

Maxwell velocity distribution revisited

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

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

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

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

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 $\vec{p}_k$.

$$P(\vec{P}_k) = \prod_i' \int d^3 \vec{q}_i \int d^3 \vec{p}_i e^{-\beta H[\vec{q}_i, \vec{p}_i]}$$

$\uparrow$
 all degrees of freedom
 except $\vec{P}_k$

$$\prod_i \int d^3 \vec{q}_i \int d^3 \vec{p}_i e^{-\beta H[\vec{q}_i, \vec{p}_i]}$$

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

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

$\uparrow$
 single particle Hamiltonian

then one has

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

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

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

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

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

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

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

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

NOTE:

1) Maxwell's probability distribution

$$E = \frac{p^2}{2m}$$

$P(E) \propto e^{-\beta E}$ is probability for a single particle to have energy E 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)

Virial Theorem - Classical systems only

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

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

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

↑ integrate by parts with respect to x_j

to be assumed from now on,

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

↑ 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 $H \propto p^2/2m \rightarrow \infty$.

- if x_j is a spatial coord q , then extremal values are at boundary of the system, where the potential energy confining the particle to the volume V becomes infinite.

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

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

$$\Rightarrow \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\beta} \delta_{ij} \frac{\int dx_k \int dp_k e^{-\beta H}}{\int dx_k \int dp_k e^{-\beta H}}$$

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

If $x_i = x_j = p_i$ then

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

If $x_i = x_j = q_i$, then

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

where we used Hamilton's eq's of motion

$$\partial H / \partial p_i = \dot{q}_i \quad \text{and} \quad \partial H / \partial q_i = -\dot{p}_i$$

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

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

Equipartition Theorem - Classical systems only

Suppose the Hamiltonian is quadratic in
some particular degree of freedom x_j (x_j is either
a coord or a momentum)

$$H[g_i, p_i] = H'[g_i, p_i] + \alpha_j x_j^2$$

↑
depends on all degrees of freedom
except x_j

$$\text{Then } \langle H \rangle = \langle H' \rangle + \alpha_j \langle x_j^2 \rangle$$

↑
Contribution to total average
energy from the degree of
freedom x_j

$$\langle x_j^2 \rangle = \frac{\prod_i \int dg_i dp_i x_j^2 e^{-\beta(H' + \alpha_j x_j^2)}}{\prod_i \int dg_i dp_i e^{-\beta(H' + \alpha_j x_j^2)}}$$

$$= \frac{\left(\prod_i' \int dg_i dp_i e^{-\beta H'} \right) \int dx_j x_j^2 e^{-\beta \alpha_j x_j^2}}{\left(\prod_i' \int dg_i dp_i e^{-\beta H'} \right) \int dx_j e^{-\beta \alpha_j x_j^2}}$$

where $\prod_i'$ is over all degrees of freedom except x_j

$$\langle x_j^2 \rangle = \frac{\int dx_j x_j^2 e^{-\beta \alpha_j x_j^2}}{\int dx_j e^{-\beta \alpha_j x_j^2}} = \frac{1}{2\beta \alpha_j} = \frac{1}{2} \frac{k_B T}{\alpha_j}$$

(follows from $\int dx e^{-x^2/2\sigma^2} = \sqrt{2\pi\sigma^2}$ and $\frac{\int dx e^{-x^2/2\sigma^2} x^2}{\sqrt{2\pi\sigma^2}} = \sigma^2$)

So the contribution to $\langle H \rangle$ from the degree of freedom x_j

$$\text{is } \alpha_j \langle x_j^2 \rangle = \alpha_j \frac{1}{2} \frac{k_B T}{\alpha_j} = \frac{1}{2} k_B T$$

$\Rightarrow$ each quadratic degree of freedom in the Hamiltonian contributes $\frac{1}{2} k_B T$ to the total average energy.

Ideal gas: $H = \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m}$

There are $3N$ quadratic degrees of freedom:
the three momenta $\vec{p}_i$ components for each particle

$$\Rightarrow E = \langle H \rangle = \frac{3N}{2} k_B T$$

or average energy per particle

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

as we saw earlier from the simple kinetic theory of the ideal gas

Elastic Vibrations of a Solid

We can imagine the Hamiltonian for the periodic array of atoms in a solid to be

$$H = \sum_i \frac{\vec{p}_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} U(\vec{r}_i - \vec{r}_j)$$

↑
pair wise interactions between the atoms.

