2} \beta \hbar \omega} \frac{1}{1 - e^{-\beta \hbar \omega}}$$

$\Rightarrow$ free energy

$$F(\beta) = -\frac{1}{\beta} \log Z(\beta)$$

$$-34- \quad = \frac{1}{2} k\omega + \frac{1}{\beta} \log(1 - e^{-\beta k\omega})$$

$$\Psi(\beta) = \beta F(\beta) = \frac{1}{2} k\omega \beta + \log(1 - e^{-\beta k\omega})$$

Mean energy

$$U = \frac{\partial}{\partial \beta} \Psi = \frac{1}{2} k\omega + \frac{k\omega e^{-\beta k\omega}}{1 - e^{-\beta k\omega}}$$

$$= \frac{1}{2} k\omega + \frac{k\omega}{e^{\beta k\omega} - 1}$$

↑
Zero-point
energy

↑
Bose-Einstein
statistics

$$\Psi = \beta U - S$$

$$\Rightarrow S = -\Psi + \beta U$$

$$= -\log(1 - e^{-\beta k\omega}) + \frac{\beta k\omega}{e^{\beta k\omega} - 1}$$

Small temperatures

$$kT \ll k\omega \Leftrightarrow \frac{1}{\beta} \ll k\omega$$

$$k\omega/\beta \gg 1$$

System dominated by ground state
energy $E_0 = \frac{1}{2} k\omega$

(Zero-point energy)

Large temperatures

-35-

$$k\omega\beta \ll 1$$

$$e^{\beta k\omega} = 1 + \beta k\omega + \frac{1}{2}\beta^2 k^2 \omega^2 + \dots$$

$$\Rightarrow \frac{k\omega}{e^{\beta k\omega} - 1} = \frac{\cancel{k\omega}}{\beta \cancel{k\omega} (1 + \frac{1}{2}\beta k\omega) + \dots}$$

$$= \frac{1}{\beta} (1 - \frac{1}{2}\beta k\omega) + \dots$$

$$= \frac{1}{\beta} - \frac{1}{2}k\omega$$

$$\Rightarrow U = \frac{1}{2}k\omega + \frac{1}{\beta} - \frac{1}{2}k\omega + \dots$$

$$= \frac{1}{\beta} + \dots = kT + \dots$$

System dominated by thermal energy

Energy fluctuations:

Remember

$$\frac{\partial \psi}{\partial \beta} = U$$

$$\frac{\partial^2 \psi}{\partial \beta^2} = - \overset{\text{expectation}}{\downarrow} (\langle E^2 \rangle - \langle E \rangle^2)$$

$$U = \langle E \rangle$$

Generally variance of a RV

$$\langle (E - \langle E \rangle)^2 \rangle$$

$$= \langle (E^2 - 2E\langle E \rangle + \langle E \rangle^2) \rangle$$

$$= \langle E^2 \rangle - 2\langle E \rangle^2 + \langle E \rangle^2$$

$$= \langle E^2 \rangle - \langle E \rangle^2$$

Then

$$\frac{\partial^2}{\partial \beta^2} \psi = \frac{\partial}{\partial \beta} U = - \underbrace{\frac{(k\omega)^2}{(e^{\beta k\omega} - 1)^2}}_{\langle E^2 \rangle - \langle E \rangle^2}$$

Ideal gas

Consider N particles in 3d space.

Positions $\vec{x}_1, \dots, \vec{x}_N$
momenta $\vec{p}_1, \dots, \vec{p}_N$ } make up a $6N$ -dim space 'phase space'

Energy of such a given microstate is given by Hamiltonian function

$$H(\vec{x}_1, \dots, \vec{x}_N, \vec{p}_1, \dots, \vec{p}_N) = H(\vec{x}, \vec{p})$$

Ideal gas: Only the kinetic energy $E = \frac{1}{2} m \vec{v}^2 = \frac{\vec{p}^2}{2m}$

of each particle contributes to the -37-
Hamiltonian:

$$H = \frac{1}{2m} \sum_{j=1}^N \vec{p}_j^2$$

Canonical distribution

$$w(\vec{x}_1, \dots, \vec{x}_N; \vec{p}_1, \dots, \vec{p}_N)$$

$$= \frac{1}{Z(\beta)} e^{-\beta H(\vec{x}_1, \dots, \vec{x}_N; \vec{p}_1, \dots, \vec{p}_N)}$$

symbol w used since p denotes momentum already

Partition function

$$Z(\beta, V) = \frac{1}{h^{3N}} \int d\vec{x}_1 \dots d\vec{x}_N \int_{-\infty}^{\infty} d\vec{p}_1 \dots d\vec{p}_N e^{-\beta H(\vec{x}, \vec{p})}$$

$V \leftarrow$ volume of container

h : Planck's constant

(makes partition function dimensionless,
since h has the dimension of an
action (position $\cdot$ momentum))

Remember

$$\Delta x \Delta p \gtrsim \frac{h}{2}$$

uncertainty relation

To do stat. mech., evaluate free energy

$$F = -\frac{1}{\beta} \log Z(\beta)$$

$$F = F(\beta, V) \quad \text{in this case}$$

$$\Rightarrow Z(\beta, V)$$

$$= \frac{1}{h^{3N}} \cdot V^N \int_{-\infty}^{\infty} d\vec{p}_1 \dots d\vec{p}_N e^{-\frac{\beta}{2m} \sum_{j=1}^N \vec{p}_j^2}$$

$$\vec{p}_j = \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix}$$

$$\Rightarrow \vec{p}_j^2 = p_x^2 + p_y^2 + p_z^2$$

for each particle

$$\Rightarrow Z(\beta, V) = \frac{1}{h^{3N}} V^N \underbrace{\left(\int_{-\infty}^{\infty} dy e^{-\mu y^2} \right)^{3N}}_{\leftarrow \sqrt{\frac{\pi}{\mu}}}$$

y : 1-d integration variable

$$\mu = \frac{\beta}{2m}$$

$$= \frac{1}{h^{3N}} V^N \left(\sqrt{\frac{\pi}{\mu}} \right)^{3N}$$

$$= \frac{1}{h^{3N}} V^N \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

$$F(\beta, V) = -\frac{1}{\beta} \log Z(\beta, V) \quad -39-$$

$$= -\frac{1}{\beta} N \cdot \log \left\{ \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}} \right\}$$

$$\Psi = \beta F = -N \log \left\{ \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}} \right\}$$

$$U = \frac{\partial \Psi}{\partial \beta} = -N \frac{-\frac{3}{2} \beta^{-\frac{5}{2}} \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}}}{\frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}}}$$

$$= \frac{3}{2} N \beta^{-1} = \frac{3}{2} N K T$$

(indep. of V)

Define pressure as

$$p = - \frac{\partial F}{\partial V}$$

(Gibbs fundamental eq.

$$dF = -SdT - p dV,$$

$$\Rightarrow p = \frac{N}{\beta} \frac{1}{V}$$

$$\Rightarrow pV = NKT$$

eq. of state of ideal gas