

Statistical Thermodynamics. Objectives of the Theory

- Creating a bridge between theory of the microworld (theory of individual molecules and their interactions) and theory of macroscopic phenomena
- Explanation (quantitative) of the properties of macroscopic systems (e.g. thermodynamic functions) using the knowledge of the properties of individual molecules (obtained from molecular spectroscopy or quantum chemistry)
- Providing rigorous definitions of thermodynamic quantities and derivations of the laws of thermodynamics from the laws of quantum mechanics
- Obtaining information on the properties of single molecules and their interaction from the knowledge of macroscopic (bulk) properties of matter (mainly of historical significance)

Example

Phenomenological thermodynamics (Boyle, Carnot, Joule, Clausius) :

Free energy (Helmholtz): $F(T, V) = E - TS$.

$$\begin{aligned} dF &= -S dT - p dV \\ &\Downarrow \\ S &= - \left(\frac{\partial F}{\partial T} \right)_V & p &= - \left(\frac{\partial F}{\partial V} \right)_T \\ &\Downarrow \\ \left(\frac{\partial S}{\partial V} \right)_T &= \left(\frac{\partial p}{\partial T} \right)_V \end{aligned}$$

The functions $S = S(T, V)$ i $p = p(T, V)$ for any substance.

Statistical thermodynamics (Maxwell, Boltzmann, Einstein, Smoluchowski):

Free energy: $F = -kT \ln Q$, where $Q = \sum_I e^{-E_I/kT}$ (statistical sum)

In the case of the gas of N atoms of mass m we have:

$$p(T, V) = \frac{NkT}{V}, \quad S(T, V) = Nk \ln \frac{(2\pi mkT)^{3/2} V}{h^3 N} + \frac{5}{2} Nk$$

Statistical Thermodynamics. Subject of Research

Using the universal constants (such as k , h , c , e , m_e) and „material parameters” specific for the molecules of the considered substance, such as:

- masses and spins of atomic nuclei (<http://www.nist.gov>)
- molecular bond lengths
- angles between the bonds
- force constants
- electronic excitation energies
- intermolecular potentials

the formalism of statistical thermodynamics allows us to predict:

- thermodynamic functions (entropy, free enthalpy, heat capacity, etc.)
- equilibrium constants
- equation of state
- rates of chemical reactions
- electric and magnetic properties of molecules
- temperatures and heats of phase transitions
- parameters characterizing critical phenomena

Statistical Thermodynamics. Subfields of Theory

Statistical thermodynamics, and generally statistical mechanics is a very large field in exact sciences. It can be divided into:

- classical statistical thermodynamics
- quantum statistical thermodynamics

or into:

- statistical thermodynamics of equilibrium states
- statistical thermodynamics of irreversible processes

With regards to calculation techniques we have a different division:

- theories using analytical
- computer simulation methods (Monte Carlo, molecular dynamics).

Recommended literature:

1. F. Reif *Fizyka statystyczna*, PWN, 1973. Chapters. 3, 4, 6. (available in English)
2. H. Buchowski *Elementy termodynamiki statystycznej*, WNT, 1998. Rozdz. 1, 3.
3. R. Hołyst, A. Poniewierski, A. Ciach *Termodynamika*, WNT, 2005, Rozdz. 13, 16, 17, 18.

Specific properties of macroscopic systems

Macroscopic systems exhibit three important properties (features) distinguishing them from microscopic systems:

1. In macroscopic systems occur irreversible processes leading to equilibrium states in which the properties of the system do not depend on time (and there are no mass flows).
2. The equilibrium states are uniquely specified by a very small number of parameters (for one-component systems only three parameters are sufficient, e.g. T, V, N).
3. Properties of macroscopic systems are in general random variables with small relative fluctuations. Usually these fluctuations decrease with the size of the system as $1/\sqrt{N}$.

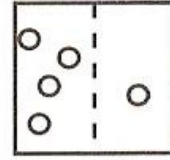
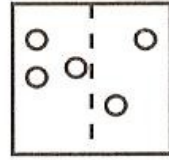
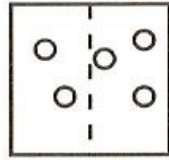
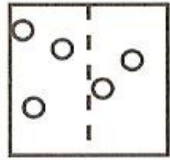
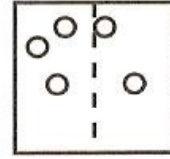
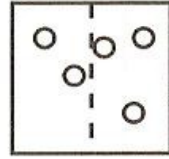
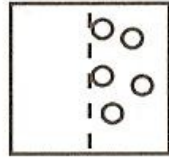
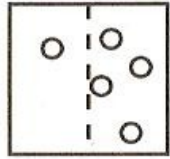
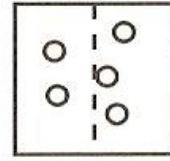
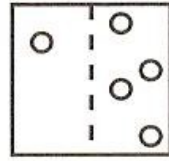
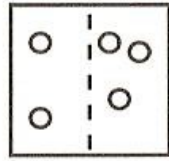
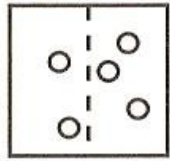
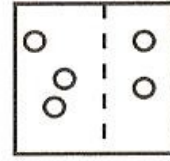
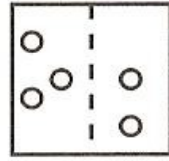
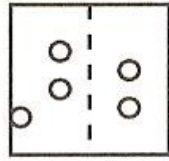
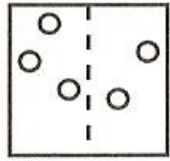
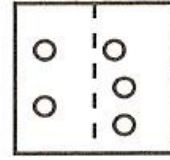
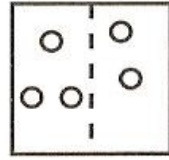
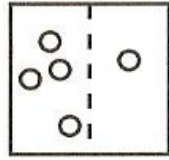
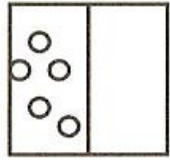
Relative fluctuation $\delta(X)$ of random variable X is defined as :

$$\delta(X) = \frac{\sqrt{\sigma^2(X)}}{\langle X \rangle} = \frac{\sigma(X)}{\langle X \rangle}$$

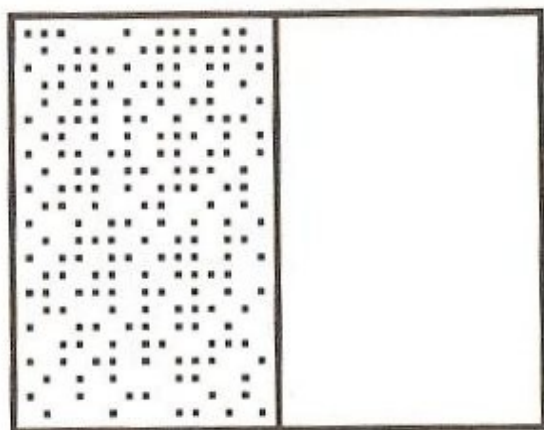
where $\langle X \rangle$ denotes the average value of the variable X , and $\sigma^2(X)$ is the **variance** of this variable (the square of the **standard deviation** σ):

$$\sigma^2(X) = \langle (X - \langle X \rangle)^2 \rangle = \langle X^2 \rangle - \langle X \rangle^2$$

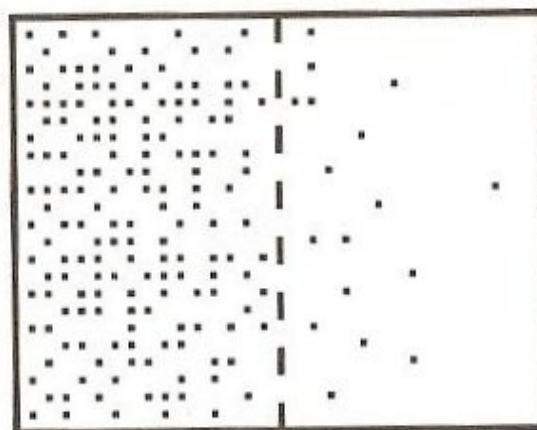
Property 1 contradicts the Poincare theorem, which states the any confined dynamical system of finite energy returns arbitrarily close to its initial state.



