Lorentz Local Field

In computing the local field, \( E^* \), experienced by a molecule surrounded by others in an applied electric field, it is necessary to compute the average dipole moment, \( \mu_{\text{avg}} \), from alignment of permanent dipoles of magnitude \( \mu_{\text{perm}} \):

\[
\mu_{\text{avg}} = \int_0^{2\pi} \mu_{\text{perm}} \cos(\theta) P(\theta) d\theta
\]

where \( P(\theta) \) is the probability that the permanent dipole is oriented at angle \( \theta \) from the applied field. This is given by a Boltzmann term involving the potential energy of the dipole in a field relative to the thermal energy, \( kT \). Show that

\[
\mu_{\text{avg}} = \frac{\mu_{\text{perm}}^2 E^*}{3kT}
\]

in the high-temperature limit. Don’t skip steps like the notes do.

The equation is deceptive because it hides the fact that a dipole can orient in three dimensions. Suppose the \( E \) field lies along the \( z \)-axis. The dipole orientation is as shown. Many values of \( \phi \) share the same \( \theta \). The probability of finding the tip of vector \( \mu \) at \( \theta \pm d\theta \) is proportional to the area of the curved ring. This is largest at \( \theta = 90^\circ \) but then \( \cos(\theta) = 0 \). The differential area is small at low \( \theta \), but then \( \cos(\theta) \) is large.

Note: \( \mu_{\text{perm}} = \mu = |\mu| \)
The probability of the dipole tip being at $\theta \pm \frac{d\theta}{2}$ is also proportional to the Boltzmann term, $e^{-\frac{U}{kT}}$, where:

$$U = -pE^* \cos \theta$$

\[
\begin{array}{c|c|c|c|c}
\theta & 0 & U & -pE & 0 \\
90 & 180 & 180 & pE & 0 \\
-90 & 0 & 0 & -pE & 90 \\
p & \theta & p & 0 & 0 \\
\end{array}
\]

High Boltzmann prob.

$$\mu_{\text{avg}} = \frac{\int_0^{2\pi} \int_0^{2\pi} \frac{1}{\mu^2 \sin \theta} e^{pE^* \cos \theta / kT} d\theta d\phi}{\int_0^{2\pi} \int_0^{2\pi} \frac{1}{\mu^2 \sin \theta} e^{pE^* \cos \theta / kT} d\theta d\phi}$$

Let $A = \frac{pE^*}{kT}$

$$\mu_{\text{avg}} = \frac{\int_0^{\pi} A \cos \theta \sin \theta d\theta \cos \theta e^{-A \cos \theta}}{\int_0^{\pi} \sin \theta d\theta \cos \theta e^{-A \cos \theta}}$$
The denominator is easy
\[
\int_{\theta=0}^{\pi} e^{A \cos \theta \sin \theta} d\theta
\]

Let \( u = \cos \theta \) \( du = -\sin \theta d\theta \)

\[\Rightarrow -\int e^{Au} du = -\frac{1}{A} e^{Au} \bigg|_{0}^{\pi} = \frac{1}{A} (e^{A} - e^{-A})\]

The numerator is done using integration by parts.
\[
\int_{\theta=0}^{\pi} \cos \theta e^{A \cos \theta \sin \theta} d\theta
\]

Now let \( u = x \) \( du = dx \)

\[ dv = e^{Ax} dx \quad \Rightarrow \quad N = \frac{1}{A} e^{Ax} + \text{constant} \]

\[ \int u dv = uv - \int v du \]

\[ \Rightarrow \frac{x}{A} e^{Ax} - \int \frac{1}{A} e^{Ax} dx \]

\[ \text{neglect for definite integral we desire.} \]
Putting in the limits:

\[ \Rightarrow \frac{\nu}{A} \left[ e^{A} - 1 \right] - \frac{1}{A^2} \left( e^{A} - e^{-A} \right) \]

\[ = \frac{1}{A} \left( e^{A} + e^{-A} \right) - \frac{1}{A^2} \left( e^{A} - e^{-A} \right) \]

\[ \mu_{\text{avg}} = p \frac{\text{Numerator}}{\text{Denominator}} = p \left[ \frac{e^{A} + e^{-A}}{e^{A} - e^{-A}} - \frac{1}{A} \right] \text{ where } A = -\frac{pE^*}{kT} \]

If \( pE << kT \) we can expand exponentials, but is this approximation fine?

