

STATISTICAL MECHANICS IN QUANTUM THEORY: MOST PROBABLE STATE

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problems 5.26 & 5.27.

We've seen the number of possible configurations in which N particles can be distributed among a set of energy states, where each energy state can be degenerate. There are different formulas for distinguishable particles, fermions and bosons. Although the number of particles n_j in state j is a discrete variable, in practice we can take it to be continuous since, for any macroscopic substance, the numbers involved will be enormous.

The fundamental assumption in statistical mechanics is that all configurations that satisfy the constraints that the total number of particles is N and the total energy is E are equally probable. The most probable distribution, then, is the one with the largest number of configurations. That is, given the number of states $S(\{n_j\})$ as a function of the numbers n_j , we want to find the maximum of this function with respect to variations in n_j , subject to the number and energy constraints above. That is, we want to find solutions of

$$\frac{\partial S}{\partial n_j} = 0 \quad (1)$$

subject to the constraints

$$\sum_{j=1}^{\infty} n_j = N \quad (2)$$

$$\sum_{j=1}^{\infty} n_j E_j = E \quad (3)$$

The standard method for finding the extrema of a function subject to constraints is the method of Lagrange multipliers. We won't derive the method here (it should be covered in any calculus textbook), but we'll state how the method works.

For a function $f(\{x_j\})$ of a set of variables $\{x_j\}$ subject to a number of constraints $c_k(\{x_j\}) = 0$, we form the compound function

$$G \equiv f + \sum_k \lambda_k c_k \quad (4)$$

We now take the derivatives with respect to all the x_j and all the λ_k and set them equal to zero, and then solve the resulting set of simultaneous equations for the x_j and λ_k .

As an example, suppose we want to find the rectangle with the largest area that can be inscribed within an ellipse with equation

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 \quad (5)$$

Since the ellipse is centred at the origin, any rectangle inscribed within it will have its corners at $(\pm x, \pm y)$ and have an area of $A = 4xy$. The problem is then to maximize $4xy$ (or equivalently, just xy) subject to the constraint $c(x, y) = \frac{x^2}{a^2} + \frac{y^2}{b^2} - 1 = 0$. The Lagrange multiplier function is then

$$G = xy + \lambda \left(\frac{x^2}{a^2} + \frac{y^2}{b^2} - 1 \right) \quad (6)$$

The three derivatives are

$$\frac{\partial G}{\partial x} = y + \frac{2x\lambda}{a^2} = 0 \quad (7)$$

$$\frac{\partial G}{\partial y} = x + \frac{2y\lambda}{b^2} = 0 \quad (8)$$

$$\frac{\partial G}{\partial \lambda} = \frac{x^2}{a^2} + \frac{y^2}{b^2} - 1 = 0 \quad (9)$$

(The derivatives with respect to the multipliers λ_k will always just give us the constraint equations.)

We can use the first two equations to eliminate λ and we get

$$\lambda = \pm \frac{ab}{2} \quad (10)$$

$$y = \pm \frac{b}{a}x \quad (11)$$

Substituting the latter equation into the constraint, we get

$$x = \pm \frac{a}{\sqrt{2}} \quad (12)$$

$$y = \pm \frac{b}{\sqrt{2}} \quad (13)$$

The four combinations of these solutions give the four corners of the rectangle, so the resulting area is $A = 2ab$.

Applying this method to distinguishable particles to find the most probable state, we start with the number of states for a given configuration

$$S_d(\{n_j\}) = N! \prod_{j=1}^{\infty} \frac{d_j^{n_j}}{n_j!} \quad (14)$$

where d_j is the degeneracy of the state j . (We've taken the upper limit of the product to be infinity, since for any unoccupied states $n_j = 0$ and $d_j = 1$, so they contribute nothing to the product.)

It turns out it's a bit easier to maximize the logarithm of this function subject to the constraints above, which means the Lagrange function is

$$G = \ln S_d + \alpha \left(N - \sum_{j=1}^{\infty} n_j \right) + \beta \left(E - \sum_{j=1}^{\infty} n_j E_j \right) \quad (15)$$

$$= \ln N! + \sum_{j=1}^{\infty} [n_j \ln d_j - \ln n_j! - \alpha n_j - \beta n_j E_j] + \alpha N + \beta E \quad (16)$$

where α and β are the Lagrange multipliers.

Since we're assuming that n_j is very large, we can use Stirling's approximation for factorials, which is

$$\ln z! \approx z \ln z - z \quad (17)$$

For $z = 10$, the approximation gives $\ln 10! = 13.02585$, while the exact value is $\ln 3,628,800 = 15.1044$. The approximation is thus 86.2% of the actual value.

