

Some terms, concepts, constants, and laws of thermodynamics and statistical mechanics (in order of appearance in 3760 course)

**Temperature (phenomenological definition)**

Temperature is a measure of the tendency of an object to spontaneously give up or get energy from its surroundings. Units K (Kelvin)

**Pressure**

$P = \vec{F} \cdot \vec{n} / S$ ,  $\vec{F}$  -force,  $\vec{n}$  -normal unit vector to the surface,  $S$  -area  
Units Pascal. 1 Pa=1N/1m<sup>2</sup>

**Absolute zero**

Lowest possible temperature, 0 K, -273.15 °C

**Ideal gas law**

$$PV = nRT, PV = NkT, PV = \frac{m}{\mu} RT$$

$P$  – pressure,  $V$ - volume,  $T$ - temperature,  $n$  – number of moles,  $\mu$  – atomic mass

**Gas constant**  $R=8.31$  J / mole K

**Avogadro number**  $N_A=6.02 \times 10^{23}$  number of molecules in 1 mole of compound

**Boltzmann constant**  $k=1.38 \times 10^{-23}$  J/K

**Kinetic energy**  $K = \frac{1}{2}mv^2$

**Root-mean-square...**  $X_{rms} = \sqrt{X^2}$

**Degrees of freedom**

In classical mechanics, the dynamics of the system of  $N$  particles can be described by the set of  $3N$  coordinates ( $x,y,z$  for each particle) and the set of  $3N$  momentums ( $mv_x, mv_y, mv_z$  for each particle). We say that such system of  $N$  particle has  $3N$  *translational degrees of freedom*. When particles (atoms) form molecules we distinguish 3 *translational degrees of freedom* that describe the translational motion of a molecule as a whole, 3 *rotational* degree of freedom correspond to rotation of a molecule (2 for axial molecules like  $N_2$ ). The rest,  $3N-3-f_R$ , are *vibration* degrees of freedom. For all degrees of freedom formula for energy is quadratic function of coordinate or velocity.

**Equipartition theorem**

At temperature  $T$ , the average energy of any *translational* and *rotational* degree of freedom is  $\frac{1}{2}kT$ , the

average energy of *vibrational* degree of freedom is  $kT$ . Equipartition theorem is a result of classical statistical mechanics. Because of the energy quantization, rotational and vibration degrees of freedom can be “frozen out” at low temperatures.

**1<sup>st</sup> law of thermodynamics**

$\Delta U = Q - W$  (definition the most physics textbooks,  $\Delta U$  –change in internal energy,  $Q$ -heat,  $W$ - work done by the system.)

$\Delta U = Q + W$  (definition in Schroeder textbook,  $W$ - work done on system)

**Internal energy, heat, work**

**Internal energy** – sum of all “fundamental” energies. We can connect each contribution to mechanical motion or some fundamental interaction.

**Heat**- energy flow between bodies as a result of temperature difference.

**Work** – all other flows of energy. We can usually find external “agent” that actively pumps energy into a system.

**Isothermal process**  $T = \text{const}$

**Adiabatic process**

$Q = \text{const}$  (no heat exchange with surroundings). For ideal gas in adiabatic process  $VT^{f/2} = \text{const}$

**Adiabatic exponent**

For ideal gas  $PV^\gamma = \text{const}$  in adiabatic process,  $\gamma = \frac{f+2}{f}$  -adiabatic exponent,  $f$  – number of active degrees of freedom.

**Heat capacity, specific heat capacity**

$C \equiv \frac{\Delta Q}{\Delta T}$ ,  $c = C/m$  ( $m$  is mass)-specific heat capacity of just specific heat.

