Benjamin Vest
benjamin.vest@institutoptique.fr
Correction au 26 septembre 2025

Master QLMN - Université Paris-Saclay

TD 1 - Non-equilibrium Statistical Physics

Linear response theory - CORRECTION

1 Polarizability Fluctuations for a Dielectric Particle

We consider a dielectric particle much smaller than the excitation wavelength. In presence of a static electric field E_0, the particle has a dipole moment $\mathbf{p_0}$ given by its static susceptibility χ_0. When the electric field is switched off, the amplitude of the dipole moment decays exponentially with a time constant $\tau = 1/\gamma$.

Derive the relaxation function Ψ and the linear response $\chi(t)$(t) .

Let's define the origin of time when the electric field is switched off. For $t < 0$, we have the relation $\mathbf{p_0} = \chi_0 \mathbf{E_0}$. For $t > 0$, the dipole decays exponentially and we can write

$$\mathbf{p}(t) = \chi_0 \mathbf{E_0} \exp(-\frac{t}{\tau})$$

The relaxation function is therefore : $\Psi(t) = \chi_0 e^{-\frac{t}{\tau}}$.

Following the textbook results, the response is given by :

$$\chi(t) = -\frac{d\psi(t)}{dt} H(t)$$

where $H(t)$ is the Heaviside function. We obtain immediately $\chi(t) = \frac{\chi_0}{\tau} e^{-\frac{t}{\tau}}$.

Derive the complex susxeptibility $\chi(\omega)$.

The complex susceptibility is given by the Fourier transform of the linear response :

$$\begin{aligned}
\chi(\omega) &= \int_{-\infty}^{+\infty} \chi(t') e^{i\omega t'} dt' \\
&= \int_{0}^{+\infty} \frac{\chi_0}{\tau} e^{-\frac{t'}{\tau} + i\omega t'} dt' \\
&= \frac{\chi_0}{\tau} \frac{-1}{-\frac{1}{\tau} + i\omega} = \frac{\chi_0}{1 - i\omega\tau}
\end{aligned}$$

There is a direct connection between the relaxation model (how does a function decay) and the susceptibility (i.e. the response in the frequency domain). With this form of the complex susceptibility, we see that when choosing $\omega \ll \frac{1}{\tau}$, the susceptibility is non-dispersive. This corresponds to the application of a slowly varying force.

2 Polarization of a particle

We consider a system of volume V that can be polarized when an electric field $\mathcal{E}$ is applied. The dipole moment of the system has a fixed mean value $\bar{\mathbf{p}}$.

We can rephrase this situation in the framework of statistical physics : in this problem, our system exchange an extensive quantity, here some dipole moment, through interaction with a reservoir, defined by a conjugated quantity that rules the exchange between the system and the reservoir and sets the system state at equilibrium : here, the conjugated quantity is the electric field $\mathcal{E}$.

Therefore, we can deal with the following problem using the frame and tools of the statistical grand canonical ensemble, defined for a system exchanging energy and dipole moment with a reservoir defined by its temperature and electric field. The work exerted by the reservoir on the system is given by $dW = -\mathrm{d}\mathbf{p} \cdot \mathcal{E}$.

Deriving the probability of a state A possible state r is defined by its probability P_r, its energy E_r and its dipole moment $\mathbf{p_r}$, who has three components along x,y, and z. The corresponding ensemble average values of the system are denoted as $\overline{E}$ and $\overline{\mathbf{p}}$.

Those quantities fulfill the following relations : $\sum P_r = 1$, $\sum E_r P_r = \overline{E}$, and $\sum \mathbf{p_r} P_r = \overline{\mathbf{p}}$.

The Lagrange multipliers method is based on the minimization of the system entropy. the entropy can be expressed as :

$$S = -k_B \sum_r P_r \ln P_r$$

By taking the derivative :

$$\frac{\partial}{\partial P_{r_0}} \left(-k_B \sum_r P_r \ln P_r + \lambda_1 (\sum_r P_r - 1) + \lambda_2 (\sum E_r P_r - \overline{E}) + \sum_i \lambda_{3,i} (\sum_r p_{r,i} P_r - \overline{p_i}) \right) = 0$$

where i denotes the directions x,y,z.

$$-k_B (\ln P_{r_0} + 1) + \lambda_1 + \lambda_2 E_{r_0} + \sum_i \lambda_{3,i} p_{r_0,i} = 0$$

The state probability P_{r_0} can therefore be casted in the form :

$$P_{r_0} = \frac{\exp(-\beta E_{r_0} - \sum_i \alpha_i p_{r_0,i})}{Z}$$

where we introduced the coefficients $\beta = \lambda_2 / k_B$, etc...

