

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

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

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

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

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

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

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

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

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

$$\approx \frac{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V} + \frac{\gamma SE^3}{N^2 k_B T}} SE}{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V} + \frac{\gamma SE^3}{N^2 k_B T}}}$$

$$\approx \frac{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma SE^3}{N^2 k_B T}\right) SE}{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma SE^3}{N^2 k_B T}\right)}$$

$$\approx \frac{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma SE^3}{N^2 k_B T}\right) SE}{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma SE^3}{N^2 k_B T}\right)}$$

where we expanded $e^{\frac{\gamma SE^3}{N^2 k_B T}} \approx 1 + \frac{\gamma SE^3}{N^2 k_B T}$
for $N \rightarrow \infty$

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

$$\langle SE \rangle \approx \frac{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}} \cdot \left(\frac{\gamma}{N^2 k_B T}\right) SE^4}{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}}}$$

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

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

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

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

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

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

(2)

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

$$\begin{aligned}
 U'(x) &= -1 + \frac{n}{x} &\Rightarrow & \begin{cases} U(\bar{x}) = -n + n \ln n \\ \bar{x} = n \text{ is the maximum} \end{cases} \\
 U''(x) &= -\frac{n}{x^2} &\Rightarrow & U''(\bar{x}) = -\frac{1}{n} \\
 U'''(x) &= \frac{2n}{x^3} && U'''(\bar{x}) = \frac{2}{n^2} \\
 U^{(4)}(x) &= -\frac{6n}{x^4} && U^{(4)}(\bar{x}) = -\frac{6}{n^3}
 \end{aligned}$$

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

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

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

$$I = \int_0^{\infty} dx e^{-n + n \ln n} e^{-\delta x^2 / 2n} e^{\frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3}}$$

expand for small δx

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

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

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

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

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

$$\begin{aligned} \ln n! &= n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi + \ln\left(1 + o\left(\frac{1}{n}\right)\right) \\ &= \underbrace{n \ln n - n}_{\text{these are the leading terms}} + \underbrace{\frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi}_{\text{these are next order corrections}} + o\left(\frac{1}{n}\right) \end{aligned}$$

Factorization of canonical partition function - the ideal gas

Consider a system of N noninteracting particles

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

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

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

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

factor the exponential

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

↑
factor for particle i is
identical to factor for particle j

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

where Q_1 is the one particle partition function

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

Apply to the ideal gas.

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

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

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

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

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

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

$$A(T, V, N) = -k_B T \ln Q_N$$

$\ln N! = N \ln N - N$
using Stirling's formula

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

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

Compute average energy

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

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

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

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

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

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

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

Because in computing Ω_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 Ω_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 microcanonical because in the $N \rightarrow \infty$ (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 introduce 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 $N \rightarrow \infty$

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 $N \rightarrow \infty$. Rather it is the distribution

$p(e \equiv E/N)$, the probability density to have an energy per particle e , that approaches a delta function as $N \rightarrow \infty$

Maxwell velocity distribution revisited

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

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

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

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

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

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 particular state $\{\vec{q}_i, \vec{p}_i\}$ is

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

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

$$P(\vec{P}_k) = \frac{\prod_i' \int d^3 q_i \int d^3 p_i e^{-\beta H[\vec{q}; \vec{P}_i]}}{\substack{\uparrow \\ \text{all degrees of freedom} \\ \text{except } \vec{P}_k} \prod_i \int d^3 q_i \int d^3 p_i e^{-\beta H[\vec{q}; \vec{P}_i]}}$$

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

$$H[\vec{q}; \vec{P}_i] = \sum_i H^{(i)}(\vec{q}_i, \vec{P}_i)$$

\uparrow
 single particle Hamiltonian

then one has

$$e^{-\beta H[\vec{q}; \vec{P}_i]} = e^{-\beta \sum_i H^{(i)}(\vec{q}_i, \vec{P}_i)} = \prod_i e^{-\beta H^{(i)}(\vec{q}_i, \vec{P}_i)}$$

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

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

$$= \frac{\int d^3 q_k e^{-\beta H^{(k)}(\vec{q}_k, \vec{P}_k)}}{\int d^3 q_k \int d^3 p_k e^{-\beta H^{(k)}(\vec{q}_k, \vec{P}_k)}}$$

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

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

$$P(\vec{p}_n) = \frac{e^{-\beta |\vec{p}_n|^2 / 2m}}{\int d^3p e^{-\beta |\vec{p}|^2 / 2m}} = \frac{e^{-|\vec{p}_n|^2 / 2mk_B T}}{(2\pi m k_B T)^{3/2}}$$

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

NOTE:

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

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

2) The probability to be in a particular state i with total energy 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 total energy and " i " specifies a state of the entire system (NOT just one particle in the system)