**Heat capacity at constant volume and pressure**

$C_V = \left( \frac{\partial U}{\partial T} \right)_V$ , for ideal gas  $C_V = \frac{f}{2} Nk$

$C_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P = C_V + P \left( \frac{\partial V}{\partial T} \right)_P$ , for ideal gas  $C_P = C_V + Nk$

**Latent heat**

Heat needed to accomplish phase transformation  $L \equiv Q/m$

**Multiplicity function. Gaussian distribution**

Number of states having the same specific arrangement such as spin excess, number of molecules in left box, etc....). For a system of  $N$  magnets with spin excess  $2s = N_\uparrow - N_\downarrow$ ,

$$g(N, s) = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{\left(\frac{N}{2} + s\right)! \left(\frac{N}{2} - s\right)!}$$

When  $N$  is large  $g(N, s)$  is well approximated by the **Gaussian distribution**

$$g(N, s) = (2/\pi N)^{1/2} 2^N \exp(-2s^2/N)$$

For more complicated systems multiplicity has different usually more complicated expression.

**Fundamental assumption**

A **closed system** is equally likely to be in any of the quantum states **accessible** to it. We treat all q. states as accessible if they are not excluded by the specification of the system and the time scale of the measurement process.

**Closed system**

A closed system will have constant energy, a constant number of particles, constant volume and constant values of all external parameters that may influence the system, including gravitational, electric, and magnetic field...

**Entropy (definition of stat. mech.)**

$S = k \ln(g)$ , where  $g$  is multiplicity function

**Temperature (stat. mech. definition)**

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_V \quad \text{or} \quad T = \left( \frac{\partial U}{\partial S} \right)_V$$

### Thermodynamic identity

$$dU = TdS - PdV, \quad dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV, \quad P = - \left( \frac{\partial U}{\partial V} \right)_S$$

### Efficiency of heat engine. Carnot cycle. Efficiency of Carnot cycle.

Efficiency  $\eta = \frac{W}{Q_{in}}$ ,  $W$  is work done by the engine over the cycle,  $Q_{in}$  is heat taken in by the engine. The

Carnot cycle produces maximum possible efficiency for a heat engine. It is formed by two isotherms and two adiabats. Its efficiency is  $\eta_{Carnot} = 1 - \frac{T_C}{T_H}$ , where  $T_C$  is the temperature of heat sink and  $T_H$  is the temperature of heat source.

### Boltzmann factor

$$\exp(-E_i / kT)$$

### Partition function for quantum systems in a thermal contact with a reservoir at temperature T

$$Z = \sum_s \exp(-E_s / kT) \quad ; \text{ sum is taken over all quantum states.}$$

$$Z = \sum_l g_l \exp(-E_l / kT) \quad \text{different way of writing the above expression. Here the sum is taken over}$$

different energy levels.  $g_l$  is degeneracy of the level, that is, the number of quantum states that have this energy. For example the ground state of electron in hydrogen atom (1S) has degeneracy 2, corresponding to spin up and spin down quantum states. The first excited state has degeneracy 8. In the first excited state an electron can occupy 2S orbital with two-fold spin degeneracy or 2P orbital with 6-fold degeneracy ( $6=2 \times 3$ , where factor 2 from spin degeneracy and factor 3 from orbital degeneracy  $L_z = +1, 0, -1$ )

### Probability (occupation number) of quantum state, energy level

$$P(s) = \frac{\exp(-E_s / kT)}{Z} \quad \text{probability of quantum state } s \text{ to be occupied}$$

$$P(E_l) = \frac{g_l \exp(-E_l / kT)}{Z} \quad \text{probability of energy level } E_l \text{ to be occupied, } g_l \text{ is degeneracy of the level.}$$

### Average energy of the system from partition function

$$\langle E \rangle = - \frac{1}{Z} \frac{\partial Z}{\partial \beta}, \quad \text{where } \beta = \frac{1}{kT}$$

### (Helmholtz) free energy. Its relation to entropy, pressure and partition function.

$$F = U + TS, \quad dF = -SdT - pdV, \quad S = - \left( \frac{\partial F}{\partial T} \right)_V, \quad P = - \left( \frac{\partial F}{\partial V} \right)_T \quad F = -kT \ln(Z)$$

### Splitting of angular momentum in magnetic field. Energy of the levels.

When atom with non-zero angular momentum  $J$  is placed in magnetic field the degenerate energy level corresponding to  $J$  splits into several levels that have different projection of  $J_z$  on the direction of magnetic field usually chosen as z-axis. For example the level with  $J=1$  will split into 3 levels with  $J_z = -1, 0, 1$ .

