Statistical Physics

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10 Classical statistical mechanics

10.1 Motivation and derivation from quantum mechanics

Several times in the previous chapters we have taken the limit $V/N \gg \lambda^3$, equivalently $e^{-\beta\mu} \gg 1$, calling it interchangeably the high T limit or the classical limit. We always recovered classical results from quantum results. Here we show that we can take this limit directly from the canonical quantum partition function, obtaining a classical partition function which depends on the classical Hamiltonian. In this way, very similar statistical mechanics builds a bridge between microscopic degrees-of-freedom, now taken to be truly classical, and macroscopic thermodynamics. Of course this route historically preceded the quantum treatment we have utilised throughout this course. This is actually a sufficient approach when dealing with the classical regime. We only need the quantum treatment when $V/N \sim \lambda^3$.

Consider for a moment the partition function of a single quantum particle in 1 dimension as the sum of the Boltzmann factor for all microstates r

$$z \;=\; \sum_r e^{-\beta\varepsilon_r} \;=\; \sum_r \langle r|e^{-\beta\hat{H}}|r\rangle \tag{10.1.1}$$

insert 2 complete sets of coordinate eigenstates

$$\begin{aligned} z \;&=\; \sum_r \langle r| \left[\int \mathrm{d}q\,|q\rangle\langle q|\right] e^{-\beta\hat{H}} \left[\int \mathrm{d}q'\,|q'\rangle\langle q'|\right] |r\rangle \\ &=\; \int \mathrm{d}q\,\mathrm{d}q'\,\langle q|e^{-\beta\hat{H}}|q'\rangle \sum_r \langle q'|r\rangle\langle r|q\rangle\,. \end{aligned}$$

Summing over r gives $\langle q'|q\rangle = \delta(q'-q)$, so

$$z \;=\; \int \mathrm{d}q\,\langle q|e^{-\beta\hat{H}}|q\rangle \tag{10.1.2}$$

Let $\hat{H}(\hat{p},\hat{q}) = \hat{K}(\hat{p}) + \hat{V}(\hat{q})$

$$e^{-\beta\hat{H}} \;=\; e^{-\beta\hat{K}(\hat{p})}e^{-\beta\hat{V}(\hat{q})} \;+\; \mathcal{O}(\hbar) \tag{10.1.3}$$

We can only write the exponential of a sum as the product of exponentials if the summands commute. Recalling that $[\hat{q},\hat{p}] = i\hbar$. Then if we are only interested in terms which do not vanish in the $\hbar \to 0$ limit, we can commute coordinate and conjugate momentum operators.

Having separated the kinetic and potential terms, we can evaluate the partition function in the classical limit

$$\begin{aligned} z \;&=\; \int \mathrm{d}q\,e^{-\beta V(q)}\langle q|e^{-\beta\hat{K}(\hat{p})}|q\rangle \\ &=\; \int \mathrm{d}q\,e^{-\beta V(q)}\langle q|\int \mathrm{d}p\,\mathrm{d}p'|p\rangle\langle p|e^{-\beta\hat{K}(\hat{p})}|p'\rangle\langle p'|q\rangle \\ &=\; \int \mathrm{d}q \int \mathrm{d}p\,|\langle q|p\rangle|^2\,e^{-\beta K(p)}e^{-\beta V(q)} \\ &=\; \frac{1}{2\pi\hbar}\int \mathrm{d}q\,\mathrm{d}p\,e^{-\beta H(p,q)} \end{aligned} \tag{10.1.4}$$

$H(p,q)$ is the classical Hamiltonian. Above we used

$$\langle q|p\rangle \;=\; \frac{1}{\sqrt{2\pi\hbar}}\, e^{ipq/\hbar} \tag{10.1.5}$$

Note that (10.1.4) integrates over all points in classical phase space. This is the classical analogue of summing over all quantum microstates. The factor of $1/(2\pi\hbar)$ for each pair of coordinate and conjugate momentum serves to satisfy Nernst's theorem, that the entropy is zero at $T=0$. It is considered to be part of the integration measure. We can drop it at the expense of carrying an additive shift in S.

