



AN ELEMENTARY APPROACH TO QUANTUM STATISTICAL PROBLEMS



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Introduction

In order to derive the relation between macroscopic thermodynamic quantities and the quantum mechanical properties of atoms or atomic unions, statistical thermodynamics is usually applied. It is considered a necessary means of solving problems of this type because »classical thermodynamics as a *macroscopic* theory is not able to make statements about atomic systems on principle«. To correct this entrenched prejudice is the aim of this presentation.

Prerequisites

Apart from the well-known relations of quantum mechanics, only the chemical potential and its concentration and energy dependence are needed (the added names may ease quotation):

$$\mu = \underbrace{\mu_0 + RT \ln \frac{c}{c_0}}_{\text{»massing term«}} \quad \text{»mass action formula«,}$$

$$\mu(\varepsilon) = \underbrace{\mu(0) + \frac{\varepsilon}{\tau}}_{\text{»boosting term«}} \quad \text{»excitation formula.«}$$

The second equation is valid on condition that all molecules of a substance are put into an activated state, which is higher in energy by the same value ε , without otherwise altering them or their environment (type of solvent, temperature, pressure, concentrations, field strengths etc.; $\tau = 1.661 \cdot 10^{-24}$ mol is the amount of substance n represented by one particle [1]).

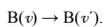
Applications

1. Freezing of a molecular vibration

We take a diatomic gas B and consider all gas particles, being in the same state of vibration with the vibrational quantum number v , as molecules of a substance B(v) and the entire gas as a mixture of these substances [2]. For sake of simplicity we regard the vibration as harmonic and the energy levels as equidistant $\varepsilon(v) = v \cdot h\nu$ (ν frequency, h Planck constant). Since the different substances B(v) are not distinguishable chemically, we assign to them — apart from the »boosting term« $\varepsilon(v)/\tau$ — the same standard potential μ_0 :

$$\mu_0(v) = \mu_0(0) + \frac{v \cdot h\nu}{\tau}$$

Changes of the state of vibration caused by collisions between the particles appear as reactions of the following type



All these reactions will be in equilibrium within a short period of time. The chemical potential μ becomes identical for all substances:

$$\underbrace{\mu = \mu(0)}_{\mu_0(0) + RT \ln \frac{c(0)}{c_0}} = \underbrace{\mu(v)}_{\mu_0(v) + RT \ln \frac{c(v)}{c_0}} \quad \text{»mass action formula«}$$

$$\underbrace{\mu_0(0) + RT \ln \frac{c(0)}{c_0}}_{\mu_0(0) + \frac{v \cdot h\nu}{\tau}} = \underbrace{\mu_0(v) + RT \ln \frac{c(v)}{c_0}}_{\mu_0(0) + \frac{v \cdot h\nu}{\tau}} \quad \text{»excitation formula«}$$

By resolving the equation for $c(v)$ and replacing $R\tau$ with k (Boltzmann constant) we obtain

$$c(v) = c(0) \cdot e^{-\frac{h\nu}{kT} v} = c(0) \cdot a^v$$

$a < 1$

By summing up all $c(v)$ we derive for the total concentration c of gas B:

$$c = \sum_{v=0}^{\infty} c(0) \cdot a^v = c(0) \cdot \frac{1}{1-a} = c(0) \cdot \frac{1}{1 - e^{-h\nu/(kT)}}$$

q_{vib}

q_{vib} is the partition function for a linear harmonic vibrator. For the fraction $x(0) = c(0)/c$ of the molecules B(0) in the ground state we find (fig. 1):

$$x(0) = 1 - e^{-\frac{h\nu}{kT}}$$

If we reversely introduce $c(0) = c \cdot x(0)$ into the »mass action formula« for substance B(0), we get:

$$\mu = \underbrace{\mu_0(0) + RT \ln \left(1 - e^{-h\nu/(kT)}\right)}_{\mu_{\text{vib}}(T)} + RT \ln \frac{c}{c_0}$$

The term $\mu_{\text{vib}}(T)$ describes the contribution of the molecular vibration to the chemical potential of B.

By derivation once or twice with respect to T we may derive a relation for the contribution of the molecular vibration to the molar entropy $S_{\text{vib}} = -d\mu_{\text{vib}}/dT$, or to the molar heat capacity $C_{\text{vib}} = -T(d^2\mu_{\text{vib}}/dT^2)$ respectively (fig. 2).

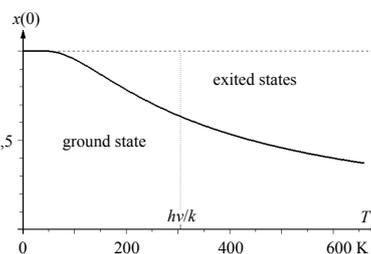


Fig. 1: Freezing of a molecular vibration. The curve shows for I₂ vapour the fraction $x(0)$ of the number of molecules in the ground state of vibration ($v=0$) related to the total number of I₂ molecules. For temperatures below 50 K practically all molecules are in the ground state.

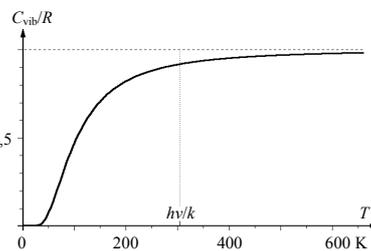


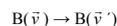
Fig. 2: Freezing of a molecular vibration. Contribution C_{vib} of the molecular vibration to the molar heat capacity of I₂ vapour.