Choose a "big" E-field: \( 10^4 \text{ volt/cm} = 10^6 \text{ volt/m} = 10^6 \frac{\text{Joule}}{\text{Coul.m}} \)

Let \( p = 1 \text{ electron} \times 1 \text{Å}^2 \)

\[ = 1.6 \times 10^{-19} \text{ Coul} \times 10^{-10} \text{ m} = 1.6 \times 10^{-29} \text{ Coul.m} \]

So \( p \equiv \left[ 1.6 \times 10^{-29} \text{ Coul.m} \right] \left[ 10^6 \frac{\text{J}}{\text{Coul.m}} \right] = 1.6 \times 10^{-23} \text{ J} \)
\[ kT = 1.38 \times 10^{-23} \frac{J}{K} \times 300 K = 4 \times 10^{-21} J = 400 \times 10^{-23} J \]

So... \( kT \) truly is much bigger than \( \mu E \), even in this case of a pretty high applied field.

Since \( \mu E / kT \) is very small, we can expand the exponentials:

\[ e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots \]

This is just for fun: get function at \( x = 1 \):

\[
\frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} \quad \overset{x=1}{\rightarrow} \quad \frac{e + \frac{1}{e} - 1}{e - \frac{1}{e}}
\]

\[
= \frac{e + \frac{1}{e}}{e - \frac{1}{e}} \approx \frac{2/e}{e - \frac{1}{e}} \approx \frac{2}{e}
\]

\[
\approx \frac{\frac{2}{e^2 - 1}}{e \approx 7.3} \approx \frac{2}{6.7} \approx \frac{1}{3}
\]
\[
\frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = 2 \left( 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots \right) - \left[ 1 - \frac{x^2}{2!} - \frac{x^4}{4!} + \cdots \right]
\]

\[
= 2x + 2\frac{x^3}{3!} + 2\frac{x^5}{5!}
\]

\[
= 2x \left( 1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots \right)
\]

\[
\frac{\text{NUM}}{\text{DENOM}} = 2 \left( 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots \right)
\]

\[
\approx \frac{1}{x} \left( 1 + \frac{x^2}{2!} \right) \left( 1 - \frac{x^2}{3!} \right) = \frac{1}{x} \left( 1 + \frac{x^2}{2!} - \frac{x^2}{3!} - \frac{x^4}{2!3!} \right)
\]

\[
\approx \frac{1}{x} \left( 1 + x^2 \left( \frac{1}{2} - \frac{1}{6} \right) \right) = \frac{1}{x} \left( 1 + \frac{x^2}{3} \right)
\]
So finally \( \frac{\text{NUM}}{\text{DENOM}} = \frac{1}{x} \)

\[ = \frac{1}{x} \left( 1 + \frac{x^2}{3} \right) - \frac{1}{x} \approx \frac{x}{3} \]

In fact this works OK all the way up to \( x \approx 1 \).

\[ L(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} \] is called the Langevin function.
Finally our answer has arrived:

\[ \mu_{\text{avg}} = \rho \left( \frac{e^{\frac{A}{kT}} + e^{-\frac{A}{kT}}}{e^{\frac{A}{kT}} \cdot e^{-\frac{A}{kT}}} - \frac{1}{4} \right) \]

\[ = \frac{\rho A}{3} \]

But \( A = \frac{\rho E^*}{kT} \)

So \[ \mu_{\text{avg}} = \frac{\rho^2 E^*}{3kT} \]