

Summary of SI1162 Statistical Physics

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Abstract

This is a summary of SI1161 Statistical physics. It contains discussions of the relevant theory.

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1 Handy Mathematics

Stirling's Formula In the limit of large n , Stirling's formula gives

$$\ln n! \approx n \ln n - n.$$

2 Combinatorics

Combinations and permutations Permutations are sequences of some kind. Combinations are permutations where order does not matter. From a collection of n elements, the number of possible permutations of k elements is

$$\Omega = \frac{n!}{(n-k)!}$$

and the number of possible combinations is

$$\Omega = \binom{n}{k}.$$

3 Basic Concepts in Statistical Physics

Avogadro's Number Statistical physics discusses systems of many particles. A relevant measure of the number of particles to be studied is $N_A = 6.022 \times 10^{23}$.

Molar Mass The molar mass of a substance is defined as $M = mN_A$, where m is the mass of a single atom or molecule.

Atomic Units When discussing atoms and molecules, we use relative units. These units are relative to the atomic mass unit a.u. = 1.66×10^{-27} kg, defined as $\frac{1}{12}$ the mass of ^{12}C . This happens to be close to the mass of a hydrogen atom.

The Thermodynamic Limit The thermodynamic limit is the limit of the statistical consideration of a system when the number of particles is large. In this limit, quantities such as temperature, pressure and density can be defined as we know them and macroscopic equilibria can be achieved.

Intensive and Extensive Variables Intensive variables do not depend on the size of the system, whereas extensive variables do. Examples of the former are pressure and temperature, and examples of the latter are volume and total energy.

Heat Heat is the flow of energy.

Microstates A microstate of a system is any complete description of all particles in a system, for instance a specification of all positions and velocities of the particles in a gas.

Macrostates A macrostate of a system is a description of the macroscopic properties of a system.

Multiplicity The multiplicity of a macrostate is the number of microstates that yield the same macrostate.

The Fundamental Postulate The fundamental hypothesis of statistical mechanics is that all microstates available to a system have equal probability.

Equilibrium and Multiplicity Combining the fundamental postulate with our knowledge of thermodynamics, it is clear that a system in thermal equilibrium has maximal multiplicity.

The Boltzmann constant Consider two systems which are not in contact. The total energy and multiplicity is given by

$$E = E_1 + E_2, \quad \Omega = \Omega_1(E_1)\Omega_2(E_2).$$

At equilibrium, the total multiplicity is maximal. Differentiating with respect to E_1 gives

$$\partial_{E_1} \Omega = \Omega_2 \frac{d\Omega_1}{dE_1} + \Omega_1 \frac{d\Omega_2}{dE_2} \frac{dE_2}{dE_1}.$$

The total energy is fixed, yielding

$$\frac{1}{\Omega_1} \frac{d\Omega_1}{dE_1} = \frac{1}{\Omega_2} \frac{d\Omega_2}{dE_2},$$

which we can rewrite as

$$\frac{d \ln \Omega_1}{dE_1} = \frac{d \ln \Omega_2}{dE_2}.$$

We define this to be equal to $\frac{1}{k_b T}$.

The Boltzmann Factor Consider a thermal bath in contact with a small system. The energy of the small system is ε , so that the bath has energy $E - \varepsilon$. Taylor expanding the multiplicity yields

$$\ln \Omega(E - \varepsilon) \approx \ln \Omega(E) - \varepsilon \frac{d \ln \Omega}{dE} = \ln \Omega(E) - \frac{\varepsilon}{k_b T},$$

with solution

$$\Omega(E - \varepsilon) = \Omega(E) e^{-\frac{\varepsilon}{k_b T}}.$$

This exponential factor is called the Boltzmann factor.

We note that the probability of finding the small system in the macrostate with energy ε is, according to the fundamental hypothesis, proportional to $e^{-\frac{\varepsilon}{k_b T}}$.

4 Ensembles

Definition For a given system, an ensemble is a collection of all possible states of the system such that a certain set of quantities are preserved.

The Microcanonical Ensemble The microcanonical ensemble has N , V and E preserved.

The Canonical Ensemble The canonical ensemble has N , V and T preserved.

Grand Canonical Ensembles The grand canonical ensemble has μ , V and T preserved.

5 Gases

The Maxwell-Boltzmann Velocity Distribution Consider a system of n (approximately) non-interacting particles. Assuming the separations to be much larger than the particle size and neglecting rotational and vibrational degrees of freedom, each particle has total energy $E = \frac{1}{2}mv^2$. We can now treat each particle as a small system in contact with a heat reservoir (namely the other particles). The results concerning the Boltzmann factor thus hold for this molecule. A single velocity component is thus described by the probability distribution

$$g(v_i) = \sqrt{\frac{m}{2\pi k_b T}} e^{-\frac{mv_i^2}{2k_b T}}.$$

This is of course true for all particles in the gas, meaning that the fraction of molecules with v_i in the range v_i to $v_i + dv_i$ is equal to $g(v_i) dv_i$.

