Average energy $\langle E \rangle$ vs. the most probable energy $\bar{E}$ in the canonical ensemble.

In our earlier discussion of fluctuations in the canonical ensemble we expanded

$$E - TS(E) \cong A_{micro}(T) + \frac{\delta E^2}{2TC_V}$$

now we continue the expansion to $O(\delta E^3)$

$$E - TS(E) \cong A_{micro}(T) + \frac{\delta E^2}{2TC_V} - \frac{1}{3!}\, T \frac{\partial^3 S}{\partial E^3}\bigg|_{E=\bar{E}} \delta E^3$$

Note $\frac{\partial^3 S}{\partial E^3} \sim \frac{1}{N^2}$ since $S \sim N$ and $E \sim N$ are both extensive

So we can write

$$E - TS(E) \cong A_{micro}(T) + \frac{\delta E^2}{2TC_V} - \frac{\gamma}{N^2}\, \delta E^3$$

where γ is some constant that does not increase with N (it can depend on T)

Now compute $\langle \delta E \rangle = \langle E \rangle - \bar{E}$

$$\langle \delta E \rangle = \frac{\int \frac{d\delta E}{\Delta}\, e^{-(E - TS(E))/k_B T}\, \delta E}{\int \frac{d\delta E}{\Delta}\, e^{-(E - TS(E))/k_B T)}}$$

$$\simeq \frac{\int d\delta E\, e^{-\frac{\delta E^2}{2k_B T^2 C_V} + \frac{\gamma\, \delta E^3}{N^2 k_B T}}\, \delta E}{\int d\delta E\, e^{-\frac{\delta E^2}{2k_B T^2 C_V} + \frac{\gamma}{N^2}\frac{\delta E^3}{k_B T}}}$$

$$\simeq \frac{\int d\delta E\, e^{-\frac{\delta E^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma\, \delta E^3}{N^2 k_B T}\right) \delta E}{\int d\delta E\, e^{-\frac{\delta E^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma\, \delta E^3}{N^2 k_B T}\right)}$$

where we expanded $e^{\frac{\gamma \delta E^3}{N^2 k_B T}} \approx 1 + \frac{\gamma\, \delta E^3}{N^2 k_B T}$ for $N \to \infty$

For a Gaussian distribution, only the even moments are non-vanishing

$$\langle \delta E \rangle \simeq \frac{\int d\delta E\, e^{-\frac{\delta E^2}{2k_B T^2 C_V}} \cdot \left(\frac{\gamma}{N^2 k_B T}\right) \delta E^4}{\int d\delta E\, e^{-\frac{\delta E^2}{2k_B T^2 C_V}}}$$

$$= \left(\frac{\gamma}{N^2 k_B T}\right) \cdot \left(k_B T^2 C_V\right)^2 \cdot 3$$

where we used $\dfrac{\int_{-\infty}^{\infty} dx\, e^{-\frac{1}{2}\frac{x^2}{\sigma^2}} x^4}{\int_{-\infty}^{\infty} dx\, e^{-\frac{1}{2}\frac{x^2}{\sigma^2}}} = 3\sigma^4$

But the main point is $C_V \sim N$

so $\langle \delta E \rangle \sim \frac{1}{N^2} \cdot N^2 \sim O(1)$

The relative difference between average and most probable energy therefore scales as

$$\frac{\langle E \rangle - \bar{E}}{\langle E \rangle} = \frac{\langle \delta E \rangle}{\langle E \rangle} \sim \frac{1}{N} \to 0 \quad \text{as } N \to \infty$$

Stirling's Formula

In lecture we used the saddle point approx to discuss the relation between the Helmholtz free energy in the canonical vs. the micro canonical ensemble. The saddle pt approx is also how one derives Stirling's approx for $n!$

Consider the integral

$$I = \int_0^\infty dx\, x^n e^{-x}$$

integrate by parts

$$I = -x^n e^{-x}\Big]_0^\infty + \int_0^\infty n x^{n-1} e^{-x}\, dx$$

boundary term vanishes at its limits so

$$I = \int_0^\infty dx\; n x^{n-1} e^{-x}$$

integrate by parts again

$$I = \int_0^\infty dx\; n(n-1)\, x^{n-2} e^{-x}$$

and so on to get

$$I = \int_0^\infty dx\; n(n-1)(n-2)\cdots(1)\, e^{-x} = n!$$

Now evaluate I in saddle pt approx.