All terms that do not depend on r_0 are now merged within Z which is the partition function. The partition function ensures that the closure relation $\sum P_r = 1$ is correctly fulfilled, and acts as a normalization, dimensionless constant. We can indeed write :

$$Z = \sum_r e^{-\beta E_r - \sum_i \alpha_i p_{r,i}}$$

which can be written in a more compact fashion using vector notations :

$$Z = \sum_r e^{-\beta E_r - \alpha \cdot \mathbf{p_r}}$$

Identifying the quantities As explained earlier, the entropy is given by $S = -k_B \sum_r P_r \ln P_r$. We can now use the expression of the state probability to derive the expression of the entropy :

$$\begin{aligned} S &= -k_B \sum_r P_r \ln P_r \\ &= -k_B \sum_r \frac{e^{-\beta E_r - \alpha \cdot \mathbf{p_r}}}{Z} (-\beta E_r - \alpha \cdot \mathbf{p_r} - \ln Z) \\ &= k_B \beta \overline{E} + k_B \alpha \cdot \overline{\mathbf{p}} + k_B \ln Z \end{aligned}$$

where we used the definition of the ensemble average values of energy and dipole moment. We can deduce the expression of the generalized potential by rearranging the previous expression :

$$\begin{aligned} A &= -k_B T \ln Z \\ &= k_B T \beta \overline{E} + k_B T \alpha \cdot \overline{\mathbf{p}} - TS. \\ &= \overline{E} - TS + k_B T \alpha \cdot \overline{\mathbf{p}}, \end{aligned}$$

The grand potential A (also called generalized free energy) is the sum of the free energy and the work, here produced by the exchange of dipole moment. In other words, one can write as well :

$$A = E - TS - \mathcal{E} \cdot \mathbf{p}$$

We can directly identify $\alpha = \beta \mathcal{E}$. Using the expression for entropy, we know that :

$$\alpha_i = \frac{1}{k_B} \frac{\partial S}{\partial \overline{p_i}},$$

Or :

$$\mathcal{E}_i = -T \frac{\partial S}{\partial p_i} = k_B T \alpha_i.$$

Average value and fluctuations We now want to calculate the average value of the components of the dipole moment. Starting from the most general expression :

$$\begin{aligned}
\overline{p_i} &= \sum_r P_r p_{r,i} \\
&= \frac{1}{Z}\sum_r e^{-\beta E_r - \alpha\cdot\mathbf{p_r}} p_{r,i} \\
&= \frac{-1}{Z}\frac{\partial Z}{\partial \alpha_i} = -\frac{\partial \ln Z}{\partial \alpha_i}
\end{aligned}$$

We can also replace the parameter α by its newly found expression $\alpha = -\beta\mathcal{E}$: We can therefore connect directly the average value of the dipole moment, that this the dipole moment at equilibrium, to its conjugated quantity, the electric field setting the conditions of equilibrium between the systelm and the reservoir :

$$\begin{aligned}
\overline{p_i} &= \sum_r P_r p_{r,i} \\
&= \frac{1}{Z}\sum_r e^{-\beta E_r + \beta\mathcal{E}\cdot\mathbf{p_r}} p_{r,i} \\
&= \frac{1}{\beta Z}\frac{\partial Z}{\partial \mathcal{E}_i} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathcal{E}_i}
\end{aligned}$$

where $\mathcal{E}_i$ denotes the components of the electric field. Let's move now to the derivation of the standard deviation of the fluctuations of the dipole moment $\sigma_{p_i}^2 = \overline{p_i^2} - \overline{p_i}^2$.

$$\begin{aligned}
\overline{p_i^2} &= \sum_r P_r p_{r,i}^2 \\
&= \frac{1}{Z}\sum_r e^{-\beta E_r + \beta\mathcal{E}\cdot\mathbf{p_r}} p_{r,i}^2 \\
&= \frac{1}{Z}\frac{1}{\beta^2}\frac{\partial^2 Z}{\partial \mathcal{E}_i^2}
\end{aligned}$$

The fluctuations can now be expressed as :

$$\begin{aligned}
\sigma_{p_i}^2 &= \overline{p_i^2} - \overline{p_i}^2 \\
&= \frac{1}{\beta^2}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial \mathcal{E}_i^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \mathcal{E}_i}\right)^2\right) \\
&= \frac{1}{\beta^2}\frac{\partial^2 \ln Z}{\partial \mathcal{E}_i^2}
\end{aligned}$$

The last equality can be easily checked. The mean value and the fluctuations at equilibrium of the exhanged quantity (dipole moment) can be thus derived either from $\ln Z$, taking successive derivatives with respect to the Lagrange multiplier (here, α), or taking derivatives of the grand potential $A = -k_B T \ln Z$ to the conjugated quantity (here electric field $\mathcal{E}$).