It can be shown that

$$\langle v_i \rangle = 0, \quad \langle |v_i| \rangle = \sqrt{\frac{2k_b T}{m}}, \quad \langle v_i^2 \rangle = \frac{k_b T}{m}.$$

The Maxwell-Boltzmann Speed Distribution Consider instead the distribution of the particle speed. The distribution satisfying that the fraction of particles with speed in the range v to $v + dv$ is

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_b T} \right)^{\frac{3}{2}} v^2 e^{-\frac{v^2}{2k_b T}},$$

where the quadratic factor arises due to the integration volume.

It can be shown that

$$\langle v \rangle = \sqrt{\frac{8k_b T}{\pi m}}, \quad \langle v^2 \rangle = \frac{3k_b T}{m}$$

and that f has a maximum for

$$v = \sqrt{\frac{2k_b T}{m}}.$$

Directions and the Speed Distribution Because the velocity distribution is isotropic, the fraction of molecules whose trajectories lie in some solid angle range $d\Omega$ is given by $\frac{d\Omega}{4\pi}$. In three dimensions we can choose some direction and define an azimuthal angle θ relative to that direction, yielding that a fraction

$$\frac{1}{2} n f(v) \sin \theta dv d\theta$$

are travelling close to the angle θ to the chosen direction with a speed close to v per unit volume (n is the amount of particles per volume).

The Ideal Gas Law Consider a wall with area A with a gas on one side. In a time interval dt the molecules travelling at angle θ to the wall normal sweep out a volume $A \cos \theta v dt$. This means that the number of molecules hitting the wall during dt is given by

$$A \cos \theta v dt \cdot \frac{1}{2} n f(v) \sin \theta dv d\theta.$$

Per unit area this number becomes

$$\cos \theta v dt \cdot \frac{1}{2} n f(v) \sin \theta dv d\theta.$$

Each particle imparts a momentum $2mv \cos \theta$ to the wall. The total momentum imparted to the wall per unit area by particles travelling at a specified speed and direction is thus

$$2mv \cos \theta \cdot \cos \theta v dt \cdot \frac{1}{2} n f(v) \sin \theta dv d\theta,$$

meaning that the impulse per area, i.e. the pressure, from these particles is

$$dp = 2mv \cos \theta \cdot \cos \theta v \cdot \frac{1}{2} n f(v) \sin \theta dv d\theta.$$

Integrating this, the total pressure is

$$p = \frac{1}{3} n m \langle v^2 \rangle = n k_b T.$$

Using the fact that $n = \frac{N}{V}$ we finally obtain the ideal gas law

$$pV = N k_b T.$$

Dalton's Law For a mixture of ideal gases, the partial pressures of each gas can be added. This is due to the fact that the number of particles can be added.

Gas Flux and Effusion We define the particle flux of a gas as the number of molecules striking a unit area per time. We can integrate a previously obtained expression to obtain

$$\Phi = \frac{p}{\sqrt{2\pi m k_b T}}.$$

The velocity distribution of molecules effusing out of a container is modified by a factor v . This can be noted from the form of the expression for the number of particles striking a unit area.

Collision Time Consider a gas, where we (for now) treat all particles but one as stationary. This particle has velocity v and collision cross-section σ (to be discussed later, but it is essentially the area of the particle with which other particles can collide). In a time dt the particle sweeps out an area $\sigma v dt$, meaning that a collision occurs within dt is $n\sigma v dt$. We define $P(t)$ to be the probability of the particle not colliding up to time t . According to our reasoning, we must have $P(t + dt) = P(t)(1 - n\sigma v dt)$. Comparing this to a Taylor expansion of P , we obtain

$$P(t) + dP = P(t)(1 - n\sigma v dt).$$

This has the solution

$$P(t) = e^{-n\sigma v t},$$

assuming our consideration started at $t = 0$. The probability of not colliding up to t and colliding during the next dt is

$$P'(t) = n\sigma v e^{-n\sigma v t},$$

which is normalized. Using this, we compute the collision time

$$\tau = \frac{1}{n\sigma v}.$$

Collision Cross-Section Consider two spherical particles of radius a_1 and a_2 interacting with a hard-sphere potential. Imagining a particle of type 1 moving in the vicinity of type 2 particles, the movement of the type 1 particle sweeps out a tube of radius $a_1 + a_2$ such that if type 2 particles enter the tube, a collision occurs. The area of this tube is the collision cross-section, and is in this case given by

$$\sigma = \pi(a_1 + a_2)^2.$$

Mean Free Path The mean free path is the mean distance a particle can move without colliding. It should be proportional to the collision time and some velocity, but which velocity? It turns out that to include the effects of all particles moving, we must use the relative velocity between the considered particle and the other particles. We have

$$v_r^2 = v_1^2 + v_2^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2.$$

The expected value of the cross-term is 0 due to symmetry, and hence

$$\langle v_r^2 \rangle = 2 \langle v^2 \rangle.$$

We approximate $\langle v_r \rangle$ and $\langle v \rangle$ to be their RMS counterparts. Hence the mean free path is

$$\lambda = \langle v_r \rangle \tau = \frac{\sqrt{\langle v_r^2 \rangle}}{n\sigma v} = \frac{\sqrt{2} \langle v \rangle}{n\sigma v} = \frac{1}{\sqrt{2}n\sigma} = \frac{k_b T}{\sqrt{2}p\sigma}.$$