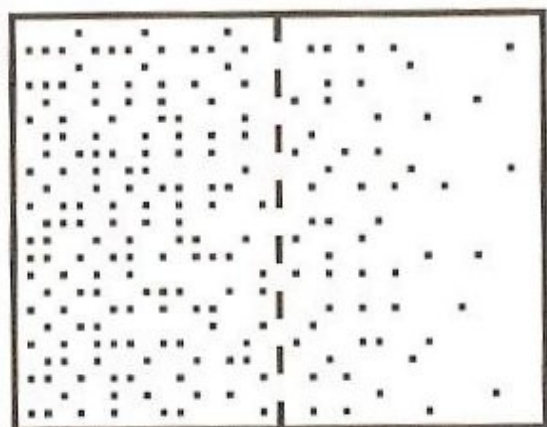
Irreversible process: decompression of the gas of 200 atoms into the vacuum



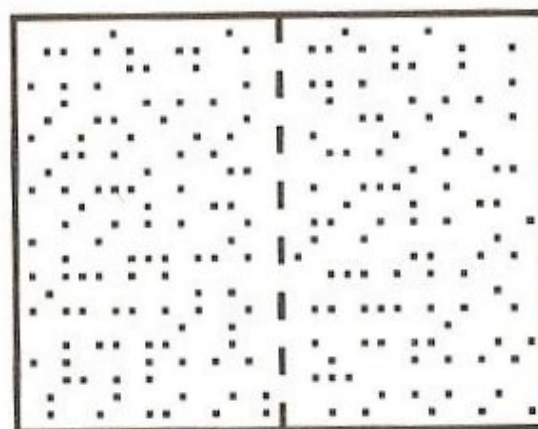
(a)



(b)



(c)

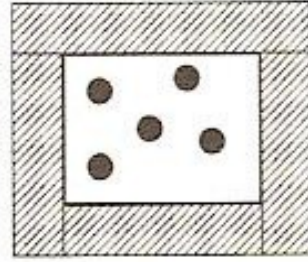


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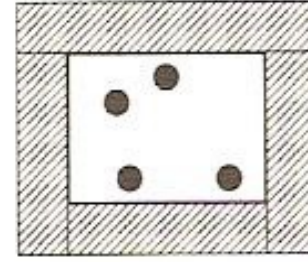
Density fluctuations, experiment



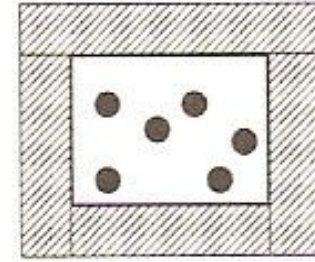
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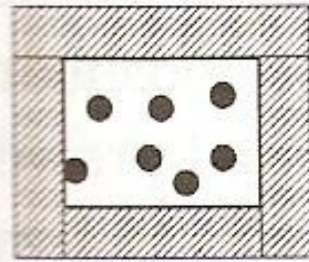
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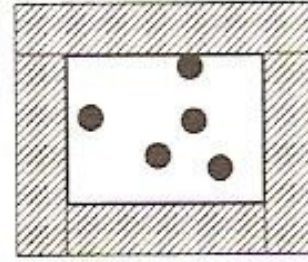
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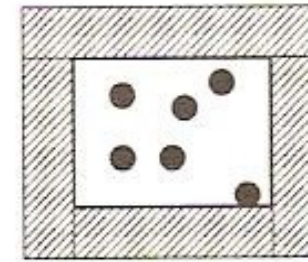
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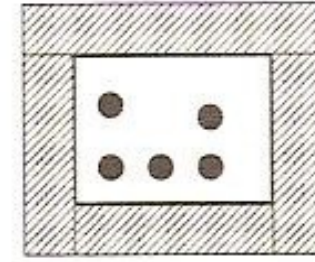
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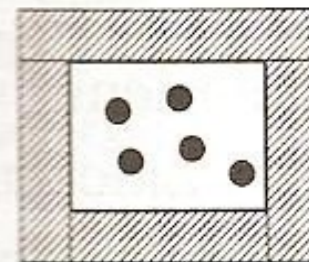
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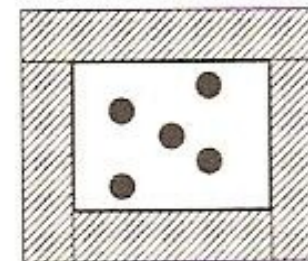
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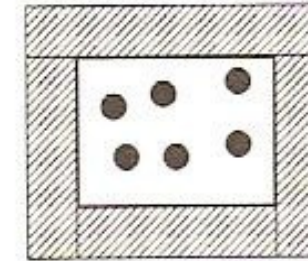
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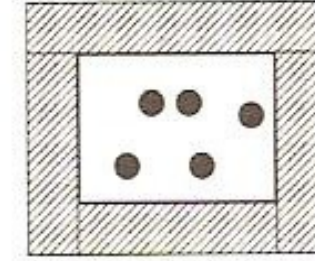
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Density fluctuations, theory

As an example we compute the fluctuation of the number of particles in a small volume element v in a larger container of volume V .

If we had only one particle then:

$$P_{n=1} = v/V \equiv p \quad P_{n=0} = 1 - v/V \equiv 1 - p \quad P_{n>1} = 0,$$

where $P_{n=k}$ denotes the probability of finding k particles in volume v . Thus,

$$\langle n \rangle = \langle n^2 \rangle = 0 \cdot (1 - p) + 1 \cdot p = p$$

$$\sigma^2(n) = \langle n^2 \rangle - \langle n \rangle^2 = p - p^2 = p(1 - p)$$

If we have N particles then $P_{n=k}$, $\langle n \rangle$ and $\sigma^2(n)$ can be obtained from the Bernoulli distribution but there is not need for that. It is sufficient to define N **independent random variables** n_i , where n_i is the number of particles with the number (label) i in the volume v :

$$n = \sum_{i=1}^N n_i$$

Then

$$\langle n_i \rangle = p, \quad \sigma^2(n_i) = p(1 - p), \quad \langle n \rangle = Np, \quad \sigma^2(n) = Np(1 - p)$$

and finally

$$\delta(n) = \frac{\sqrt{\sigma^2(n)}}{\langle n \rangle} = \sqrt{\frac{1 - p}{Np}} = \sqrt{\frac{1 - p}{\langle n \rangle}}$$

Postulates and three most important probability distributions

Definitions:

Macrostate: is defined as the macroscopic state of the system specified by a small number of parameters need to defined it

Microrstate: is defined as a specific quantum state of the system (in quantum mechanics) or a small cell in the phase space (in classical machanics)

Postulates:

Postulate 1: In a isolated macroscopic system spontaneous processes occur such that the number of possible microstates increases

Postulate 2: If an isolated system (of fixed energy) is in a state of equilibrium then

all microstates of this energy are equally probable

Distributions (Ensembles) :

1. Microcanonical. For isolated system. Fixed E, V, N .
2. Canonical (Gibbs). For thermostatic system. Fixed T, V, N .
3. Grand canonical (Gibbs). For open systems. Fixed μ, T, V , where μ denotes the chemical potential.

