Dielectric susceptibility

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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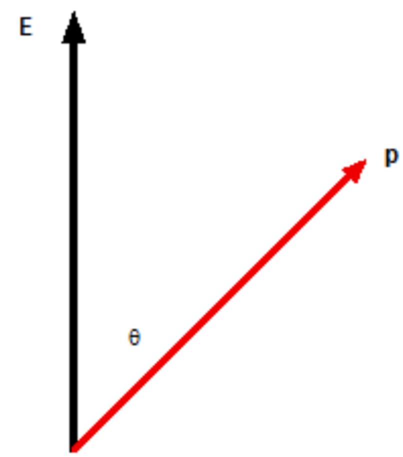
Langevin-Debye formula

We assume that an electric dipole moment p of each molecule in the presence of an electric field. The potential energy is given by

$$U = -\boldsymbol{p}\cdot\boldsymbol{E} = -pE\cos\theta$$

N is the number of molecules per unit volume and θ is the angle between $\boldsymbol{p}$ and $\boldsymbol{E}$. The polarization



The polarization P is given by

$$P = Np\langle\cos\theta\rangle$$

where

$$\langle\cos\theta\rangle = \frac{\int e^{-\frac{U}{k_BT}}\cos\theta d\Omega}{\int e^{-\frac{U}{k_BT}}d\Omega} = \frac{\int_0^\pi e^{\frac{pE\cos\theta}{k_BT}}\cos\theta(2\pi\sin\theta d\theta)}{\int_0^\pi e^{\frac{pE\cos\theta}{k_BT}}(2\pi\sin\theta d\theta)}$$

and k_B is the Boltzmann constant.

For simplicity we put $x = \frac{pE}{k_BT}$ and $s = \cos\theta$. Then we have

$$\langle \cos\theta \rangle = \frac{\int_{-1}^{1} e^{sx} s ds}{\int_{-1}^{1} e^{sx} ds} = \coth x - \frac{1}{x} = L(x)$$

where $L(x)$ is the Langevin function.

((**Mathematica**)) Derivation of the Langevin-Debye formula

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f1 = ∫_{-1}^{1} Exp[s x] s ds / ∫_{-1}^{1} Exp[s x] ds // Simplify
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$$-\frac{1}{x} + \mathrm{Coth}[x]$$

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Plot[f1, {x, 0, 5}, AxesLabel → {"x = pE/k_BT", " L(x)"},
 PlotStyle → {Red, Thick}, Background → LightGray]
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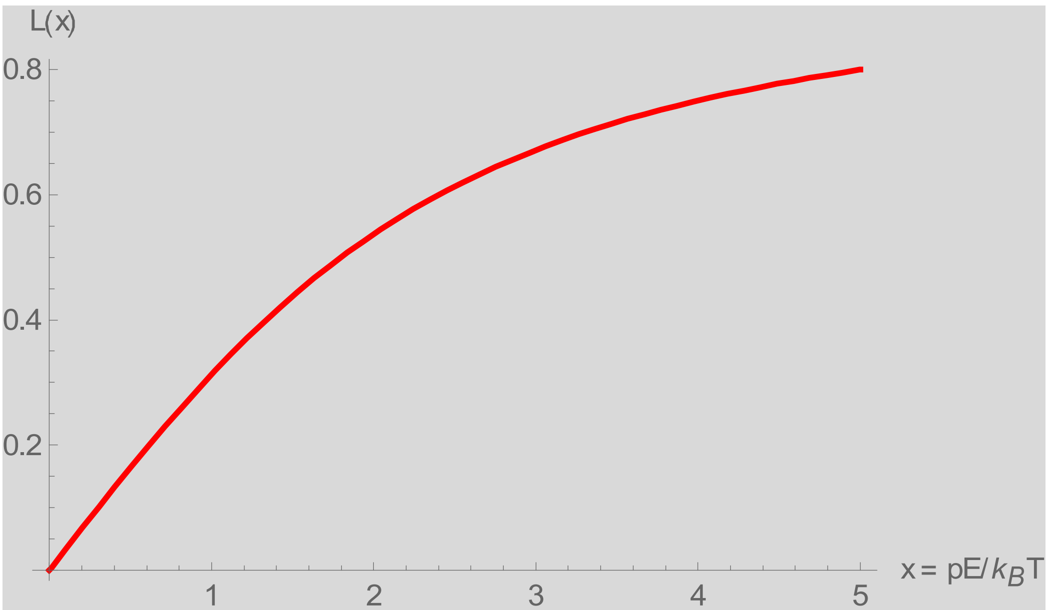


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Series[f1, {x, 0, 10}]
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$$\frac{x}{3} - \frac{x^3}{45} + \frac{2\,x^5}{945} - \frac{x^7}{4725} + \frac{2\,x^9}{93\,555} + O[x]^{11}$$

For x<<1, the Langevin function is approximated as

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + ... \approx \frac{x}{3}$$

and the derivative d$L(x)$/dx at $x = 0$ is equal to 1/3. Using this we have a Langevin-Debye formula,

$$P = Np\frac{x}{3} = \frac{Np^2 E}{3k_B T} = N\alpha E$$

where $\alpha = \frac{p^2}{3k_B T}$ is called the polarizability.

2. The use of partition function

The one-particle partition function is given by

$$\begin{aligned}
Z_{C1} &= \frac{1}{4\pi}\int d\Omega e^{\beta pE\cos\theta} \\
&= \frac{1}{4\pi}\int_0^\pi 2\pi\sin\theta d\theta e^{\beta pE\cos\theta} \\
&= \frac{1}{2}\int_0^\pi \sin\theta d\theta e^{\beta pE\cos\theta}
\end{aligned}$$

We substitute $x = \cos\theta$, so that $dx = -\sin\theta d\theta$. Thus we have

$$\begin{aligned}
Z_{C1} &= \frac{1}{2}\int_{-1}^{1} e^{\beta pEx}dx \\
&= \int_0^1 \cos(\beta pEx)dx \\
&= \frac{\sin(\beta pE)}{\beta pE}
\end{aligned}$$

Suppose that there are N electric dipoles in the volume V. P is the average of the total electric dipole moment per unit volume. The isothermal dielectric susceptibility is defined by

$$\chi_e = \frac{\partial P}{\partial E}$$

We note that

$$dF = -SdT - PdE$$

Using

$$
\begin{aligned}
F &= -\frac{k_B T}{V}\ln Z_{CN} \\
&= -\frac{N}{V}k_B T\ln Z_{C1} \\
&= -nk_B T\ln Z_{C1}
\end{aligned}
$$

and

$$\ln Z_{CN} = N\ln Z_{C1}, \qquad n = \frac{N}{V}$$

we get

$$
\begin{aligned}
P &= -\left(\frac{\partial F}{\partial E}\right)_T \\
&= nk_B T\left(\frac{\partial \ln Z_{C1}}{\partial E}\right)_T \\
&= np[\coth(x) - \frac{1}{x}]
\end{aligned}
$$

where

$$
\begin{aligned}
\left(\frac{\partial \ln Z_{C1}}{\partial E}\right)_T &= \beta p[\coth(\beta pE) - \frac{1}{\beta pE}] \\
&= \beta p[\coth(x) - \frac{1}{x}] \\
&= \beta pL(x)
\end{aligned}
$$

and

$$x = \beta pE$$