Take-home message : the partition function is a crucial quantity, that contains all the information regarding the values of the different physical quantities at equilibrium : knowing the partition function, you virutally know everything of your system at equilibrium under the specific constraints of the problem.

Deriving the partition function. The external constraint here is the application of an external electric field.

We can imagine that, without this field, the system reaches a specific equilibrium situation. From this point, applying a field makes the system move *out* of this equilibrium.

If the amplitude of the applied field remains "small", i.e. if the work exerted on the system remains small compared to its energy at rest ($k_B T$), then we can make a connection between the previous equilibrium state (with no field applied) and the new one (with field applied).

It is rather intuitive to understand that this connection involves the amplitude of the linear response of the system, in other words, its susceptibility. But we will see that the fluctuations of the system at equilibrium with no force applied also play a role.

We now derive the partition function when a field is applied as an expansion of the partition function *with no external field.*

The approximation suggested in the text writes $\overline{\mathbf{p}} \cdot \mathcal{E} \ll \frac{1}{k_B T}$. In the derivation of the partition, we have to deal with a summation over all possible states, displaying individual values of the dipole moment $\mathbf{p}_r$. We will assume that we are in the thermodynamic limit. In this regime, satistical fluctuations around the average value of the dipole moment are extremely small. An astonishingly large number of microstate have their dipole moment $\mathbf{p}_r$ close to the average, so that almost all terms of the sum fulfill the approximation. Few states do not fulfill it, but do not weigh statistically.

We can then use the approximation to expand the exponential term :

$$
\begin{aligned}
Z &= \sum_r e^{-\beta E_r + \beta \mathcal{E} \cdot \mathbf{p_r}} \\
&\approx \sum_r e^{-\beta E_r} [1 + \beta \mathcal{E} \cdot \mathbf{p_r} + \frac{1}{2} \beta^2 (\mathcal{E} \cdot \mathbf{p_r})^2] \\
&\approx \sum_r e^{-\beta E_r} + \beta \sum_i \left(\mathcal{E}_i \sum_r p_{r,i} e^{-\beta E_r} \right) + \frac{\beta^2}{2} \sum_{i,j} \left(\mathcal{E}_i \mathcal{E}_j \sum_r p_{r,i} p_{r,j} e^{-\beta E_r} \right)
\end{aligned}
$$

Let us now consider a situation where no electric field is applied. The partition function in this case is written $Z_0 = \sum_r e^{-\beta E_r}$. So when looking at the other terms in the expression, we identify the expectation value of the dipole moment of the system **when no electric field is applied** : $\frac{\sum_r p_{i,r} e^{-\beta E_r}}{Z_0} = \overline{p_{i,0}}$, where the subscript "$i, 0$" accounts for $\mathcal{E}_i = 0$.

Similarly, the last term is the expectation value of the square of the dipole moment in the absence of an external electrid field : $\sum_r p_{r,i} p_{r,j} e^{-\beta E_r} \approx Z_0 \overline{p_{i,0} p_{j,0}}$. We will suppose that cross-correlations are zero in our problem ($\overline{p_{i,0} p_{j,0}} = 0$ for $i \neq j$), but diagonal correlations remain :

$$
\sum_r p_{r,i}^2 e^{-\beta E_r} \approx Z_0 \overline{p_{i,0}^2}
$$

We can cast the partition function in the form :

$$
\begin{aligned}
Z &= Z_0 + Z_0\beta\sum_i \mathcal{E}_i\overline{p_{i,0}} + Z_0\frac{\beta^2}{2}\sum_i \mathcal{E}_i^2\overline{p_{i,0}^2} \\
&= Z_0[1 + \frac{\overline{\mathbf{p_0}}\cdot\mathcal{E}}{k_BT} + \frac{\overline{(\mathbf{p_0^2}}\cdot\mathcal{E}^2)}{2(k_BT)^2}]
\end{aligned}
$$

