

9/15

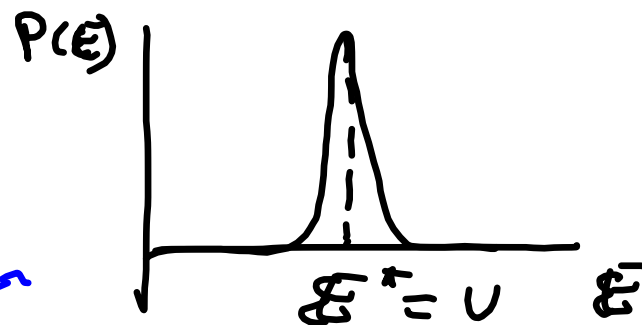
Last time:

We found that

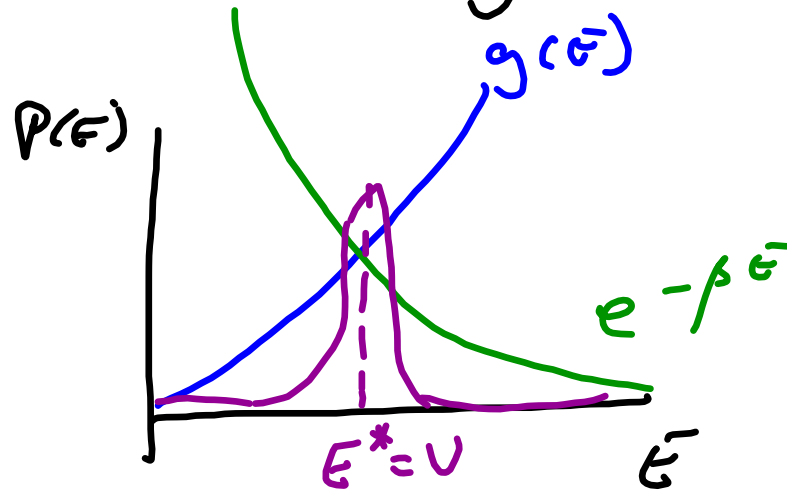
$$\frac{\sqrt{(\Delta E^2)^2}}{\langle E \rangle} = \frac{\sqrt{kT^2 C_V}}{U} \propto \frac{1}{\sqrt{N}} \rightarrow 0 \text{ as } N \rightarrow \infty$$

Let's now consider the continuous expression of $P(E)$

We will see that
 $P(E)$ is a very sharp
 gaussian



$$P(\bar{\epsilon}) d\bar{\epsilon} \propto g(\bar{\epsilon}) e^{-\beta \bar{\epsilon}} d\bar{\epsilon}$$



Very sharp peak
 in $P(\bar{\epsilon})$ also
 has a maximum
 at $\bar{\epsilon}^*$.

Let's find $\bar{\epsilon}^*$:

$$0 = \left. \frac{\partial P(\bar{\epsilon})}{\partial \bar{\epsilon}} \right|_{\bar{\epsilon} = \bar{\epsilon}^*} = \left. \frac{\partial}{\partial \bar{\epsilon}} (e^{-\beta \bar{\epsilon}} g(\bar{\epsilon})) \right|_{\bar{\epsilon} = \bar{\epsilon}^*} \Rightarrow$$

$$-\beta e^{-\beta \bar{\epsilon}} g(\bar{\epsilon}) + \frac{\partial g}{\partial \bar{\epsilon}} e^{-\beta \bar{\epsilon}} \Big|_{\bar{\epsilon} = \bar{\epsilon}^*} = 0$$

$$\left[\beta = \frac{1}{g(\bar{\epsilon})} \frac{\partial g}{\partial \bar{\epsilon}} \Big|_{\bar{\epsilon} = \bar{\epsilon}^*} = \frac{\partial \ln g(\bar{\epsilon})}{\partial \bar{\epsilon}} \Big|_{\bar{\epsilon} = \bar{\epsilon}^*} \right] \quad (1)$$

But $Z_N(\beta) = \int g(\bar{\epsilon}) e^{-\beta \bar{\epsilon}} d\bar{\epsilon}$

If $\bar{\epsilon}$ is fixed in the system $g(\bar{\epsilon}) \equiv \Omega$
 # of accessible microstates
 then $S(\bar{\epsilon}) = k \ln g(\bar{\epsilon})$

Also from thermodynamics $\beta = 1/kT$

$$dE = TdS - PdV + Nd\mu \Rightarrow \left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{1}{T} =$$

Then Eq. ① becomes:

$$\beta = \left. \frac{\partial \ln g(\bar{E})}{\partial \bar{E}} \right|_{\bar{E} = \bar{E}^*} \equiv \frac{1}{k} \left. \frac{\partial S}{\partial E} \right|_{V, N} \equiv \frac{1}{k} \left. \frac{\partial S}{\partial E} \right|_{\bar{E} = U}$$

\therefore We can identify $\bar{E}^* = U$ most probable energy is equal to the thermodynamic energy of the system which is U the ensemble average.

