We give the numerical constants :
Electron charge –e where e $\approx$ 1.6x10⁻¹⁹C
Boltzmann constant $k_B \approx 1.4 \times 10^{-23}$ m² kg s⁻² K⁻¹

$$\frac{1}{4\pi\varepsilon_0} \approx 9 \times 10^9 \, SI$$

Orientation of dipolar molecules. Orientational susceptibility

We consider in the following N dilute and independent molecules placed in a volume Ω and maintained at thermal equilibrium characterized by a temperature T. One such molecule is composed of atoms. Because of the partly polar nature of the chemical bonds in most of the molecules, these atoms bear charges +q_{i+}, 1≤ i ≤p_+ and charges –q_{j-}, 1≤ j ≤ p_-. Both q_{i+} and q_{j-} are ≥0. Each molecule is neutral:

$$\sum_{i=1}^{p_+} q_{i+} = \sum_{j=1}^{p_-} q_{j-}$$

We call $\vec{r}_{i+}(\vec{r}_{j-})$ the position vectors of the charge q_{i+}(-q_{j-}).

The molecules are subjected to a constant and homogeneous electric field $\vec{F}$.

1) What is the electrostatic potential $\varphi(\vec{r})$ associated with the electric field $\vec{F}$?

2) Deduce the interaction energy $U_{ext}(\vec{F})$ of one molecule with the electric field $\vec{F}$ and show that it can be written:

$$U_{ext}(\vec{F}) = -\vec{D}.\vec{F}$$

where $\vec{D}$ is the dipole moment of the molecule:

$$\vec{D} = \sum_{i=1}^{p_+} q_{i+}\vec{r}_{i+} - \sum_{j=1}^{p_-} q_{j-}\vec{r}_{j-}$$

3) Show that $\vec{D}$ is independent of the origin of the coordinates.

Because it is impossible to follow the positions of all the atoms in all the molecules at every time, we use a probabilistic description and consider that the vector $\vec{D}$ has a fixed length but a random orientation. We shall call $(\theta,\varphi), 0 \le \theta \le \pi, 0 \le \varphi \le 2\pi$ the two angles that are needed to specify the orientation of $\vec{D}$ (see fig.(1)).

In order to be able to apply the Boltzmann law, we must find out, besides U_{ext}, for a given molecule the various parts of its energy. They are associated with its motion (kinetic energy) or the internal potential energy of the various atoms that constitute the molecule and give rise to the molecular binding.

Consider then the $(p_+ + p_-)$ atoms that constitute the molecule. Their kinetic energy is:

$$K = \sum_{i=1}^{p_+} \frac{p_{i+}^2}{2m_{i+}} + \sum_{j=1}^{p_-} \frac{p_{j-}^2}{2m_{j-}}$$

We define the center of mass of the molecule $\vec{R}_{CM}$ as:

$$M\vec{R}_{CM} = \left(\sum_{i=1}^{p_+} m_{i+} + \sum_{j=1}^{p_-} m_{j-} \right) \vec{R}_{CM} = \sum_{i=1}^{p_+} m_{i+}\vec{r}_{i+} + \sum_{j=1}^{p_-} m_{i-}\vec{r}_{i-}$$

4) Show that the kinetic energy of the molecule can be written:

$$K = \frac{P_{CM}^2}{2M} + K_{rel}$$

where K_{rel} is the kinetic energy of the atoms that form the molecule in the center of mass reference frame and. Hint: for each atom write:

$$\vec{r}_{atom} = \vec{R}_{CM} + \vec{r}_{rel}$$

5) The kinetic energy of the relative motion K_{rel} adds to the atom-atom potential energy V_{rel}. Therefore, when the center of mass of the molecule is at rest, the molecule energy reads:

$E_{rel} = K_{rel} + V_{rel}$

Quantum mechanics associates to this energy an operator, the Hamiltonian H_{rel}, such that the energy levels are the eigenvalues of this operator. The lower energy levels are discrete. We call E_0 the ground state, E_1 the first excited state etc.

For a molecule absorbing visible photons (for example at $h\nu = 2eV$ where h is the Planck constant and ν the frequency of the electromagnetic wave) that correspond to optical transitions between the ground and first excited state of the relative motions, find the ratio between $h\nu$ and the thermal agitation energy $k_B T$ at T= 300K . Conclusion?
Same question if the molecule is probed by infrared light with a wavelength $\lambda = 60$ µm.

In the following, we neglect the internal degrees of freedom and we set $E_0 = 0$.