Define $U(x) = -x + n \ln x$

$$I = \int_0^\infty dx \; e^{U(x)}$$

expand $U(x)$ about its maximum

$$U'(x) = -1 + \frac{n}{x} \Rightarrow \begin{cases} U(\bar{x}) = -n + n \ln n \\ \bar{x} = n \quad \text{is the maximum} \end{cases}$$

$$U''(x) = -\frac{n}{x^2} \Rightarrow U''(\bar{x}) = -\frac{1}{n}$$

$$U'''(x) = \frac{2n}{x^3} \qquad U'''(\bar{x}) = 2/n^2$$

$$U''''(x) = \frac{-6n}{x^4} \qquad U''''(\bar{x}) = -6/n^3$$

For $\delta x = x - \bar{x}$,

$$U(x) \simeq -n + n \ln n - \frac{\delta x^2}{2n} + \frac{1}{6}\frac{2}{n^2}\delta x^3 - \frac{1}{24}\frac{6}{n^3}\delta x^4 + \ldots$$

$$= -n + n \ln n - \frac{\delta x^2}{2n} + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \ldots$$

$$I = \int_0^\infty dx \; e^{-n+n\ln n} \; e^{-\delta x^2/2n} \; \underbrace{e^{\frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3}}}_{\text{expand for small } \delta x}$$

$$\approx \int_{-\infty}^{\infty} d\delta x \; e^{-n+n\ln n} \; e^{-\delta x^2/2n} \left[1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + O(\delta x^6) \right]$$

$$= e^{-n+n\ln n} \int_{-\infty}^{\infty} d\delta x \; e^{-\delta x^2/2n} \left[1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \ldots \right]$$

$$= e^{-n+n\ln n} \sqrt{2\pi n} \left[1 + \frac{\langle \delta x^3 \rangle}{3n^2} - \frac{\langle \delta x^4 \rangle}{4n^3} + \ldots \right]$$

Now $\langle \delta x^3 \rangle = 0$, $\langle \delta x^4 \rangle \sim n^2$, So

$$I = n! = e^{-n + n\ln n} \sqrt{2\pi n} \left[1 + O\left(\tfrac{1}{n}\right) \right]$$

$$\ln n! = n\ln n - n + \tfrac{1}{2}\ln n + \tfrac{1}{2}\ln 2\pi + \ln\left(1 + O\left(\tfrac{1}{n}\right)\right)$$

$$= \underbrace{n\ln n - n}_{\text{these are the leading terms}} + \underbrace{\tfrac{1}{2}\ln n + \tfrac{1}{2}\ln 2\pi}_{\text{these are next order corrections}} + O\left(\tfrac{1}{n}\right)$$

Factorization of canonical partition function – the ideal gas

Consider a system of N noninteracting particles

$$\rightarrow \mathcal{H}[\vec{q}_j, \vec{p}_i] = \sum_{i=1}^{N} \mathcal{H}^{(1)}(\vec{q}_i, \vec{p}_i)$$

where $\mathcal{H}^{(1)}$ is the single particle Hamiltonian that depends only on the three coordinates $\vec{q}_i$ and three momenta $\vec{p}_i$ of particle i.