2. Molecular speed distribution

To determine the distribution of the molecular velocities in a gas, we regard all particles with the same velocity \vec{v} as molecules of a substance B(\vec{v}) and the entire gas as a mixture of many such substances. Different energies $\varepsilon(\vec{v}) = \frac{1}{2}mv^2$ caused by different velocities $v = |\vec{v}|$ are taken into account by a corresponding »boosting term« $\varepsilon(\vec{v})/\tau = \frac{1}{2}Mv^2$ (m mass of a particle, $m/\tau = M$ molar mass of substance B). Since particles which are moving with different speeds or in different directions are not distinguishable chemically, we assign to them — apart from the term $\varepsilon(\vec{v})/\tau$ — the same standard potential μ_0 :

$$\mu_0(\vec{v}) = \mu_0(0) + \frac{1}{2}Mv^2$$

The velocity modifications, caused by multiple collisions between each other or with the walls, appear as a reaction of the following type:



In equilibrium, the chemical potential becomes identical for all substances B(\vec{v}):

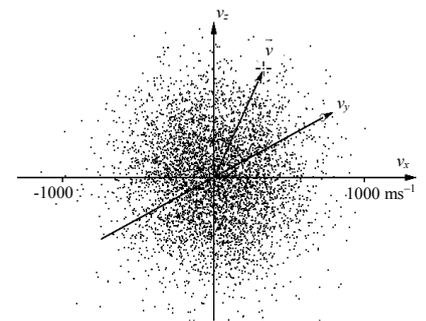
$$\underbrace{\mu = \mu(0)}_{\mu_0(0) + RT \ln \frac{c(0)}{c_0}} = \underbrace{\mu(\vec{v})}_{\mu_0(\vec{v}) + RT \ln \frac{c(\vec{v})}{c_0}} \quad \text{»mass action formula«}$$

$$\underbrace{\mu_0(0) + RT \ln \frac{c(0)}{c_0}}_{\mu_0(0) + \frac{1}{2}Mv^2} = \underbrace{\mu_0(\vec{v}) + RT \ln \frac{c(\vec{v})}{c_0}}_{\mu_0(0) + \frac{1}{2}Mv^2} \quad \text{»excitation formula«}$$

If this equation is resolved for $c(\vec{v})$, we attain the distribution law ($M/R = m/k$):

$$c(\vec{v}) = c(0) \cdot \exp\left(-\frac{\frac{1}{2}Mv^2}{RT}\right) \Rightarrow c(\vec{v}) = c(0) \cdot e^{-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}}$$

If we plot the concentration $c(\vec{v})$ of the particles with equal velocity \vec{v} as point density in the three-dimensional velocity space, we get a spherical point cloud shown in figure 3.



3. Boltzmann distribution

We choose again a (mono- or polyatomic) gas B, and consider all gas particles, being in the same state (ε, i) as molecules of a substance B(ε, i) and the entire gas as a mixture of these substances in equilibrium (i. e. μ identical for all components). The parameter i , that we take to be discrete, stands for some characteristic (spatial orientation, spin orientation, conformation, etc.) by which — apart from the energy ε — the individual types of particles can be distinguished. Now we interpret the concentration $c(\varepsilon, i)$ of the substance B(ε, i) as a measure of the probability $p(\varepsilon, i)$ to find a molecule B in the state (ε, i) . That means formally $p(\varepsilon, i) \sim c(\varepsilon, i)$. One needs only to combine our two starting formulas and solve for $c(\varepsilon, i)$ in order to get the desired result:

$$\mu = \underbrace{\mu_0(\varepsilon, i) + RT \ln \frac{c(\varepsilon, i)}{c_0}}_{\mu_0(0,0) + \frac{\varepsilon}{\tau}} \quad \text{»mass action formula«}$$

$$c(\varepsilon, i) = c_0 \cdot \exp\left(\frac{\mu - \mu_0(0,0)}{RT}\right) \cdot e^{-\frac{\varepsilon}{kT}} \Rightarrow p(\varepsilon, i) = e^{-\frac{\varepsilon}{kT}}$$

Outlook

The chosen examples presented here are simple. We skipped over details, which seem to be less important in this context, to emphasize the basic idea. The same approach can be used in many other cases including systems of macroscopic or microscopic dimensions, of non-interacting or interacting particles, of fermions or bosons. Surface chemistry gives us clear examples of systems with Fermi-Dirac and Bose-Einstein distributions and therefore recommends itself for a start into this subject. Some further examples may be mentioned:

- Contribution of translation, rotation, vibration to the thermodynamic properties of ideal gases
- Van der Waals gas
- Barometric altitude formula
- Equilibrium of sedimentation in a centrifuge
- Single-layer and multi-layer adsorption
- Fermi-Dirac and Bose-Einstein distributions
- Black body radiation
- Double layers on electrode surfaces
- Theory of inter-ionic interaction
- Properties of paramagnetic substances
- Debye model for the heat capacity of solids

[1] $\tau = 1.661 \cdot 10^{-24}$ mol represents the elementary quantum of the amount of substance n , like $e = 1.602 \cdot 10^{-19}$ C the elementary quantum of the amount of electricity Q . To use the reciprocal $\tau = N_A$ instead of the AVOGADRO constant N_A was suggested first by G. Falk: *Konzepte eines zeitgenössischen Physikalischen Lehrbuchs*, Teil 2, Schroedel, Hannover (1978) p. 9.

[2] To regard substances as equilibrium mixtures as above has a long tradition (see for instance A. EINSTEIN, *Verhandlungen der Deutschen Physikalischen Gesellschaft* 12 (1914) 820).