6) In this part we take F = 0.
Hence, with $E_0 = 0$ from 5), the molecular Hamiltonian contains only terms related to the center of mass motion:

$$H = \frac{P_{CM}^2}{2M}$$

H does not depend on $\mathbf{R}_{CM}$. But a classical state is specified by giving both the position and the linear momentum of the center of mass : $\mathbf{R}_{CM}$, $\mathbf{P}_{CM}$.

The Boltzmann law then tells us that the probability density to find such a state is:

$$dP = \frac{1}{Z} \frac{d^3 R_{CM} d^3 P_{CM}}{h^3} \exp\left(-\frac{H}{k_B T}\right)$$

where $1/Z$ is a normalization constant that ensures that P is normalized:

$$\int dP = 1$$

Compute Z as a function of Ω, T, M. We give:

$$\int_{-\infty}^{+\infty} dx \exp(-x^2) = \sqrt{\pi}$$

7) Compute the average kinetic energy *<H>* due to the translation of the center of mass of the molecule where:

$$\langle H \rangle = \int H dP$$

8) Suppose that by some means the molecules are constrained to move on a plane (bi-dimensional motion). How would the result found in 7) be modified? Same question if the molecules were moving on a line.

9) Compute the mean square fluctuation ΔH of the molecule kinetic energy:

$$\Delta H = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}$$

<p style="text-align:center; color:blue;">The electric field is now non zero: F ≠ 0.</p>

10) The molecular Hamiltonian is:

$$H(\vec{F}) = \frac{P_{CM}^2}{2M} - \vec{D}.\vec{F}$$

A state of the system is specified by the knowledge of:

$$\vec{R}_{CM}, \vec{P}_{CM}, \theta, \varphi$$

The probability density to find such a state is:

$$dP = \frac{1}{Z} \frac{d^3 R_{CM} d^3 P_{CM}}{h^3} \sin\theta d\theta d\varphi \exp\left(-\frac{H(\vec{F})}{k_B T}\right)$$

11) Show that Z factorizes in a contribution Z_{CM} due to the center of mass translation by one Z_{dip} due to the dipolar degrees of freedom.

12) Consequently, show that if one is interested in the dipolar degrees of freedom (essentially the average value of **D**), one can eliminate the center of mass degrees of freedom and consider that the probability density of finding the dipole in a given state is:

$$dP_{dip} = \frac{1}{Z_{dip}} \sin\theta d\theta d\varphi \exp\left(\frac{DF\cos\theta}{k_B T}\right)$$

13) Evaluate Z_{dip}.

14) We call z the electric field direction. What are the average values of D_x, D_y?

15) Show that the average value of D_z can be written:

$$\langle D_z \rangle = DL(x) \quad ; \quad L(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x}$$

$$x = \frac{DF}{k_B T}$$

16) Find a typical value of the parameter x if F = 10^7V/m, T = 300K. Either you know or you will have to guess a typical order of magnitude for D. Deduce that under most circumstances x <<1.

17) What is the behavior of L(x) at low x (first non vanishing term of the Taylor expansion)?

18) Would the previous results have changed if the molecules would not have been electrically neutral?

Measurement of the molecular polarizability of chlorine substituted methane ($CH_{4-n}Cl_n$), n = 0, 1, 2, 3, 4.

We assume that the electric field is weak: x << 1. Compute the polarization **P** of the medium. Hint: the polarization **P** is the number of dipoles per unit volume. Show that **P** can be written:

$$\vec{P} = \varepsilon_0 \chi_{orient} \vec{F}$$

where ε_0 is the vacuum dielectric constant and χ_{orient} is the electrical susceptibility (a c-number). The static dielectric constant of a substance is related to its electrical susceptibility by:

$$\varepsilon_r = 1 + \chi$$

We admit that besides χ_{orient} there exist other sources of polarizability that are temperature independent.

Fig.(2) shows a plot of (ε_r -1) versus 1/T for the chlorine substituted methane of chemical formula $CH_{4-n}Cl_n$.

19) Show that these experimental results allow to determine the magnitude of the dipole D of individual molecules.