A completely equivalent approach is to write a Taylor expansion of the partition function, noting that it is an explicit function of the electric field :

$$
\begin{aligned}
Z &= Z(\mathcal{E}=\mathbf{0}) + \sum_i \mathcal{E}_i\left(\frac{\partial Z}{\partial \mathcal{E}_i}\right)_{\mathcal{E}=\mathbf{0}} + \sum_i \frac{\mathcal{E}_i^2}{2}\left(\frac{\partial^2 Z}{\partial \mathcal{E}_i^2}\right)_{\mathcal{E}=\mathbf{0}} \\
&= Z_0 + \sum_i \mathcal{E}_i Z_0\beta\overline{p_{i,0}} + \sum_i \frac{\mathcal{E}_i^2}{2} Z_0\beta^2\overline{p_{i,0}^2} \\
&= Z_0[1 + \frac{\overline{\mathbf{p_0}}\cdot\mathcal{E}}{k_BT} + \frac{\overline{(\mathbf{p_0^2}}\cdot\boldsymbol{\mathcal{E}^2}}{2(k_BT)^2}]
\end{aligned}
$$

where we used the relations between the mean value or fluctuations of the dipole moment and the derivatives of the partition function derived earlier. Here again, the derivatives in the Taylor expansion are calculated **in the absence of electric field**, so that the expectation values of the dipole moment and the square of the dipole moments are denoted with the subscript $i, 0$.

We assume that the dipole moment above $\overline{\mathbf{p_0}}$ is zero in absence of the electric field, so that

$$
Z = Z_0[1 + \frac{\overline{(\mathbf{p_0^2}}\cdot\boldsymbol{\mathcal{E}^2}}{2(k_BT)^2}]
$$

The last term does not fall to zero : indeed, it is related to the average value of $\mathbf{p_0}^2$, or in other words, to the fluctuations of the dipole moment, at equilibrium and when the system is at rest. Those fluctuations are non-zero, as they are permanent exchanges between the system and the reservoir.

2.0.0.1 Connecting the response and the fluctuations The linear response is defined by the susceptibility :

$$
\overline{p_i} = \chi_0\mathcal{E}_i
$$

then

$$
\chi_0 = \frac{\partial\overline{p_i}}{\partial\mathcal{E}_i}
$$

From here, we can for example use the expression of the mean value of the dipole moment as the derivative of the partition function, or of the grand potential, or derive directly the previous expansion of the partition function.

Recall that :

$$\sigma^2_{p_{i,0}} = \overline{p^2_{i,0}} - \overline{p_{i,0}}^2 = \overline{p^2_{i,0}}$$

then

$$\begin{aligned}
\chi_0 = \frac{\partial \overline{p_i}}{\partial \mathcal{E}_i} &= \frac{\partial}{\partial \mathcal{E}_i}\left(\frac{1}{\beta Z}\frac{\partial Z}{\partial \mathcal{E}_i}\right) \\
&= \frac{1}{\beta}\frac{\partial^2 \ln Z}{\partial \mathcal{E}_i^2} \\
&= \frac{1}{\beta}\beta^2 \sigma^2_{p_i}
\end{aligned}$$

In other words :

$$\chi_0 = \beta \sigma^2_{p_i}$$

Alternatively, we can directly witness the role of fluctuations at rest around equilibrium by expanding the expectation value of the dipole moment itself :

$$\begin{aligned}
\overline{p_i} = \chi_0 \mathcal{E}_i = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathcal{E}_i} &= \frac{1}{\beta}\frac{1}{Z}\frac{\partial Z}{\partial \mathcal{E}_i} \\
&= \frac{1}{\beta}\frac{1}{Z}\frac{\partial}{\partial \mathcal{E}_i}\left(Z_0[1 + \beta \overline{\mathbf{p_0}} \cdot \mathcal{E} + \frac{\beta^2}{2}\overline{(\mathbf{p_0^2}} \cdot \mathcal{E}^{\mathbf{2}})]\right) \\
&= \frac{Z_0}{Z}(\overline{p_{i,0}} + \beta \overline{p^2_{i,0}} \mathcal{E}_i)
\end{aligned}$$

What does it mean ? We see that the fluctuations around equilibrium in the absence of an external electric field $\sigma^2_{p_{i,0}}$ gives us information about the linear optical response χ_0 of the dipole to a static electric field...so when an electric field is present ! This somewhat intriguing result will be extended and generalized using the Fluctuation-Dissipation theorem in the upcoming lectures.