Microcanonical distribution

Definition: **The number of states $\Omega(E, V, N)$** is the number of microstates of the system of volume V , particle number N and constant energy (contained in the interval from E to $E+\delta E$, $\delta E=10^{-30}\text{J}$).

Definition: **Statistical (quantum) definition of the temperature**

$$\frac{1}{kT} = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{V,N}$$

Definition: **Empirical definition of the temperature ($T_{t.p.}=273.16\text{ K}$)**

$$T = \frac{1}{k} \lim_{p \rightarrow 0} \frac{pV}{N}$$

Definition: **S Statistical (quantum) definition of entropy (Boltzmann, Planck)**

$$S = k \ln \Omega$$

Definicja: **Statistical (quantum) definition of pressure**

$$p = kT \left(\frac{\partial \ln \Omega}{\partial V} \right)_{E,N}$$

Canonical distribution (Gibbs)

A thermostatic system with temperature T does not have a fixed energy. Such a system can be in a quantum state i of energy E_i with probability:

$$P_i = \frac{1}{Q} e^{-E_i/kT}$$

$$Q = \sum_i e^{-E_i/kT}$$

where $Q=Q(T, V, N)$ is the statistical sum. Knowing the statistical sum we can easily obtain all thermodynamic functions of the system, for instance:

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V \qquad S = k \ln Q + \frac{E}{T}$$

$$p = kT \left(\frac{\partial \ln Q}{\partial V} \right)_T \qquad F = -kT \ln Q$$

Canonical distribution, c.d.

If we neglect the interaction between molecules and **if the temperature T is not too low** then Q has a particularly simple form:

$$Q = \frac{q^N}{N!}$$

where N is the number of molecules in the system, and q is the statistical sum for a single molecule, called also the **molecular partition function**

$$q = \sum_i e^{-\epsilon_i/kT}$$

In the definition of the partition function q the summation i goes over all quantum states ψ_i with energy ϵ_i of a single molecule

For rigid molecules q is approximately equal to the product

$$q = q_{\text{tr}} q_{\text{rot}} q_{\text{vib}} q_{\text{el}} q_{\text{nucl}}$$

of partition functions corresponding to various degrees of freedom

- translational q_{tr}
- rotational q_{rot}
- vibrational q_{vib}
- electronic q_{el}
- nuclear q_{nucl}

Canonical distribution. Calculation of the partition function q_{tr}

The factorization of Q is possible when the energy ϵ_i of the i th quantum state can be represented as a sum of the energy of translation, rotation, vibration, etc.

$$\epsilon_i = \epsilon_{n_1 n_2 n_3}^{\text{tr}} + \epsilon_{JKM}^{\text{rot}} + \epsilon_{v_1 \dots v_f}^{\text{vib}} + \epsilon_l^{\text{el}} + \epsilon_\lambda^{\text{nucl}}$$

The function q_{tr} q_{rot} q_{vib} , etc. are defined formally in the same way as q , for instance the translational partition function q_{tr} has the form:

$$q_{\text{tr}} = \sum_{n_1 n_2 n_3}^{\infty} \exp(-\epsilon_{n_1 n_2 n_3}^{\text{tr}}/kT),$$

where the energies of the translational excitations are given by the formula for the energies of a particle in the box of volume $V = L^3$:

$$\epsilon_{n_1 n_2 n_3}^{\text{tr}} = \frac{h^2}{8mL^2} (n_1^2 + n_2^2 + n_3^2)$$

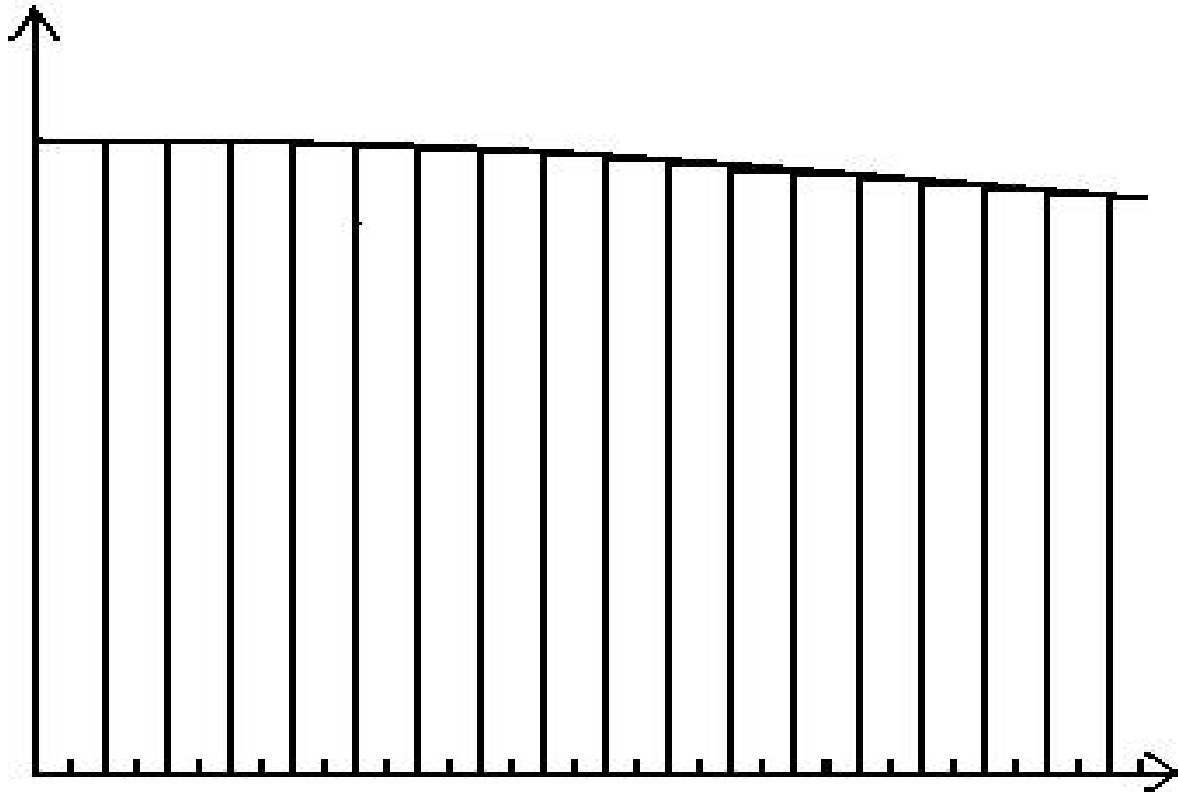
The summation over n_1, n_2, n_3 can be factorized and replaced by integration:

$$q_{\text{tr}} = \sum_{n_1 n_2 n_3}^{\infty} \exp\left(-\frac{n_1^2 + n_2^2 + n_3^2}{a^2}\right) = \left[\sum_n^{\infty} \exp\left(-\frac{n^2}{a^2}\right) \right]^3 = \left[\int_0^{\infty} \exp\left(-\frac{x^2}{a^2}\right) dx \right]^3 = \frac{\pi^{3/2} a^3}{8}$$

where $a = \sqrt{8mkT} L/h$.