With the partition function in hand, the development of classical statistical mechanics parallels quantum statistical mechanics. The integrand in (10.1.4) defines the classical statistical distribution function

$$\rho(p,q) \;=\; \frac{1}{z}\, e^{-\beta H(p,q)}\,. \tag{10.1.6}$$

Expectation values are given by

$$\langle f(p,q)\rangle \;=\; \frac{\int \mathrm{d}q\,\mathrm{d}p\, f(p,q)\, e^{-\beta H(p,q)}/(2\pi\hbar)}{\int \mathrm{d}q\,\mathrm{d}p\, e^{-\beta H(p,q)}/(2\pi\hbar)}\,. \tag{10.1.7}$$

For example, the average energy of this 1-particle "system" is given by

$$E \;=\; \langle H(p,q)\rangle \;=\; -\frac{\partial}{\partial\beta}\log z\,. \tag{10.1.8}$$

10.2 Monatomic gas

Consider an ideal classical gas of structureless particles, in other words, a monatomic gas. The Hamiltonian is simply the kinetic energy

$$H \;=\; \sum_{n=1}^{N} \frac{|\mathbf{p}_n|^2}{2m} \tag{10.2.1}$$

where we can take $\mathbf{p}_n$ to be the momentum of the nth particle in D dimensions.

The partition function for the system can be written as the product of N independent single particle partition functions

$$Z = \frac{z^N}{N!} \tag{10.2.2}$$

where

$$\begin{aligned} z \;&=\; \frac{1}{(2\pi\hbar)^D}\int \mathrm{d}^D x\; \mathrm{d}^D p\; e^{-\beta H} && (10.2.3)\\ &=\; \frac{V}{(2\pi\hbar)^D}\prod_{j=1}^{D}\int_{-\infty}^{\infty}\mathrm{d}p_j\; e^{-\beta\, p_j^2/2m} \\ &=\; \frac{V}{(2\pi\hbar)^D}\left(\frac{2m\pi}{\beta}\right)^{D/2} \\ &=\; \frac{V}{\lambda^D} && (10.2.4)\end{aligned}$$

As in our quantum derivation §4.2, the thermal wavelength $\lambda = \sqrt{2\pi\hbar^2/mkT}$ appears.

Yet again we find that

$$E \;=\; -\frac{\partial}{\partial\beta}\log Z \;=\; \frac{D}{2}\,NkT \tag{10.2.5}$$

yields the classical equipartition of energy. This is a consequence of the fact that the momentum components p_j enter the Hamiltonian quadratically.

Often, e.g. in kinetic theory, one works not with momenta, but with velocities

$$\begin{aligned} z \;&=\; \frac{V}{(2\pi\hbar)^D}\int \mathrm{d}^D p\, e^{-\beta|\mathbf{p}|^2/2m} \\ &=\; \frac{m^D V}{(2\pi\hbar)^D}\int \mathrm{d}^D v\, \exp\left(-\frac{m|\mathbf{v}|^2}{2kT}\right) \\ &=\; \frac{m^D V}{(2\pi\hbar)^D}\, S_D \int_0^\infty \mathrm{d}v\, v^{D-1}\, \exp\left(-\frac{mv^2}{2kT}\right) \end{aligned} \tag{10.2.6}$$

where S_D is the surface area of a $D-$dimensional sphere. The integrand in (10.2.6) is the **Maxwell distribution** (Fig. 20)

$$f(v) \;=\; \mathcal{N}\, v^{D-1}\exp\left(-\frac{mv^2}{2kT}\right) \tag{10.2.7}$$

with $\mathcal{N}$ a normalisation factor.

10.3 Diatomic gas

Now consider 2 structureless atoms joined together to make a diatomic molecule. In addition to translational degrees-of-freedom, the molecule can rotate in the dimensions perpendicular to its axis of symmetry.

The Lagrangian is just the kinetic energy

$$L \;=\; K \;=\; \tfrac{1}{2}m|\dot{\mathbf{x}}|^2 \;+\; \tfrac{1}{2}I\left(\dot\theta^2 \;+\; \sin^2\theta\,\dot\phi^2\right) \tag{10.3.1}$$

specialising to 3 dimensions now for simplicity. First we find the momenta conjugate to the generalised coordinates in the Lagrangian

$$p_j \;=\frac{\partial L}{\partial \dot x_j}=\; m\dot x_j \tag{10.3.2}$$

$$p_\theta \;=\frac{\partial L}{\partial \dot\theta}=\; I\,\dot\theta \tag{10.3.3}$$

$$p_\phi \;=\frac{\partial L}{\partial \dot\phi}=\; I\sin^2\theta\,\dot\phi \tag{10.3.4}$$

We obtain the classical Hamiltonian by Legendre transform

$$\begin{aligned} H \;&=\; \sum_j \dot q_j p_j \;-\; L \\ &=\; \dot x_j p_j \;+\; \dot\theta\, p_\theta \;+\; \dot\phi\, p_\phi \;-\; K \\ &=\; \frac{|\mathbf{p}|^2}{2m} \;+\; \frac{p_\theta^2}{2I} \;+\; \frac{p_\phi^2}{2I\sin^2\theta} \end{aligned} \tag{10.3.5}$$