The energy of the new levels is given as  $E_{J_z} = -g \mu_B B J_z$ , where  $g$  is so called g-factor (do not confuse

with degeneracy or multiplicity),  $\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24}$  J/T is Bohr magneton, and  $B$  is magnetic field

measured in Teslas (T).

### Maxwell distribution

Here we neglect all interaction between molecules and assume that all fields (as gravitational and so on) are equal to zero so the energy of a molecules is just kinetic energy of transverse motion  $E_k = \frac{1}{2}mv^2$ , where

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

**A)** Let's consider first just one molecule in a volume  $V$ ,

$P_1(\vec{v})d^3\vec{v}$  - is the probability for the molecule to be in **any** position within volume  $V$  and have velocity between  $\vec{v}$  and  $\vec{v} + d\vec{v}$  (that is  $x$ -component of velocity is between  $v_x$  and  $v_x + dv_x$ ,  $y$ -component is between  $v_y$  and  $v_y + dv_y$  and  $z$ -component is between  $v_z$  and  $v_z + dv_z$ ). By definition of notation  $d^3\vec{v} = dv_x dv_y dv_z$ .

$$(1) P_1(\vec{v})d^3\vec{v} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) d^3\vec{v}$$

Normalization constant  $\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}$  in eq. (1) was computed from condition that

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} P_1(\vec{v}) dv_x dv_y dv_z = 1 \quad (\text{probability to find a molecule in any position with any velocity})$$

**To compute an average value**  $\langle Q \rangle$  of some quantity  $Q(v_x, v_y, v_z)$  which is a function of the velocity, we use general rule

$$(2) \langle Q \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} Q(v_x, v_y, v_z) P_1(\vec{v}) dv_x dv_y dv_z.$$

For example, for the average square of  $x$ -component of velocity  $\langle v_x^2 \rangle$  we have

$$(3) \langle v_x^2 \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_x^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) dv_x dv_y dv_z =$$

$$\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \times \int_{-\infty}^{+\infty} v_x^2 \exp\left(-\frac{mv_x^2}{2kT}\right) dv_x \times \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_y^2}{2kT}\right) dv_y \times \int_{-\infty}^{+\infty} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z = \frac{kT}{m}$$

The following integrals are useful compute different average values:

$$I(n) = \int_0^{\infty} x^n \exp(-ax^2) dx$$

$$I(0) = \frac{1}{2} \sqrt{\frac{\pi}{a}}, \quad I(1) = \frac{1}{2} a^{-1}, \quad I(2) = \frac{1}{4} \sqrt{\pi} a^{-3/2}, \quad I(3) = \frac{1}{2} a^{-2}, \quad I(4) = \frac{3}{8} \sqrt{\pi} a^{-5/2}, \quad I(5) = a^{-3}$$

We use  $I(0)$  to compute the normalization constant in eq. (1) and  $I(0)$  and  $I(2)$  in eq. (3) to compute  $\langle v_x^2 \rangle$ .

Let us introduce probability of certain speed (magnitude of velocity)

$P_2(v)dv$  - is the probability for the molecule to be in **any** position within volume  $V$ , move in **any** direction and have the speed between  $v$  and  $v + dv$ .

To compute  $P_2(v)dv$  we have to integrate  $P_1(\vec{v})d^3\vec{v}$  over all possible direction. We first convert element volume in velocity space from Cartesian to spherical coordinates  $dv_x dv_y dv_z = \sin \theta d\theta d\varphi v^2 dv$ . After this we have

$P_1(v, \theta, \varphi) \sin \theta d\theta d\varphi v^2 dv$  - is the probability to find a molecule in **any** position within the volume  $V$  and to have the speed between  $v + dv$ , azimuthal angle between  $\varphi + d\varphi$  and polar angle between  $\theta$  and  $\theta + d\theta$ .