$$Q_N = \frac{1}{N!\, h^{3N}} \left(\prod_{i=1}^{N} \int d\vec{q}_i\, d\vec{p}_i \right) e^{-\beta \mathcal{H}}$$

$$= \frac{1}{N!} \left(\prod_{i=1}^{N} \int \frac{d\vec{q}_i\, d\vec{p}_i}{h^3} \right) e^{-\beta \sum_j \mathcal{H}^{(1)}(\vec{q}_j, \vec{p}_j)}$$

factor the exponential

$$= \frac{1}{N!} \prod_{i=1}^{N} \left(\int \frac{d\vec{q}_i\, d\vec{p}_i}{h^3} e^{-\beta \mathcal{H}^{(1)}(\vec{q}_i, \vec{p}_i)} \right)$$

factor for particle i is identical to factor for particle j

$$\rightarrow \boxed{Q_N = \frac{1}{N!} (Q_1)^N}$$ for noninteracting particles

where Q_1 is the one particle partition function

$$Q_1 = \int \frac{d\vec{q}\,d\vec{p}}{h^3}\, e^{-\beta \mathcal{H}^{(1)}(\vec{q},\vec{p})}$$

Apply to the ideal gas.

$$\mathcal{H}^{(1)}(\vec{q},\vec{p}) = \frac{p^2}{2m}$$

$$Q_1 = \int \frac{d\vec{q}}{h^3} \int d\vec{p}\; e^{-\beta \frac{p^2}{2m}}$$

$$\int d\vec{q} = V \quad \text{volume of system}$$

$$\int d\vec{p}\; e^{-\beta p^2/2m} = \left(\frac{2\pi m}{\beta}\right)^{3/2} \quad \text{3D Gaussian integral}$$

$$Q_1 = \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2}$$

$$\Rightarrow Q_N = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \left(2\pi m k_B T\right)^{3N/2}$$

$\ln N! = N\ln N - N$

$$A(T,V,N) = -k_B T \ln Q_N \quad \text{using } \underbrace{\text{Stirling's formula}}$$

$$= -k_B T\left\{ N \ln\left[\frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2}\right] - N\ln N + N\right\}$$

$$A(T,V,N) = -k_B T N - k_B T N \ln\left[\frac{V}{h^3 N}\left(2\pi m k_B T\right)^{3/2}\right]$$

Compute average energy

$$\langle E \rangle = -\frac{\partial}{\partial \beta}(\ln Q_N) = -\frac{\partial}{\partial \beta}(-\beta A)$$

$$= -\frac{\partial}{\partial \beta}\left(N + N \ln\left[\frac{V}{h^{3N}}\left(\frac{2\pi m}{\beta}\right)^{3/2}\right]\right)$$

$$= -N \frac{\partial}{\partial \beta}\left(\ln \beta^{-3/2}\right) = \frac{3}{2} N \frac{\partial}{\partial \beta} \ln \beta = \frac{3}{2} N \frac{1}{\beta}$$

$\langle E \rangle = \frac{3}{2} N k_B T$ as expected

entropy

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

$$+ k_B T N \, \frac{3}{2}\left(\frac{1}{T}\right)$$

← from derivative of log

$$S = \frac{5}{2} N k_B + N k_B \ln\left[\frac{V}{h^{3N}}(2\pi m k_B T)^{3/2}\right]$$

substitute in $k_B T = \frac{2}{3}\frac{E}{N}$ to get

$$\Rightarrow \quad S(E,V,N) = \frac{5}{2} N k_B + N k_B \ln\left[\frac{V}{h^{3N}}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right]$$

We have recovered the Sackur-Tetrode equation which we earlier derived from the microcanonical ensemble! Canonical and microcanonical approaches are equivalent.

Because in computing Q_N we sum over all states with any energy, as compared to computing Ω where we restrict the sum to states in a particular energy shell E, it is usually easier to compute Q_N, rather than Ω.

We introduced the canonical distribution as a means of describing a physical system in contact with a heat bath.

The canonical distrib gives the same result as the microcannonical because in the $N \to \infty$ (thermodynamic) limit, the canonical probability distribution

$$p(E) = \frac{\Omega(E)\, e^{-E/k_B T}}{\Delta\, Q_N(V,T)}$$

approaches a delta-function* at the most probable energy = average energy, as set by the temperature T.