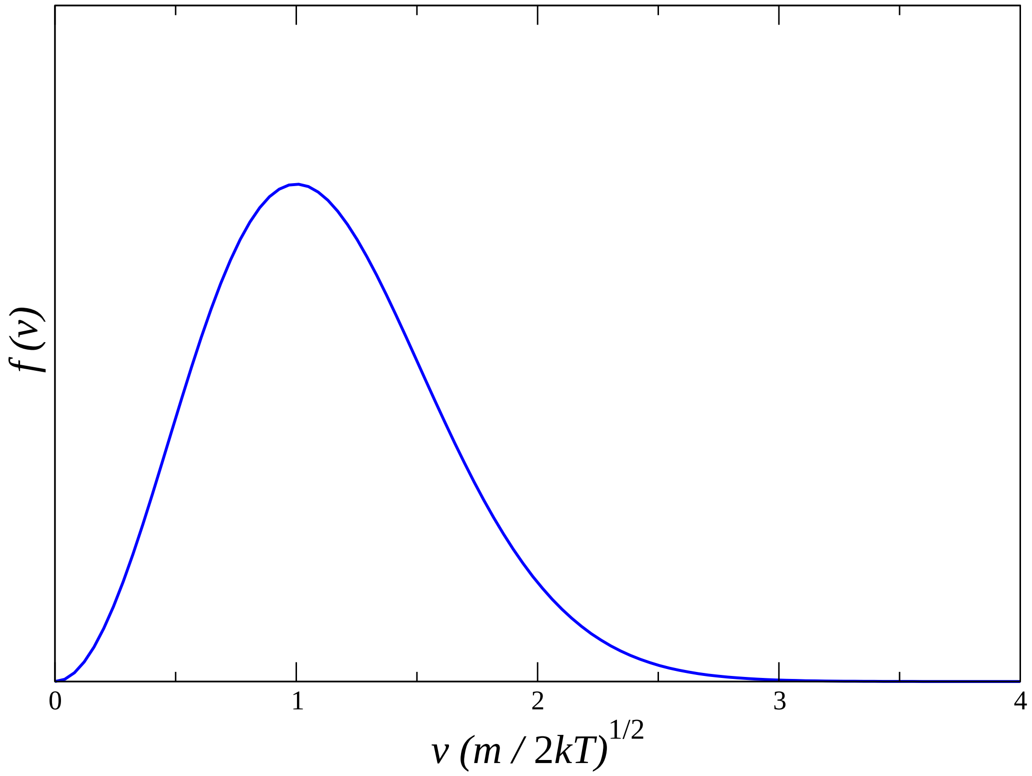

Figure 20: The Maxwell distribution.

The single particle partition function is then

$$z \;=\; \frac{1}{(2\pi\hbar)^5}\int \mathrm{d}^3p\,\mathrm{d}^3x\,\mathrm{d}p_\theta\,\mathrm{d}\theta\,\mathrm{d}p_\phi\,\mathrm{d}\phi\;e^{-\beta H} \tag{10.3.6}$$

We can factorise this into translational and rotational contributions

$$z \;=\; z_t\,z_r \tag{10.3.7}$$

where $z_t = V/\lambda^3$ as in the previous section and

$$z_r \;=\; \frac{1}{(2\pi\hbar)^2}\int \mathrm{d}p_\theta\,\mathrm{d}\theta\,\mathrm{d}p_\phi\,\mathrm{d}\phi\;\exp\left[-\frac{\beta}{2I}\left(p_\theta^2\;+\;\frac{p_\phi^2}{\sin^2\theta}\right)\right] \tag{10.3.8}$$

Doing the momentum integrals we find

$$\begin{aligned} z_r \;&=\; \frac{1}{(2\pi\hbar)^2}\sqrt{\frac{2\pi I}{\beta}}\int_0^\pi \mathrm{d}\theta\sqrt{\frac{2\pi I\sin^2\theta}{\beta}}\;\int_0^{2\pi}\mathrm{d}\phi \\ &=\; \frac{1}{(2\pi\hbar)^2}\,\frac{2\pi I}{\beta}\int_0^\pi \mathrm{d}\theta\,\sin\theta\int_0^{2\pi}\mathrm{d}\phi \;=\; \frac{2I}{\beta\hbar^2} \end{aligned} \tag{10.3.9}$$