After integration over all angles (which is the same as integration over all possible directions of the speed we have

$$P_2(v)dv = \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta P_1(v, \theta, \varphi) dv =$$

$$\int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

The average speed is computed by general method using integral I(3)

$$\langle v \rangle = \int_0^{+\infty} v P_2(v) dv = \int_0^{+\infty} v 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) dv = \sqrt{\frac{8}{\pi}} \sqrt{\frac{kT}{m}}$$

In lecture notes (L18) we considered the quantity:

$P(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r}$  - the probability for the molecule to be in position between  $\vec{r}$  and  $\vec{r} + d\vec{r}$  and to have velocity between  $\vec{v}$  and  $\vec{v} + d\vec{v}$ . From Boltzmann statistics we have

$$P(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r} = C \exp\left(-\frac{mv^2}{2kT}\right) dv_x dv_y dv_z dx dy dz$$

Normalization constant C is determined from condition

$$\int_V dx dy dz \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dv_x dv_y dv_z P(\vec{v}, \vec{r}) = 1 \quad \text{from which we find } C = \frac{1}{V} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}$$

and therefore

$$P(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r} = \frac{1}{V} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) dv_x dv_y dv_z dx dy dz$$

$$\text{Notice that } P(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r} = \frac{1}{V} P_1(\vec{v}) d^3\vec{v} d^3\vec{r}$$

**B)** Let's consider now the case when we have  $N$  molecules in the volume  $V$ . The quantity

$$f(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r} = NP(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r}$$

is then average number of molecules in position between  $\vec{r}$  and  $\vec{r} + d\vec{r}$  and to have velocity between  $\vec{v}$  and  $\vec{v} + d\vec{v}$ . Obviously the interaction of  $f(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r}$  over the volume and over all possible velocities gives us total number of molecules in the volume  $V$  and we have

$$f(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r} = \frac{N}{V} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) dv_x dv_y dv_z dx dy dz$$

$$n = \frac{N}{V} \text{ is an average concentration of molecules in the container}$$

Given the fact that  $f(\vec{v}, \vec{r})$  does not explicitly depend on  $\vec{r}$  we may introduce quantity

$$f(\vec{v}) d^3\vec{v} = \frac{f(\vec{v}, \vec{r}) d^3\vec{v} d^3\vec{r}}{d^3\vec{r}} - \text{the average number of molecules per unit volume and to have that have}$$

velocity between  $\vec{v}$  and  $\vec{v} + d\vec{v}$ .

$$f(\vec{v}) d^3\vec{v} = n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) dv_x dv_y dv_z$$

### Clausius-Clapeyron relation

(gives in differential form the line in P-T diagram at which liquid and gas phases co-exist or saturated vapor pressure at given temperature)

$$\frac{dP}{dT} = \frac{L}{T(V_g - V_L)}$$

where  $L$  latent heat (per mole) of vaporization,  $V_g$  is a gas molar volume and  $V_L$  is liquid molar volume. If we assume that gas phase follows ideal gas law and  $V_g \gg V_L$  then we can integrate the equation and get

$$P(T) = P_0 \exp(-L_0 / kT)$$

where  $L_0$  heat of vaporization of one molecule

### Radiation

Total energy of radiation inside of the cavity with volume  $V$  in thermal equilibrium is

$$\frac{U}{V} = \int_0^\infty \frac{8\pi\varepsilon^3 / (hc)^3}{\exp(\varepsilon / kT) - 1} d\varepsilon = \frac{8\pi^5 (kT)^4}{15(hc)^3}$$

Where  $\varepsilon = h\omega$  is energy of photon.

$$\text{Entropy of photon gas } \frac{S(T)}{V} = \frac{32\pi^5}{45} \left( \frac{kT}{hc} \right)^3 k$$

$$\text{Radiation pressure inside cavity with volume } V \quad P = \frac{1}{3} \frac{U}{V}$$

$$\text{Radiation power emitted by blackbody } W = \frac{2\pi^5}{15} \frac{(kT)^4}{h^3 c^2} A = \sigma_B AT^4, \text{ where}$$

$A$ -surface area of the body,  $\sigma_B = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4$  Stefan-Boltzmann constant

Emissivity  $e$  – fraction of photons emitted by a real body in comparison with blackbody

$W = e\sigma_B AT^4$ . For blackbody radiator  $e=1$ , for perfectly reflected surface  $e=0$ . More generally  $e$  is also a fraction of photons absorbed by a body with the surface emissivity  $e$ .  $(1-e)$  is reflected fraction.