Replacing summation by integration

$$\sum_{n=1}^{\infty} \exp(-n^2/a^2) \approx \int_0^{\infty} \exp(-x^2/a^2) dx = \frac{\sqrt{\pi a}}{2} \quad \text{when } a \gg 1$$



Canonical distribution. Calculation of the partition function q_{tr}

After the substitution $a = \sqrt{8mkT} L/h$ we find

$$q_{\text{tr}} = (2\pi mkT)^{3/2} \frac{V}{h^3}$$

or

$$q_{\text{tr}} = \frac{V}{\lambda_B^3}, \quad \text{where } \lambda_B = \frac{h}{\sqrt{2\pi mkT}}$$

is the so called **thermal de Broglie wave length**.

One can now calculate the translational statistical sum $Q_{\text{tr}} = (q_{\text{tr}})^N / N!$, the translational part of the internal energy E^{tr} , heat capacity C_V^{tr} , entropy S^{tr} :

Calculation of E^{tr} is particularly simple. It is enough to notice that $Q_{\text{tr}} \sim T^{3N/2}$.

We find :

$$E^{\text{tr}} = \frac{3}{2} NkT \quad C_V^{\text{tr}} = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk$$

$$S^{\text{tr}} = Nk \ln \frac{(2\pi mkT)^{3/2} V}{h^3 N} + \frac{5}{2} Nk = Nk \ln \frac{v}{\lambda_B^3} + \frac{5}{2} Nk,$$

where $v = V/N$. This is the Sackur-Tetredde equation - applicable when $v > \lambda_B^3$.

Canonical distribution. Rotation of heteronuclear diatomics

For linear molecules the energies of rotational excitations are given by:

$$\epsilon_J^{\text{rot}} = \frac{\hbar^2}{2I} J(J+1)$$

where I is the moment of inertia of a molecule ($I = \mu R^2$ for diatomics)

The rotational partition function is thus given by the formula

$$q_{\text{rot}} = \sum_{J=0}^{\infty} \sum_{M=-J}^J e^{-\epsilon_J^{\text{rot}}/kT} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\frac{\Theta_{\text{rot}}}{T}} \approx \frac{T}{\gamma \Theta_{\text{rot}}}$$

valid for $T \gg \Theta_{\text{rot}}$ where Θ_{rot} is the characteristic temperature of rotations

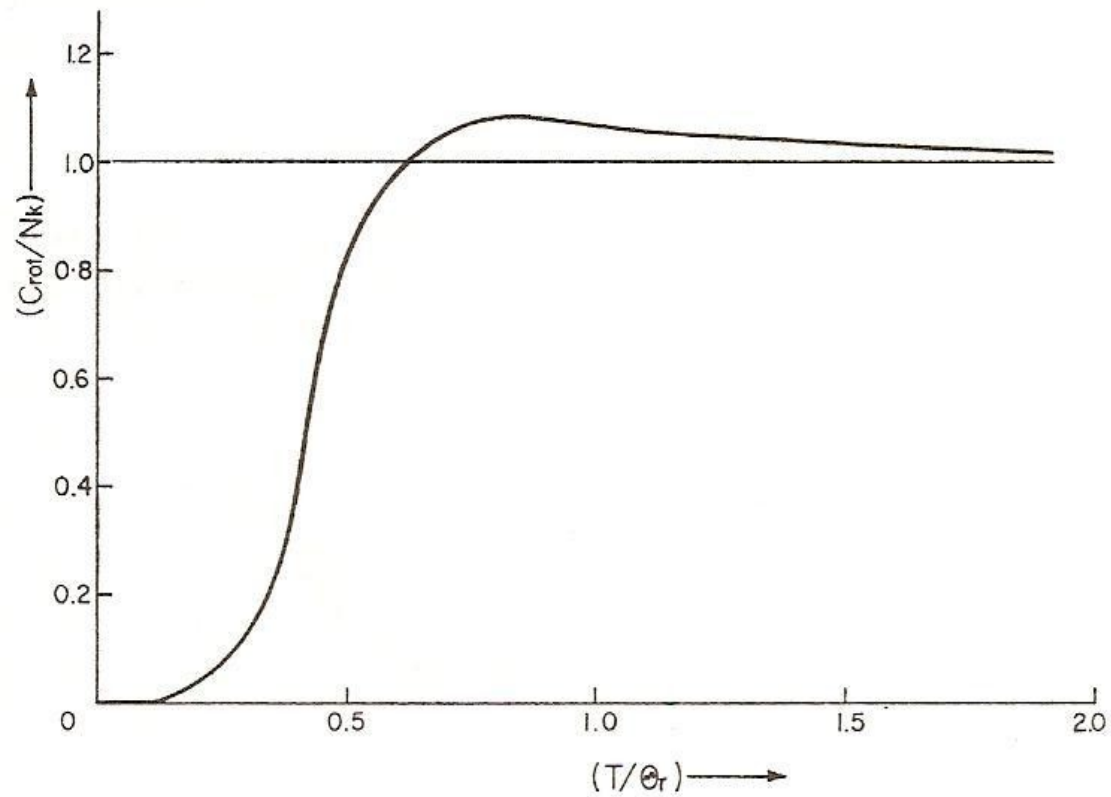
$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik}$$

This large- T formula is applicable also to homonuclear molecules with $\gamma = 2$ (for heteronuclear ones $\gamma = 1$). For $T \leq \Theta_{\text{rot}}$ the series converges very quickly. Most often $T \gg \Theta_{\text{rot}}$ since Θ_{rot} is of the order 1 K or less. For H_2 , $\Theta_{\text{rot}} = 85$ K.