Collecting all the factors of kT we find $z = z_t z_r \propto (kT)^{5/2}$. Given that $Z = z^N/N!$ we find the mean energy of a gas of diatomic molecules (with vibrations "frozen")

$$E \;=\; -\frac{\partial}{\partial\beta}\log Z \;=\; \frac{5}{2}NkT \tag{10.3.10}$$

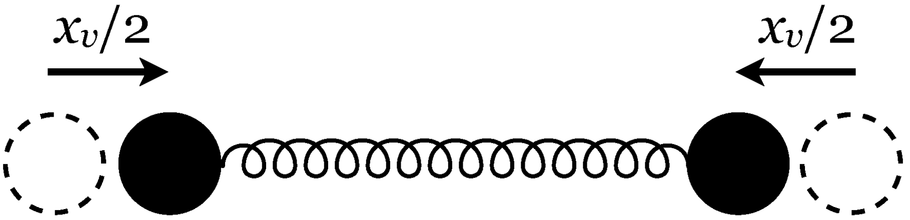

Figure 21: Vibrations in a diatomic molecule. The atoms (solid circles) are each displaced $x_v/2$ from their equilibrium positions (dashed circles); i.e. the energy stored in the spring is $m\omega^2 x_v^2/2$.

as we expect for a system with 3 translational and 2 rotational degrees-of-freedom per particle.

Now we consider vibrations. We can approximate the molecule as a harmonic oscillator (fig. 21). Let x_v be the displacement of the 2 atoms in the molecule away from their vibrational equilibrium state. The vibrational Hamiltonian is

$$H = \frac{p_v^2}{2m} + \frac{1}{2} m\omega^2 x_v^2 \tag{10.3.11}$$

and the single particle contribution to the partition function is

$$\begin{aligned} z_v &= \frac{1}{2\pi\hbar} \int \mathrm{d}p_v \, \mathrm{d}x_v e^{-\beta p_v^2/2m} \, e^{-\beta m \omega^2 x_v^2/2} \\ &= \frac{1}{2\pi\hbar} \sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{m\omega^2\beta}} = \frac{kT}{\hbar\omega} \, . \end{aligned} \tag{10.3.12}$$

Writing

$$Z = \frac{1}{N!} \left(z_t \, z_r \, z_v \right)^N \tag{10.3.13}$$

we find the mean energy of a gas of diatomic molecules to be

$$E = \frac{7}{2} NkT \tag{10.3.14}$$

In addition to the translational and rotational degrees-of-freedom, we add 2 degrees-of-freedom (x_v and p_v) for the harmonic vibrations.

10.4 Magnetism and thermodynamics

In previous discussions of thermodynamics we had 2 independent variables, for example entropy and volume, and 2 dependent variables, pressure and temperature in this example. We can introduce external independent variables like an external magnetic field **B**. The response of the system to this new external variable will be a change in the system energy with some response coefficient. In the case of a magnetic field

$$\mathrm{d}E|_{S,V} \; = \; -\,\mathbf{M}\cdot\mathrm{d}\mathbf{B} \tag{10.4.1}$$

where $\mathbf{M}$ is the **magnetisation**. For the moment we will consider $\mathbf{M}$ parallel to a constant $\mathbf{B}$ for simplicity. In this case

$$\mathrm{d}E \; = \; T\mathrm{d}S \; - \; P\,\mathrm{d}V \; - \; M\,\mathrm{d}B \tag{10.4.2}$$

Recalling that the free energy $F = E - TS = -kT\log Z$ we find

$$\mathrm{d}F \; = \; -\,S\mathrm{d}T \; - \; P\,\mathrm{d}V \; - \; M\,\mathrm{d}B \tag{10.4.3}$$

implies the magnetisation can be calculated as

$$M \; = \; -\left.\frac{\partial F}{\partial B}\right|_{T,V} \; = \; kT\left.\frac{\partial}{\partial B}\log Z\right|_{T,V} \tag{10.4.4}$$

As promised, the magnetisation is the response of the free energy to a varying magnetic field B.