The smallest integer for which Stirling's approximation comes within 1% the correct value can be worked out by plugging numbers into Maple (most pocket calculators won't calculate factorials higher than 69!), and we find that the first number is 90, where the approximation gives 99.004% of the correct value. Incidentally, although a 1% error may not sound like much, the fact that this is an error in the logarithm means that the factorial itself is incorrect by a factor of about $e^3 \approx 20$.

Returning to our main problem, we now have the approximation:

$$G \approx \ln N! + \sum_{j=1}^{\infty} [n_j \ln d_j - n_j \ln n_j + n_j - \alpha n_j - \beta n_j E_j] + \alpha N + \beta E \quad (18)$$

We can now find the derivative:

$$\frac{\partial G}{\partial n_j} = \ln d_j - \ln n_j - \alpha - \beta E_j = 0 \quad (19)$$

$$n_j = d_j e^{-\alpha - \beta E_j} \quad (20)$$

Finding α and β is a bit trickier, since we need to know the energies E_j and degeneracies d_j . These obviously depend on the potential so it might seem that these parameters will take on different meanings for different potentials. In fact, they turn out to have much the same meaning for all potentials (and in fact, for fermions and bosons too). One day I might get round to posting more about this, but for now we can sketch the argument for the 3-d infinite square well (this is the model we used for the electron gas model of a solid).

When we analyzed this model before, we found that the allowed energies are

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \quad (21)$$

$$= \frac{\hbar^2 k^2}{2m} \quad (22)$$

with

$$k^2 \equiv \frac{\pi^2 n_x^2}{l_x^2} + \frac{\pi^2 n_y^2}{l_y^2} + \frac{\pi^2 n_z^2}{l_z^2} \equiv k_x^2 + k_y^2 + k_z^2 \quad (23)$$

and l_x, l_y, l_z being the dimensions of the box. When this model is applied to a solid, the particles are electrons, which are fermions, so must satisfy the Pauli exclusion principle. We looked at the ground state and found that the energy levels fill an octant in k -space, where each energy state occupies a volume of $\pi^3/l_x l_y l_z = \pi^3/V$.

In the current case, we're dealing with distinguishable particles so there is no exclusion principle. However, the same energy states are available so for a given total energy E , the particles must occupy some combination of states in k -space so that their energy adds up to E . All states with a given value of k^2 have the same energy, so all states within the spherical shell in the first octant with radius between k and $k + dk$ will have energy $E(k)$. That is, the degeneracy is

$$d(k) = \frac{1}{8} \frac{4\pi k^2}{\pi^3/V} dk \quad (24)$$

$$= \frac{k^2 V}{2\pi^2} dk \quad (25)$$

The number constraint then becomes

$$N = \frac{V}{2\pi^2} \int_0^\infty k^2 e^{-\alpha - \beta E(k)} dk \quad (26)$$

$$= \frac{V e^{-\alpha}}{2\pi^2} \int_0^\infty k^2 e^{-\beta \hbar^2 k^2 / 2m} dk \quad (27)$$

$$= \frac{V e^{-\alpha}}{2\pi^2} \sqrt{\frac{\pi}{2}} \left(\frac{m}{\beta \hbar^2} \right)^{3/2} \quad (28)$$

$$= V e^{-\alpha} \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2} \quad (29)$$

$$e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi \beta \hbar^2}{m} \right)^{3/2} \quad (30)$$

The energy constraint is

$$E = \frac{V}{2\pi^2} \int_0^\infty k^2 e^{-\alpha - \beta E(k)} E(k) dk \quad (31)$$

$$= \frac{V \hbar^2 e^{-\alpha}}{4\pi^2 m} \int_0^\infty k^4 e^{-\beta \hbar^2 k^2 / 2m} dk \quad (32)$$

$$= \frac{V \hbar^2 e^{-\alpha}}{4\pi^2 m} \frac{3\sqrt{\pi}}{\sqrt{2}} \left(\frac{m}{\beta \hbar^2} \right)^{5/2} \quad (33)$$

$$= \frac{V \hbar^2}{4\pi^2 m} \frac{3\sqrt{\pi}}{\sqrt{2}} \left(\frac{m}{\beta \hbar^2} \right)^{5/2} \frac{N}{V} \left(\frac{2\pi \beta \hbar^2}{m} \right)^{3/2} \quad (34)$$

$$= \frac{3}{2} \frac{N}{\beta} \quad (35)$$

$$\beta = \frac{3N}{2E} \quad (36)$$

A result from classical physics is that an atom has an energy of $k_B T/2$ for each degree of freedom of motion that it has, where k_B is Boltzmann's constant and T is the absolute temperature. Thus in 3-d, an atom with 3 translational degrees of freedom would have an energy of $3k_B T/2$. From

above, the energy per atom works out to $E/N = 3/2\beta$, so it's natural to identify

$$\beta = \frac{3N}{2E} = \frac{1}{k_B T} \quad (37)$$

This can be shown in more detail, or you can (as Griffiths does) just take this to be the definition of temperature.

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