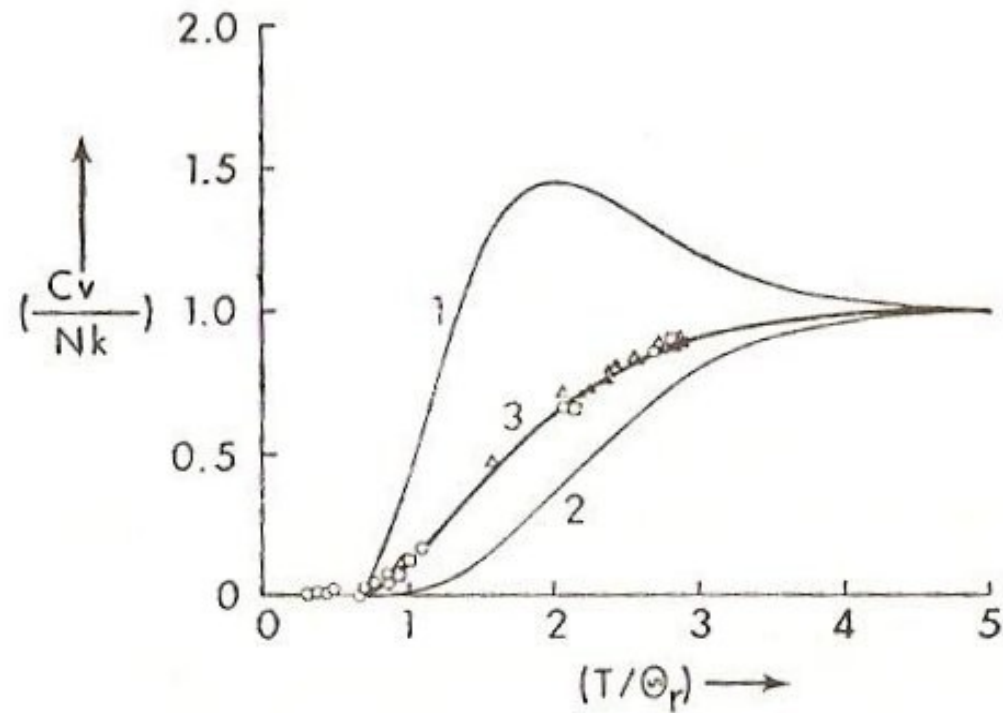
$$E^{\text{rot}} = NkT \quad C_V^{\text{rot}} = \left(\frac{\partial E}{\partial T} \right)_V = Nk$$

$$S^{\text{rot}} = Nk \ln \frac{T}{\gamma \Theta_{\text{rot}}} + Nk,$$

Rotational heat capacity. Heteronuclear molecule



Hear capacity of para (1), orto (2), and 1:3 para-orto mixture (3) for hydrogen



Para hydrogen $S_{\text{nucl}}=0, J = 0, 2, 4, 6, \dots$

Orto hydrogen $S_{\text{nucl}}=1, J = 1, 3, 5, 7, \dots$

Canonical distribution. Molecular vibration of a diatomic

For diatomic molecules the vibrational energy is given by the formula:

$$\epsilon_{\text{vib}} = nh\nu$$

The vibrational partition function takes then the form:

$$q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\frac{nh\nu}{kT}} = \frac{1}{1 - e^{-\Theta_v/T}},$$

where Θ_{vib} is the characteristic temperature of vibration

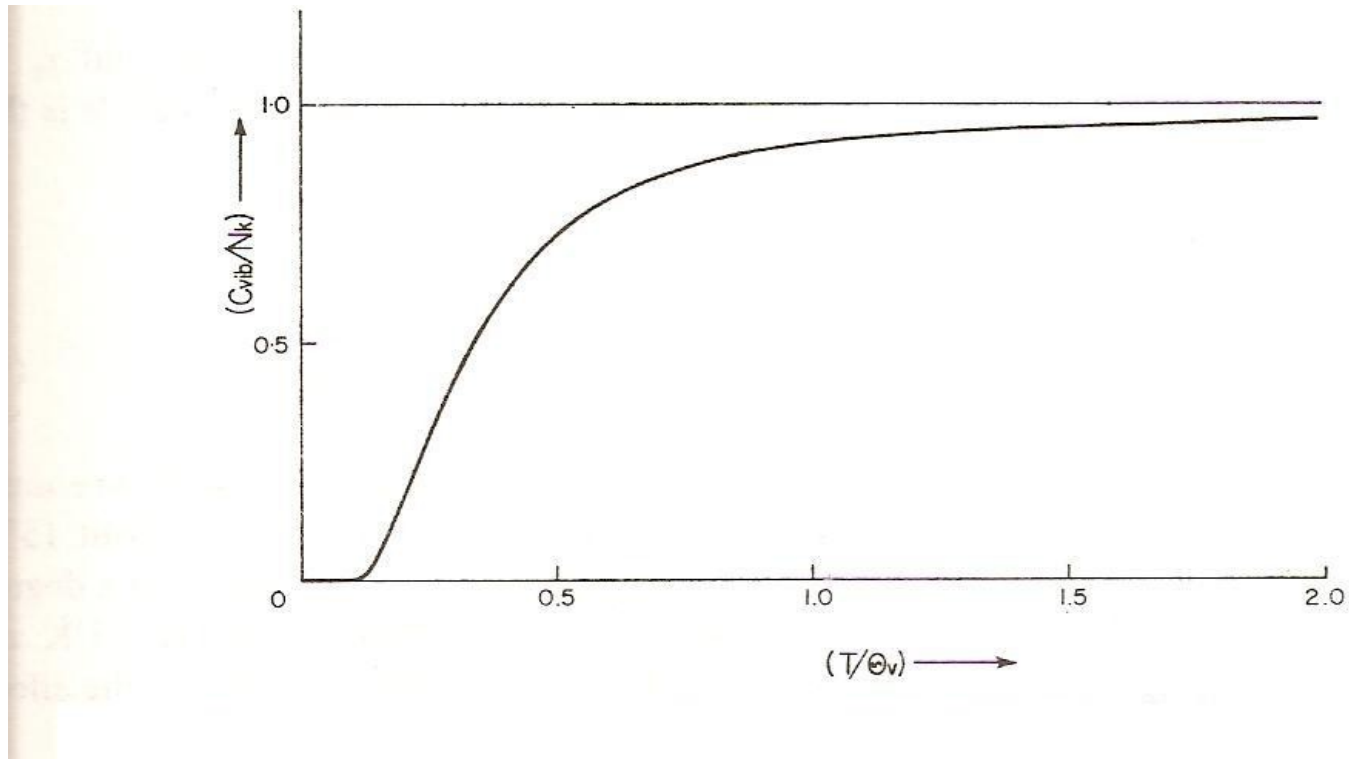
$$\Theta_v = \frac{h\nu}{k}$$

Temperatures Θ_{vib} are high: $\Theta_{\text{vib}} \approx 6000$ K for H_2 , $\Theta_{\text{vib}} \approx 3000$ K for N_2 or CO .

For the vibrational contributions to the internal energy and heat capacity we get:

$$E_{\text{vib}} = \frac{Nh\nu}{e^{h\nu/kT} - 1} \quad \Rightarrow \quad C_V^{\text{vib}} = Nk \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

Vibrational heat capacity for a diatomic molecule or for one normal mode of a polyatomic molecule



Canonical distribution. Rotations of polyatomic molecules

For a spherical, symmetric, or asymmetric top one can derive for high T :

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\gamma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}},$$

where Θ_A , Θ_B , i Θ_C are characteristic temperatures

$$\Theta_A = \frac{\hbar^2}{2I_A k}, \quad \Theta_B = \frac{\hbar^2}{2I_B k}, \quad \Theta_C = \frac{\hbar^2}{2I_C k}$$

This formula is valid only when $T \gg \Theta_A$, $T \gg \Theta_B$, and $T \gg \Theta_C$.

I_A , I_B and I_C are moments of inertia relative to principal axes of a molecule and γ is the *symmetry number* equal to the number of permutations of identical nuclei which can be effected by a rotation: $\gamma=n$ for the C_{nv} , $\gamma=2n$ for the D_{nh} , $\gamma=12$ for the T_d , $\gamma=24$ for the O_h symmetry group.