We could alternatively introduced the canonical ensemble just as a mathematical trick for computing $\Omega(E)$, removing the constraint of constant energy E by means of a Lagrange multiplier.

* since $E \sim N$ increases as $N \to \infty$
and $\langle E^2 \rangle - \langle E \rangle^2$ increases as $\sqrt{N}$
it is not really $P(E)$ that approaches a well defined function as $N \to \infty$. Rather it is the distribution
$p(e \equiv E/N)$, the probability density to have an <u>energy per particle</u> e, that approaches a delta function as $N \to \infty$

Maxwell velocity distribution revisited

We found that the canonical partition function for a gas of N particles is given by

$$Q_N(T,V) = \int \frac{dE}{\Delta}\,\Omega(E)\,e^{-\beta E} = \frac{1}{N!}\prod_{i=1}^{N}\int \frac{d^3p_i\,d^3q_i}{h^{3N}}\,e^{-\beta H[\vec{q}_i,\vec{p}_i]}$$

from which we conclude that the probability density for the system to have total energy E is

$$P(E) = \frac{\frac{\Omega(E)}{\Delta}\,e^{-\beta E}}{\int \frac{dE}{\Delta}\,\Omega(E)\,e^{-\beta E}}$$

Since $\Omega(E)$ is the number of states with total energy E, and all states with energy E are equally likely, we can conclude that the probability density for the system to be in some <u>particular</u> state $\{\vec{q}_i,\vec{p}_i\}$ is

$$P(\{\vec{q}_i,\vec{p}_i\}) = \frac{e^{-\beta H[\vec{q}_i,\vec{p}_i]}}{\prod_{i=1}^{N}\int d^3q_i\,d^3p_i\,e^{-\beta H[\vec{q}_i,\vec{p}_i]}}$$

To get the probability density that one particular particle k has momentum $\vec{p}_k$ we <u>integrate</u> $P(\{\vec{q}_i,\vec{p}_i\})$ over all degrees of freedom <u>except</u> $\vec{p}_k$.

$$P(\vec{p}_k) = \frac{\prod_i' \int d^3 q_i \int d^3 p_i \quad e^{-\beta \mathcal{H}[\vec{q}_i \vec{p}_i]}}{\prod_i \int d^3 q_i \int d^3 p_i \; e^{-\beta \mathcal{H}[\vec{q}_i \vec{p}_i]}}$$

all degrees of freedom except $\vec{p}_k$

For a general Hamiltonian with interactions between the particles, the above integrations can be very hard to do. But for non-interacting particles, it is easy! When

$$\mathcal{H}[\vec{q}_i \vec{p}_i] = \sum_i \mathcal{H}^{(1)}(\vec{q}_i \vec{p}_i)$$

single particle Hamiltonian

then one has

$$e^{-\beta \mathcal{H}[\vec{q}_i, \vec{p}_i]} = e^{-\beta \sum_i \mathcal{H}^{(1)}(\vec{q}_i \vec{p}_i)} = \prod_i e^{-\beta \mathcal{H}^{(1)}(\vec{q}_i \vec{p}_i)}$$

and the probability distribution $P(\vec{p}_k)$ becomes

$$P(\vec{p}_k) = \frac{\int d^3 q_k \, e^{-\beta \mathcal{H}^{(1)}(\vec{q}_k \vec{p}_k)} \prod_{i \neq k} \left(\int d^3 q_i \, d^3 p_i \, e^{-\beta \mathcal{H}^{(1)}(\vec{q}_i, \vec{p}_i)} \right)}{\prod_i \left(\int d^3 q_i \, d^3 p_i \; e^{-\beta \mathcal{H}^{(1)}(\vec{q}_i, \vec{p}_i)} \right)}$$

$$= \frac{\int d^3 q_k \, e^{-\beta \mathcal{H}^{(1)}(\vec{q}_k, \vec{p}_k)}}{\int d^3 q_k \, d^3 p_k \; e^{-\beta \mathcal{H}^{(1)}(\vec{q}_k, \vec{p}_k)}}$$

where all other terms for particles $i \neq k$ cancel out in numerator and denominator.