Now expand $\ln P(\bar{\epsilon})$ about $\bar{\epsilon}^* = U$:

$$\ln (e^{-\beta \bar{\epsilon}} g(\bar{\epsilon})) = (-\beta U + \underbrace{\ln g(U)}_S) + \underbrace{\frac{\partial \ln P}{\partial \bar{\epsilon}}}_{P_0} \Big|_{\bar{\epsilon}=U} (\bar{\epsilon} - U) + \frac{1}{2} \underbrace{\frac{\partial^2}{\partial \bar{\epsilon}^2} \ln \{e^{-\beta \bar{\epsilon}} g(\bar{\epsilon})\}}_{-\frac{1}{kT^2 c_V}} \Big|_{\bar{\epsilon}=U} (\bar{\epsilon} - U)^2 + \dots$$

$$\therefore P(\bar{\epsilon}) \propto e^{-\beta \bar{\epsilon}} g(\bar{\epsilon}) \approx e^{-\beta(U - T S)} e^{-\frac{(\bar{\epsilon} - U)^2}{2 k T^2 c_V}}$$

this is a gaussian distribution about $\bar{\epsilon} = U$ with dispersion $\sqrt{k T^2 c_V} \equiv \sqrt{\langle (\Delta \bar{\epsilon})^2 \rangle}$

Examples:

Ideal gas: $g(\epsilon) \propto \epsilon^{\frac{3N}{2}-1}$

$$P(\epsilon) \propto g(\epsilon) e^{-\beta\epsilon} = \epsilon^{\frac{3N}{2}-1} e^{-\beta\epsilon}$$

$$\left. \frac{\partial P}{\partial \epsilon} \right|_{\epsilon=\epsilon^*} = 0 = \epsilon^{\frac{3N}{2}-2} \left(\frac{3N}{2} - 1 \right) e^{-\beta\epsilon} - \beta \epsilon^{\frac{3N}{2}-1} e^{-\beta\epsilon}$$

$$\left(\frac{3N}{2} - 1 \right) \frac{1}{\epsilon^*} = \beta$$

$$\therefore \epsilon^* \approx \left(\frac{3N}{2} - 1 \right) kT \approx \frac{3N}{2} kT = U$$

which
we
knew!

notice that $P(\bar{\epsilon}) \approx 0$ if $\bar{\epsilon} \neq \bar{\epsilon}^*$ due to the negligible dispersion.

Partition function for ideal gas:

[Using the gaussian form of $P(\bar{\epsilon})$]

$$Z_N(U, T) = \int_0^{\infty} e^{-\beta \bar{\epsilon}} g(\bar{\epsilon}) d\bar{\epsilon} \approx e^{-\beta(U-TS)}$$

$$\int_0^{\infty} e^{-\frac{(\bar{\epsilon}-U)^2}{2kT^2 c_V}} d\bar{\epsilon} = e^{-\beta(U-TS)} \sqrt{2\pi kT^2 c_V}$$

Then

$$F = -kT \ln Z_U = kT \beta (U - TS) \propto N$$

$$-kT \ln \sqrt{2\pi kT^2 c_V} \approx U - TS$$

Correct thermodynamic expression of F.

$\ln N^{1/2}$ (negligible compared with N)

Theorems:

1) Theorem of equipartition of energy:

Find: $\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle$ (canonical average).

where $H(q, p)$ is the classical Hamiltonian
 x_i, x_j are 2 of the $6N$ generalized
 coordinates (q, p) .

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

Let's work with the numerator in $\textcircled{*}$:

Notice that

$$\frac{\partial}{\partial x_j} (x_i e^{-\beta H}) = \frac{\partial x_i}{\partial x_j} e^{-\beta H} - x_i \beta \frac{\partial H}{\partial x_j} e^{-\beta H}$$

$$\Rightarrow x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta} \frac{\partial x_i}{\partial x_j} e^{-\beta H} - \frac{1}{\beta} \frac{\partial}{\partial x_j} (x_i e^{-\beta H})$$

$$\therefore \int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} dx_j d\omega'(j) = \frac{1}{\beta} \int \underbrace{\frac{\partial x_i}{\partial x_j}}_{\delta_{ij}} e^{-\beta H} dx_j d\omega'(j)$$

$$= \frac{1}{\beta} \int \underbrace{\frac{\partial}{\partial x_j} (x_i e^{-\beta H})}_{x_i e^{-\beta H}} dx_j d\omega'(j) \Big|_{x_j^{(1)}}^{x_j^{(2)}}$$

$x_j(1)$ and $x_j(2)$ are extreme values of x_j and
 $H(x_{\text{extr}}) \rightarrow \infty \Rightarrow e^{-\beta H(x_{\text{extr}})} = 0$

Then:

$$\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} dx_j d\omega_{ij} = \int \frac{1}{\beta} \delta_{ij} e^{-\beta H} d\omega$$