Since $Q_{\text{rot}}=(q_{\text{rot}})^N$ the thermodynamic functions are:

$$E^{\text{rot}} = \frac{3}{2} N k T \quad C_V^{\text{rot}} = \frac{3}{2} N k$$

$$S^{\text{rot}} = N k \ln \left[\frac{\sqrt{\pi}}{\gamma} \sqrt{\frac{T^3}{\Theta_x \Theta_y \Theta_z}} \right] + \frac{3}{2} N k,$$

Canonical distribution. Vibrations of polyatomic molecules

For a polyatomic molecule with f normal modes of vibrations with frequencies ν_j the vibration energy is the sum of energies of all modes. Therefore, q_{vib} must be a product:

$$q_{\text{vib}} = \prod_{j=1}^f \frac{1}{1 - e^{-h\nu_j/kT}}$$

The internal energy and heat capacity per one molecule are sums of contributions from each normal mode:

$$E_{\text{vib}} = \sum_{j=1}^f \frac{h\nu_j}{e^{h\nu_j/kT} - 1}$$

A crystal consisting of N atoms can be treated as a one big molecule with $f=3N$ normal modes. If we assume that all these modes have the same frequency equal ν_E then

$$E_{\text{vib}} = 3N \frac{h\nu_E}{e^{h\nu_E/kT} - 1} \quad C_V^{\text{vib}} = 3Nk \left(\frac{h\nu_E}{kT} \right)^2 \frac{e^{h\nu_E/kT}}{(e^{h\nu_E/kT} - 1)^2}$$

This is Einstein's theory of the heat capacity of crystals - quite good for intermediate and high temperatures but poor for low temperatures.

Debye's theory of heat capacity of crystals

The assumption that all frequencies in the crystals are identical is too drastic. In reality there exists a distribution of frequencies given by the function $g(\nu)$ such that

$g(\nu)d\nu =$ the number of normal modes with frequencies between ν and $\nu+d\nu$

The sum over all normal modes can then be given by the integral:

$$E_{\text{vib}} = \int_0^{\nu_{\text{max}}} \frac{h\nu g(\nu) d\nu}{\exp(h\nu/kT) - 1}$$

Debye assumed that

$$g(\nu) = 4\pi V \left(\frac{1}{c_l} + \frac{2}{c_t} \right) \nu^2 = A\nu^2 \quad \text{for} \quad \nu < \nu_{\text{max}}$$

where c_l i c_t are the longitudinal and transverse sound velocities in the crystal. Then:

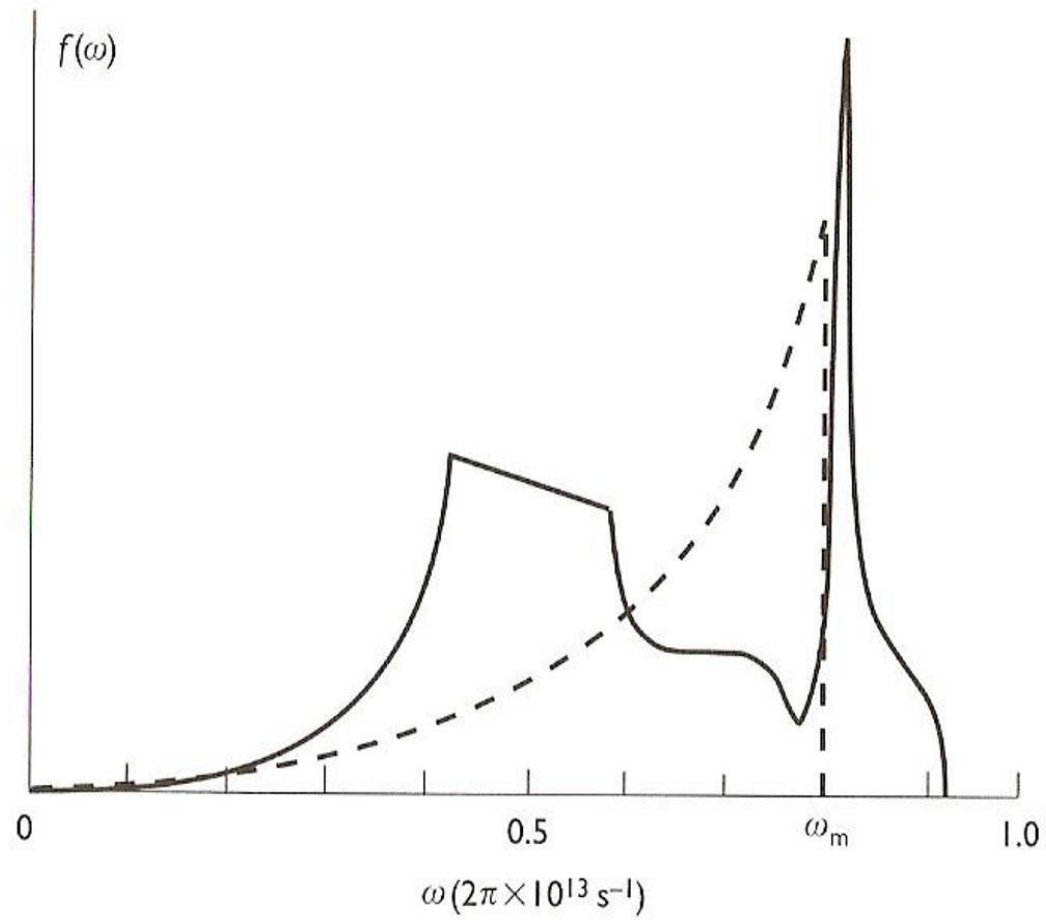
$$E_{\text{vib}} = A \int_0^{\nu_{\text{max}}} \frac{h\nu^3 d\nu}{\exp(h\nu/kT) - 1} = A \frac{k^4 T^4}{h^3} \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1}$$

where $\Theta_D = h\nu_{\text{max}}/h$ is the so called Debye temperature. When $T \ll \Theta_D$ then:

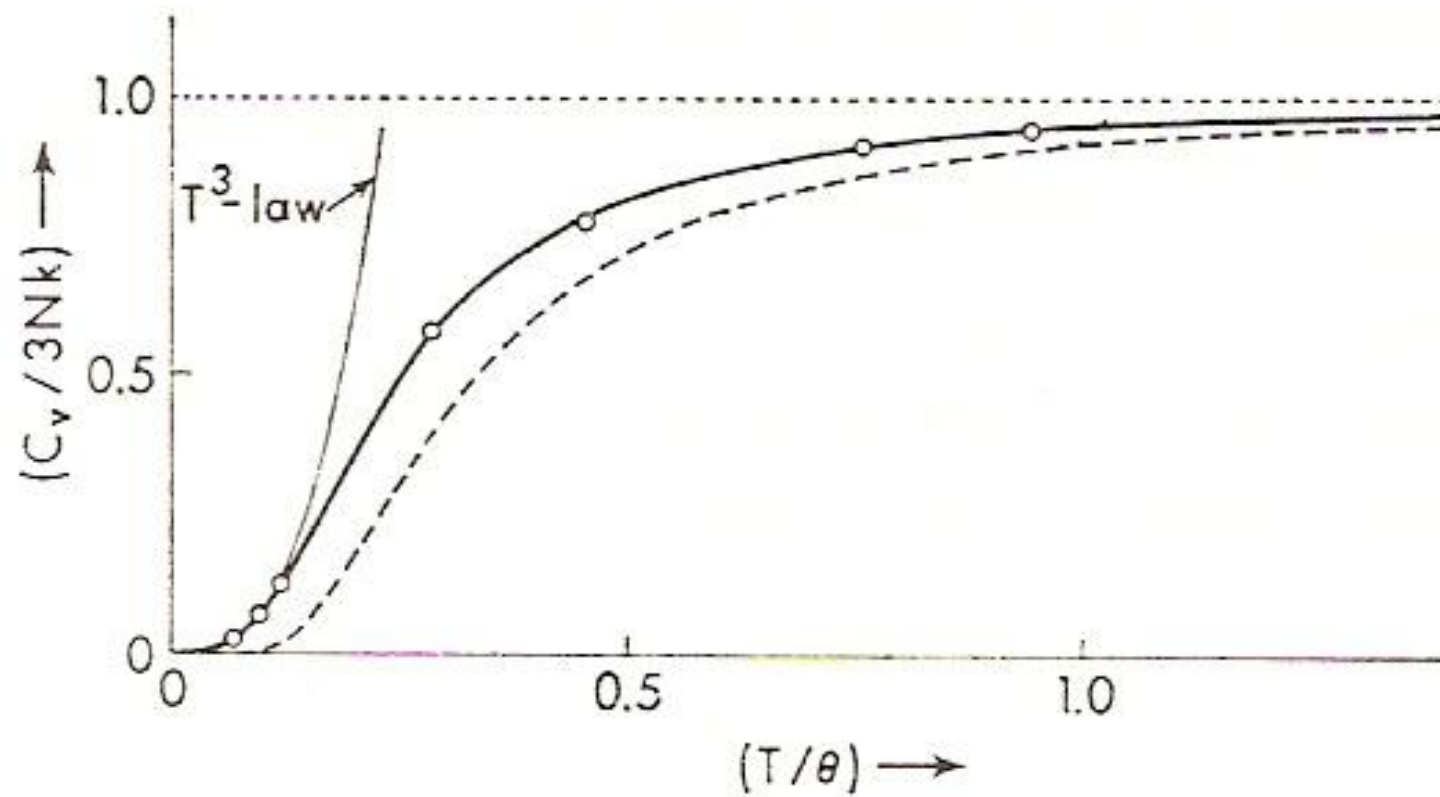
$$E_{\text{vib}} \sim T^4 \quad \text{oraz} \quad C_V \sim T^3.$$

When $\nu_{\text{max}} = \infty$ (photons) we get the Planck distribution and the Stefan law.