For the ideal gas $\mathcal{H}^{(1)}(\vec{p},\vec{p}) = \frac{|\vec{p}|^2}{2m}$ is indep of $\vec{q}$. Hence the d^3q integrals in numerator and denominator each give a factor of V and

$$p(\vec{p}_n) = \frac{e^{-\beta|\vec{p}|^2/2m}}{\int d^3p\, e^{-\beta|\vec{p}|^2/2m}} = \frac{e^{-|\vec{p}_n|^2/2mk_BT}}{(2\pi m k_BT)^{3/2}}$$

This is exactly the Maxwell velocity distribution that we derived earlier from kinetic theory!

NOTE:

1) Maxwell's probability distribution $\quad \epsilon = \frac{p^2}{2m}$

$p(\epsilon) \propto e^{-\beta\epsilon}$ is probability for a <u>single particle</u> to have energy ϵ and holds only in the limit of <u>non-interacting</u> particles

2) The probability to be in a particular state i with <u>total energy</u> E_i in the canonical distribution is

$$P_i \propto e^{-\beta E_i}$$

and holds generally for any type of system. Here E_i is the <u>total energy</u> and "i" specifies a state of the <u>entire system</u> (NOT just one particle in the system)

Virial Theorem – Classical Systems Only

Consider $\langle x_i \frac{\partial H}{\partial x_j} \rangle = \dfrac{\prod_k \int dq_k dp_k \, x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\prod_k \int dq_k dp_k \, e^{-\beta H}}$

where x_i and x_j are any of the $6N$ generalized coordinates q, p $i = 1, \dots, 3N$,

$$\prod_k \int dq_k \, dp_k \; x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = -\frac{1}{\beta} \prod \int dq_k \, dp_k \; x_i \frac{\partial}{\partial x_j}\left(e^{-\beta H}\right)$$

to be assumed from now on.

integrate by parts with ~~p~~ respect to x_j

$$= -\frac{1}{\beta} \int' dq_k \, dp_k \; x_i e^{-\beta H} \Big]_{x_j^{(1)}}^{x_j^{(2)}} + \frac{1}{\beta} \int dq_k \, dp_k \left(\frac{\partial x_i}{\partial x_j}\right) e^{-\beta H}$$

integral over all coordinates *except* x_j

$x_j^{(1)}$ and $x_j^{(2)}$ are the extremal values of x_j

the boundary integral vanishes because H becomes infinite at the extremal values of any coordinate

- if x_j is a momentum p, then extremal values are $p = \pm\infty$ and $H \propto p^2/2m \to \infty$.
- if x_j is a spatial coord q, then extremal values are at boundary of ~~sten~~ system, where the potential energy confining the particle to the volume V becomes infinite.

$$\Rightarrow \int dq_k dp_k \; x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta} \int dq_k dp_k \left(\frac{\partial x_i}{\partial x_j}\right) e^{-\beta H}$$

but $\frac{\partial x_i}{\partial x_j} = \delta_{ij}$

$$\Rightarrow \left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{1}{\beta}\delta_{ij} \frac{\int dq_k \int dp_k\, e^{-\beta\mathcal{H}}}{\int dq_k \int dp_k\, e^{-\beta\mathcal{H}}}$$

$$\boxed{\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = k_B T\, \delta_{ij}} \Leftarrow \text{Virial Theorem}$$

If $x_i = x_j = p_i$ then

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \langle p_i \dot{q}_i \rangle = k_B T$$

If $x_i = x_j = q_i$, then

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

where we used Hamiltons equ's of motion
$\partial \mathcal{H}/\partial p_i = \dot{q}_i$ and $\partial \mathcal{H}/\partial q_i = -\dot{p}_i$

$$\Rightarrow \left\langle \sum_{i=1}^{3N} p_i \dot{q}_i \right\rangle = 3N k_B T$$

$$-\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3N k_B T \quad \text{– Virial Theorem Clausius (1870)}$$