Then

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{\beta} \delta_{ij} \frac{\int e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega} = \frac{\delta_{ij}}{\beta} = kT \delta_{ij}$$

Now if $x_i = x_j = p_i$

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle \equiv \left\langle p_i \dot{q}_i \right\rangle = kT \quad \textcircled{1}$$

$$\text{If } x_i = x_j = q_i$$

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = - \left\langle q_i \dot{p}_i \right\rangle = kT$$

Now

$$\left\langle \sum_{i=1}^{3N} p_i \frac{\partial H}{\partial p_i} \right\rangle = \left\langle \sum_{i=1}^{3N} p_i \dot{q}_i \right\rangle =$$

$$= 3NkT$$

$$\left\langle \sum_{i=1}^{3N} q_i \frac{\partial H}{\partial q_i} \right\rangle = - \left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3NkT$$

If H is quadratic in its coordinates
we always can write:

$$H = \sum_j (A_j P_j^2 + B_j Q_j^2)$$

P_j and Q_j are canonically conjugated

then

$$\sum_j \left(P_j \underbrace{\frac{\partial H}{\partial P_j}}_{2 A_j P_j} + Q_j \underbrace{\frac{\partial H}{\partial Q_j}}_{2 B_j Q_j} \right) = 2 \sum_j (A_j P_j^2 + B_j Q_j^2) = 2 H \quad \textcircled{2}$$

Calculate the canonical average of $\langle Z \rangle$:

$$\frac{f k T}{2} = \langle H \rangle$$

f : # of nonvanishing A_j 's and B_j 's
it is the number of active degrees of freedom.

Theorem of equipartition of the energy:

each active degree of freedom (quadratic in H) contributes $\frac{1}{2} kT$ to the energy.

2) Virial theorem:

$$-\mathcal{V} = - \left\langle \sum_{i=1}^{3N} \mathbf{r}_i \cdot \dot{\mathbf{p}}_i \right\rangle = 3NkT$$

↳
virial

↳
from equipartition theorem.

Notice that $\dot{\mathbf{p}}_i = \frac{\partial(m\mathbf{v}_i)}{\partial t} = m\mathbf{a}_i = \mathbf{F}_i$

↳
force that acts on particle i .

Virial theorem says that

$$\boxed{\mathcal{V} = -3NkT}$$

Let's calculate \mathcal{V} for the ideal gas
(we will see that it will be useful):

only force is P on the container

Surface:

$$dF = -P dS$$

$-3NkT$ (Virial theorem)

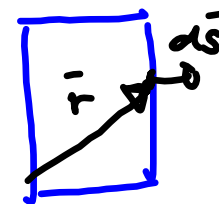
$$\mathcal{V}_0 = \left(\sum_i \mathbf{r}_i \cdot \mathbf{F}_i \right)_0 = -P \oint \bar{\mathbf{r}} \cdot d\bar{\mathbf{s}} =$$

non interactions

$$= -P \int_V \nabla \cdot \bar{\mathbf{r}} dV = -P \int_V \left(\frac{\partial x}{\partial x} + \frac{\partial y}{\partial y} + \frac{\partial z}{\partial z} \right) dV$$

$$= -P 3V$$

divergence theorem



Then

$$- 3NkT = - 3PV$$

$$PV = NkT \quad \text{ef. of state}$$

Notice that

$$P = nkT$$

$$n = N/V$$

or

$$\boxed{\frac{P}{nkT} = 1}$$

for ideal gas.

Notice that since (for ideal gas)

$$U = \frac{3}{2} NkT \equiv K \quad (\text{kinetic energy})$$

$$\Rightarrow K = -\frac{\gamma_0}{2} \quad \text{or} \quad \boxed{\gamma = -2K}$$

Now consider a non-ideal gas in which the molecules interact weakly with each other via a potential $u(r_{ij})$ (2 molecule interaction)

Let's calculate γ :

$$\begin{aligned} \bar{V} &= \left(\sum_i q_i F_i \right)_0 + \left\langle \sum_{i < j} \overline{r_{ij}} F_{ij} \right\rangle = \\ &= -3PV - \left\langle \sum_{i < j} \frac{\partial u(r_{ij})}{\partial r_{ij}} r_{ij} \right\rangle = -3NkT \end{aligned}$$

\swarrow
 $-\frac{\partial u(r_{ij})}{\partial r_{ij}}$
 \swarrow
 Virial theorem

$$\therefore P = nkT - \frac{1}{3V} \left\langle \sum_{i < j} \frac{\partial u}{\partial r_{ij}} r_{ij} \right\rangle$$

$$\therefore \frac{P}{nkT} = 1 - \frac{1}{3NkT} \left\langle \sum_{i < j} \frac{\partial u}{\partial r_{ij}} r_{ij} \right\rangle$$

Virial eq. of state (it will be used for diagrammatic expansions)