Comment on the trend observed for D in $CH_{4-n}Cl_n$ versus n. Could you explain the D values for n = 0 and n = 4? You will have to know (or reason about) the geometry of the chlorine substituted methane

20) In these experimental results Ω = 22.4x10^{-3}m^3 and N is the Avogadro number (N =6x10^{23}). Compute the numerical value of D if n = 1 (CH_3Cl).
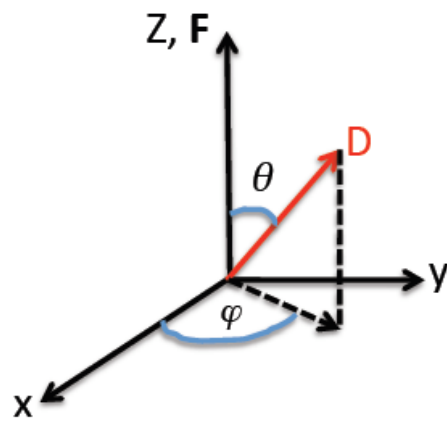
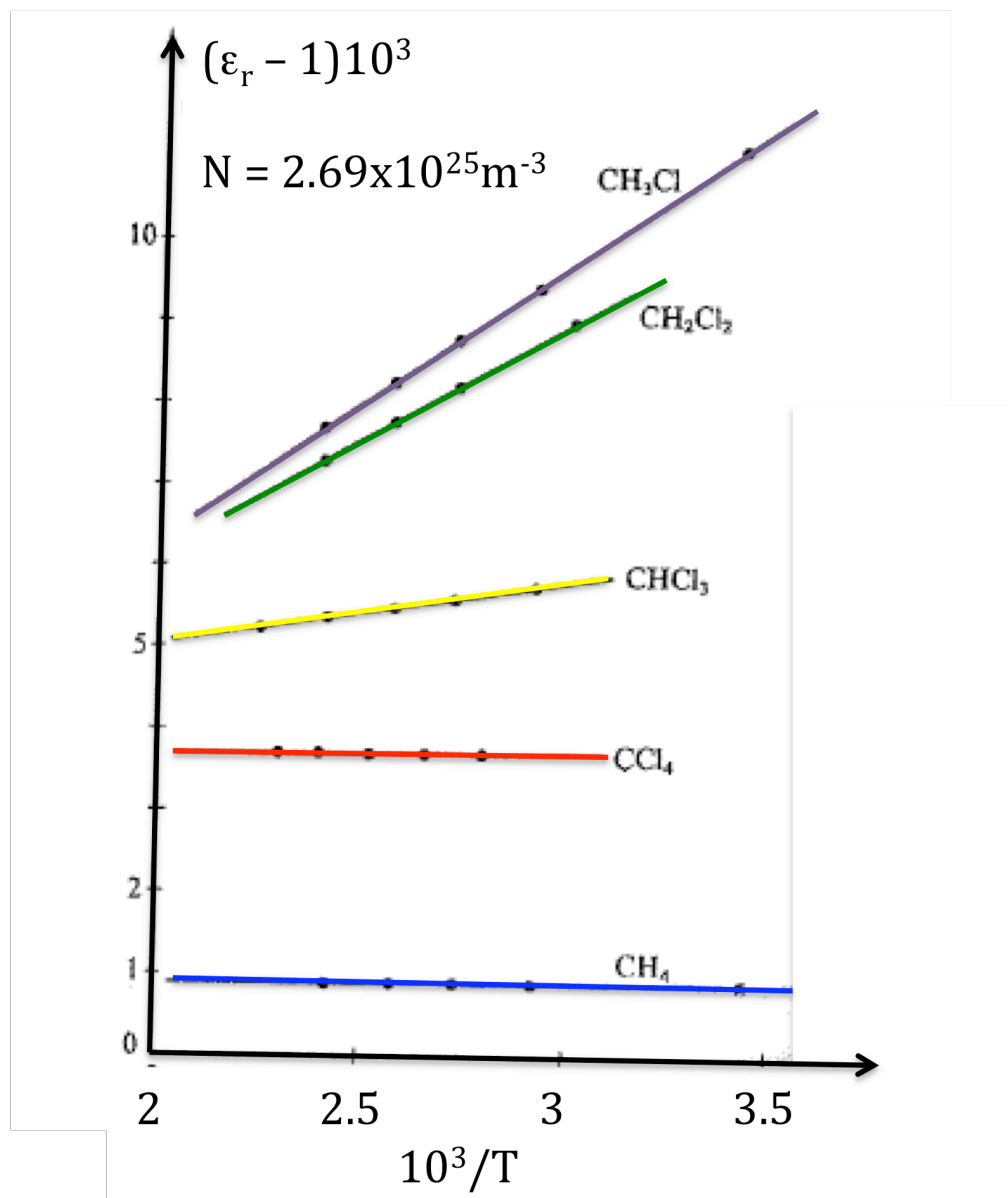Fig.(1) Definition of the angles θ, φ.

Fig.(2)   Static dielectric constant versus $10^3/T$ of chlorine substituted methane