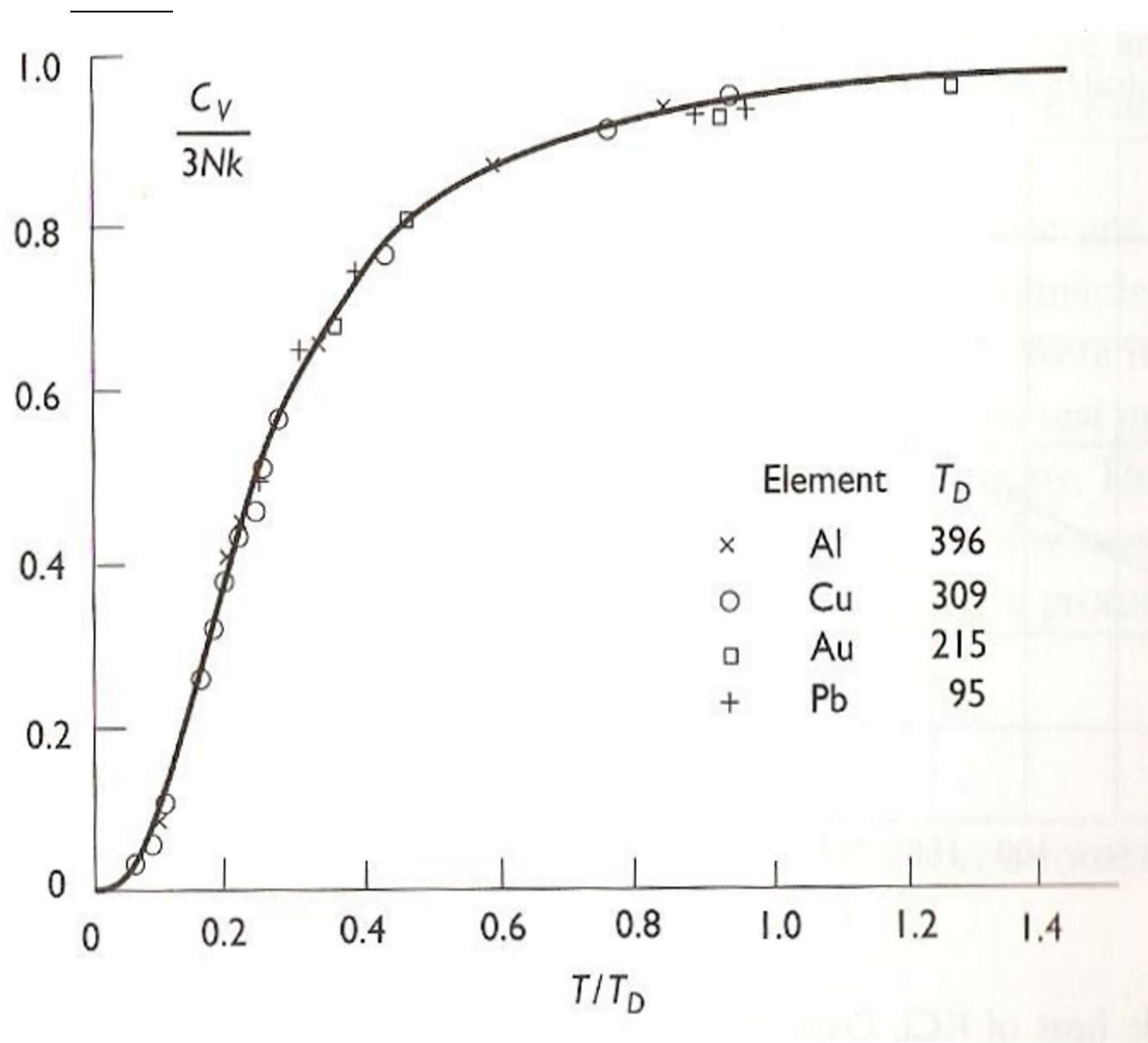
Spectral function $g(\nu)$ in a crystal



Comparison of Einstein's and Debye's theories

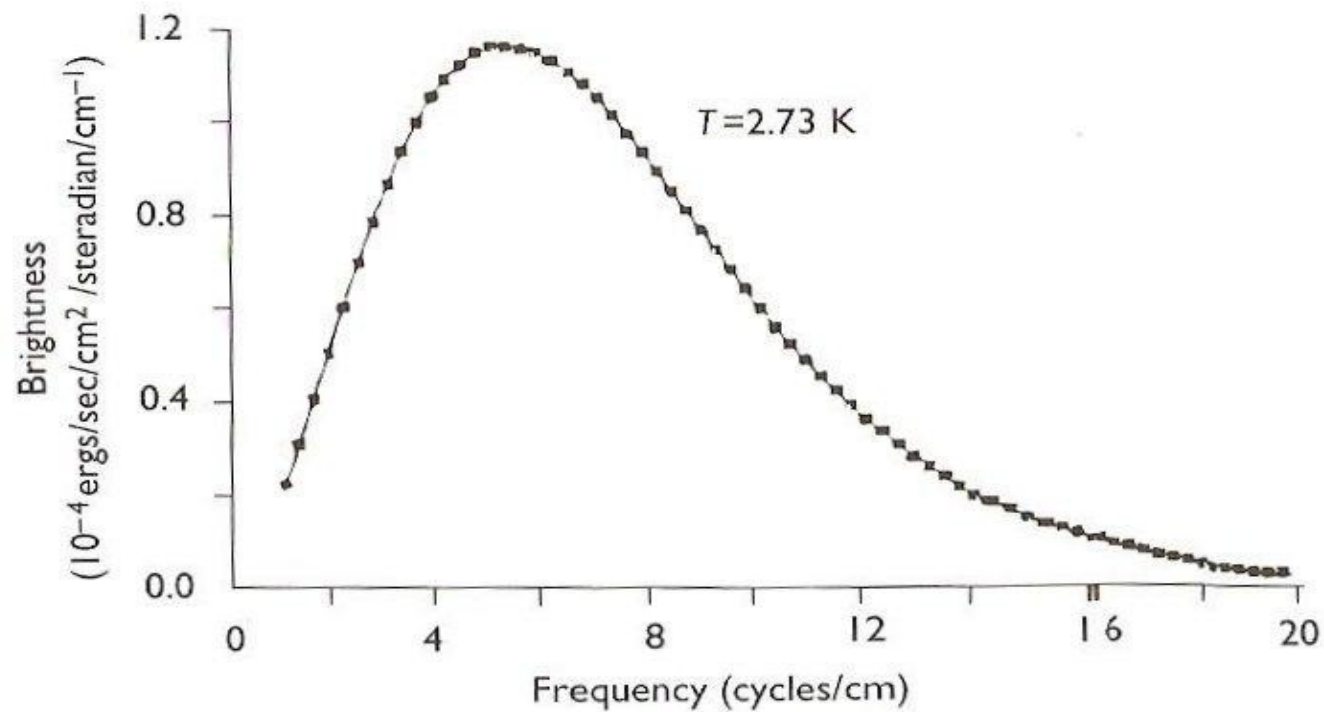


Comparison of Debye theory with experiment



Spectrum of relict radiation from a big-bang. $T=2.73\text{K}$

Comparison with Planck's distribution



Canonical distribution. Electronic excitations

Electronic partition function is computed directly from its definition performing the summation over relevant electronic states.

$$q_{\text{el}} = \sum_i e^{-\epsilon_i^{\text{el}}/kT}$$

Usually it is sufficient to include only the lowest electronic states resulting from the spin-orbit coupling. For example, for the NO molecule the ground electronic state $^2\Pi$ splits into two states $^2\Pi_{3/2}$ i $^2\Pi_{1/2}$ differing by the excitation energy equal to $\Delta\epsilon^{\text{el}}/k=178$ K. For NO q_{el} has then the form:

$$q_{\text{el}} = 2 + 2e^{-\Theta_{\text{el}}/T}$$

where $\Theta_{\text{el}} = 178$ K. Such partition function gives at $T=178$ K a characteristic maximum on the heat capacity as a function of temperature, known as Schottky anomaly.

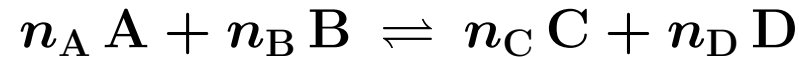
If the nuclei have a spin different from zero (e.g. the nitrogen or deuterium) then to the product of all partition functions we have to include the factor of the nuclear partition function

$$q_{\text{nucl}} = \prod_j (2s_j + 1),$$

where s_j is the spin of the j th nucleus.

Canonical distribution. Application to chemical equilibrium

The equilibrium constant for the chemical reaction



in the gas phase is defined as follows:

$$K_p(T) = \frac{p_C^{n_C} p_D^{n_D}}{p_A^{n_A} p_B^{n_B}},$$

where X is the partial pressure of substance X , $X=A, B, C, D$, and n_X is its stoichiometric coefficient. $K_p(T)$ is the *equilibrium constant in terms of pressures*. It is useful to consider also the *equilibrium constant in terms of particle numbers* $K_N(T)$, defined analogously as $K_p(T)$, but with partial pressures replaced by numbers of molecules N_X of substances:

$$K_N(T) = \frac{N_C^{n_C} N_D^{n_D}}{N_A^{n_A} N_B^{n_B}},$$

Using the equation $p = NkT/V$ connecting partial pressures with particle numbers it is easy to show that these two equilibrium constants are related as follows

$$K_p(T) = \left(\frac{kT}{V} \right)^{n_C+n_D-n_A-n_B} K_N(T).$$

Canonical distribution. Application to chemical equilibrium

Using the canonical (Gibbs) distribution one can derive the following, basic formula for the equilibrium constant $K_N(T)$:

$$K_N(T) = \frac{\tilde{q}_C^{n_C} \tilde{q}_D^{n_D}}{\tilde{q}_A^{n_A} \tilde{q}_B^{n_B}},$$

where \tilde{q}_X is the *partition function* of molecule X defined formally the same way as before

$$\tilde{q} = \sum_i e^{-\tilde{\epsilon}_i/kT}$$

but with molecular energy levels $\tilde{\epsilon}_i$ measured relative to the energy of free, separated atoms (rather than relative to the energy of the ground state of a molecule). The energy of separated atoms is higher than E_0 and differs from E_0 by the atomization energy D_0 (energy of dissociation into atoms). Thus

$$\tilde{\epsilon}_i = \epsilon_i - D_0$$

and, in consequence,

$$\tilde{q} = e^{D_0/kT} q.$$

Canonical distribution. Application to chemical equilibrium

When we use the usual partition functions q_X computed relative to the energy of the ground state then the equilibrium constant $K_N(T)$ is expressed as:

$$K_N(T) = e^{\Delta D_0/kT} \frac{q_C^{n_C} q_D^{n_D}}{q_A^{n_A} q_B^{n_B}}.$$

where

$$\Delta D_0 = n_C D_0^C + n_D D_0^D - n_A D_0^A - n_B D_0^B$$

and D_0^X is the atomization energy of the molecule X. Since D_0^X is equal to the energy of atoms minus the energy of the ground state E_0^X and since the total number of atoms does not change during the chemical reaction we have

$$\Delta D_0 = -\Delta E_0$$

where

$$\Delta E_0 = n_C E_0^C + n_D E_0^D - n_A E_0^A - n_B E_0^B$$

is the reaction energy at zero temperature ($\Delta E_0 < 0$ for exothermic reactions).

The obtained expression for $K_N(T)$ can be computed using spectroscopic data and gives usually more accurate results than measurement of $K_N(T)$.