The position of atoms can be written as

$$\vec{r}_i = \vec{R}_i + \vec{u}_i \quad \text{where } \vec{R}_i \text{ is its position in the perfect periodic array, and } \vec{u}_i \text{ is a small displacement from this position due to thermal fluctuations}$$

then we can expand

$$\begin{aligned} U(\vec{r}_i - \vec{r}_j) &= U(\vec{R}_i - \vec{R}_j + \vec{u}_i - \vec{u}_j) \\ &= U(\vec{R}_i - \vec{R}_j) + \vec{\nabla} U \cdot (\vec{u}_i - \vec{u}_j) \\ &\quad + \frac{1}{2} \sum_{\alpha, \beta=1}^3 \frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}} (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta}) \end{aligned}$$

Now assuming the positions $\vec{R}_i$ describe a stable equilibrium in the mechanical sense (i.e. the net force on each atom is zero), then $\alpha, \beta = x, y, z$

$$\sum_{i \neq j} \vec{\nabla} U \cdot (\vec{u}_i - \vec{u}_j) = 0$$

otherwise there would be some set of displacements that would lower the energy U

The Hamiltonian is then

$$H = \sum_i \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} \frac{1}{2} \frac{\partial^2 U(\vec{r}_i, \vec{r}_j)}{\partial r_{i\alpha} \partial r_{j\beta}} (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta}) + \text{constant}$$

We see that H is quadratic in the displacements $\vec{u}_i$.
We can rewrite the above as

$$H = \sum_i \frac{p_i^2}{2M} + \sum_{i \neq j} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta}$$

where the "dynamical matrix", D , is related to the $\frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}}$.
One can show that it is always possible to choose "normal coordinates", $\tilde{u}_{i\alpha} = \sum_{j\beta} C_{ij}^{\alpha\beta} u_{j\beta}$, such that the above quadratic form is diagonalized.

(see Ashcroft & Mermin for details)

$$\sum_{i \neq j} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta} = \sum_{i\alpha} \tilde{D}_i^{\alpha} \tilde{u}_{i\alpha}^2$$

Equipartition Theorem then says that each momentum $p_{i\alpha}$ gives $\frac{1}{2} k_B T$, and each normal coord $\tilde{u}_{i\alpha}$ also gives $\frac{1}{2} k_B T$.

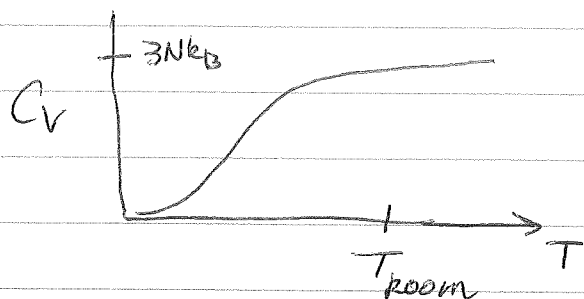
$\Rightarrow$ each of the $6N$ degrees of freedom gives $\frac{1}{2} k_B T$ towards the total average internal energy

$$\Rightarrow E = \langle H \rangle = (6N) \frac{1}{2} k_B T = \boxed{3N k_B T = E}$$

The contribution to the specific heat of a solid, due to atomic vibrations, is therefore

$$C_V = \frac{\partial E}{\partial T} = 3Nk_B \quad \text{Law of Dulong + Petit}$$

The classical result predicts a C_V that is independent of temperature. In real life however, one finds



at low T , see a clear decrease from Dulong-Petit prediction. Unexplainable classically

It was one of the early successes of quantum mechanics to explain why the Law of Dulong Petit fails at low T . This is an interesting example where the effects of quantum mechanics can be observed, not in atomic phenomena, but in the thermodynamics of macroscopic solids! And also observable at room temperature!

We will see the solution to this problem later when we discuss the statistics of bosons

Paramagnetism - Classical spins

N distinguishable spins, we ignore interaction between spins and consider only the interaction of each spin with an external magnetic field $\vec{H}$.

This could be a model for fixed magnetic impurities in a solid. The "spin" is the intrinsic magnetic dipole moment of the magnetic atom, that is fixed to sit at a particular spatial position (that the atoms cannot move is why we consider them distinguishable).

Hamiltonian of the N -spins is

$$H = - \sum_{i=1}^N \vec{\mu}_i \cdot \vec{h} \quad \leftarrow \begin{array}{l} \text{spins are} \\ \text{non-interacting} \end{array}$$

$\uparrow$
spin of atom i

energy is lowest when it is $\parallel$ to $\vec{h}$

$$= -\mu h \sum_{i=1}^N \cos \theta_i$$

where $\mu = |\vec{\mu}_i|$ is fixed and θ_i is angle of $\vec{\mu}_i$ with respect to $\vec{h}$.



Spins are distinguishable

$$\Rightarrow Q_N = (Q_1)^N \quad \text{no factor } \frac{1}{N!}$$

$$Q_1 = \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta e^{\beta\mu h \cos\theta}$$

integrate over all possible states of the single spin $\vec{\mu}$, i.e. over all possible orientations of the vector $\vec{\mu}$.

$$Q_1 = 2\pi \int_0^\pi d\theta \sin\theta e^{\beta\mu h \cos\theta}$$

make substitution of variables

$$x = -\cos\theta$$

$$dx = d\theta \sin\theta$$

$$\theta = 0 \rightarrow x = -1$$

$$\theta = \pi \rightarrow x = +1$$

$$Q_1 = 2\pi \int_{-1}^1 dx e^{\beta\mu h x} = \frac{2\pi}{\beta\mu h} \left[e^{\beta\mu h} - e^{-\beta\mu h} \right]$$

$$= \frac{4\pi}{\beta\mu h} \sinh(\beta\mu h)$$

↑
hyperbolic sin

$$\sinh x = \frac{e^x - e^{-x}}{2}$$