10.5 Model of a paramagnet

Let us consider a solid lattice of N diatomic molecules, each with magnetic dipole moment $\boldsymbol{\mu}$. (Ignore vibrations and translations of any kind.) Then the classical Hamiltonian consists just of the rotational terms from §10.3 plus a term coupling the magnetic moments to an external magnetic field $\mathbf{B}$, taken to be constant here

$$\begin{aligned} H \; &= \; \frac{1}{2I}\left(p_\theta^2 \; + \; \frac{p_\phi^2}{\sin^2\theta}\right) \; - \; \boldsymbol{\mu}\cdot\mathbf{B} && (10.5.1) \\ &= \; \frac{1}{2I}\left(p_\theta^2 \; + \; \frac{p_\phi^2}{\sin^2\theta}\right) \; - \; \mu B\cos\theta\,. && (10.5.2) \end{aligned}$$

In the last step, we chose a spherical polar coordinate system where $\mathbf{B} = B\hat{z}$. The single particle partition function is

$$\begin{aligned} z \; &= \; \frac{1}{(2\pi\hbar)^2}\sqrt{\frac{2\pi I}{\beta}}\sqrt{\frac{2\pi I}{\beta}}\,2\pi\int_0^\pi \sin\theta\,\mathrm{d}\theta\; e^{\beta\mu B\cos\theta} && (10.5.3) \\ &= \; \frac{I}{\beta\hbar^2}\frac{2\sinh y}{y} && (10.5.4) \end{aligned}$$

where $y = \beta\mu B$. The integrals over p_θ and p_ϕ are responsible for the first two square roots in (10.5.3), the integral over ϕ for the 2π, and the integration over θ is done by setting $x = \cos\theta$.

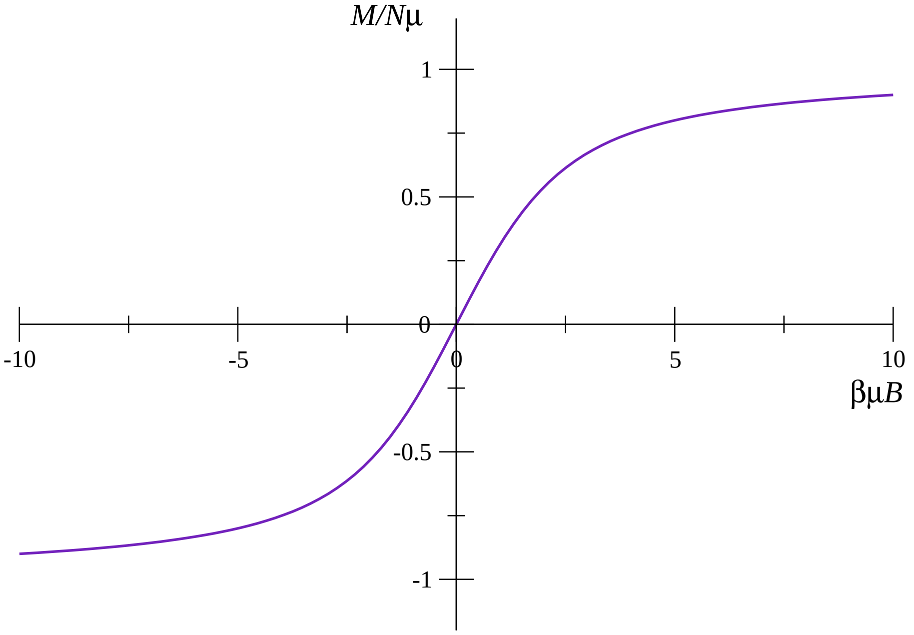

Figure 22: Magnetisation M of a classical paramagnet versus the dimensionless ration $\mu B/kT$.

The magnetisation is calculated from

$$\begin{aligned} M &= kT\,\frac{\partial}{\partial B}\log Z\bigg|_{T,V} && (10.5.5)\\ &= NkT\,\frac{\partial}{\partial B}\log\left(\frac{2I}{\beta\hbar^2}\,\frac{\sinh y}{y}\right) \\ &= NkT\,\frac{\partial}{\partial B}\Big[\log(\sinh y)-\log y\Big] && \text{recall } y=\beta\mu B\\ &= N\mu\left(\coth y-\frac{1}{y}\right)\,. && (10.5.6)\end{aligned}$$

This curve is plotted in Figure 22. For small B or high T, y is small

$$\coth y = \frac{\cosh y}{\sinh y} \simeq \frac{1+\frac{1}{2}y^2}{1+\frac{1}{6}y^3} \simeq \frac{1}{y}+\frac{y}{3} \qquad (10.5.7)$$

Therefore, for small y

$$M = N\mu\frac{y}{3} = \frac{N\mu^2 B}{3kT} \qquad (10.5.8)$$

which is known as **Curie's law**.

Further reading

1. F Reif, *Fundamentals of Thermal and Statistical Physics*, (McGraw-Hill, 1965), Ch. 7.

2. L D Landau and E M Lifshitz, *Statistical Physics*, (Pergamon Press, 1980), §47, §49, §52.
3. R K Pathria, *Statistical Mechanics*, (Pergamon Press, 1985), §3.8.