E&M Lecture 7

Topics:
(1) Polar dielectrics
(2) Potential energy of dipole in electric field
(3) Random orientation expression
(4) “low E - high T” approximation
(5) Langevin Equation
Polar dielectrics

…….molecules possess *permanent* dipole moment but, in the absence of an electric field, dipoles are randomly oriented by thermal motion: hence, no polarisation.

- e.g. HCl and H$_2$O
- …..but not CS$_2$
  no *net* dipole moment

zero field, random net $P=0$

preferential alignment but $P \neq Np$
The effect of alignment is to oppose the applied field, that is, to **reduce** the net field

The tendency to alignment is opposed by thermal effects, the balance between these two effects is determined by Boltzmann statistics: key factor is ratio of the potential energy of the dipole \((U)\) (a measure of \(E\)) to the temperature \((T)\), which enters as \(\exp(-U/kT)\)
Potential energy of dipole in $E$ field ($U$)
determines the balance between “random” and “alignment”:
$U$ depends on $\theta$.
Natural choice: $U(\theta) = 0$ when $\theta = 0$
Convention: $U(\theta) = 0$ when $\theta = 90^\circ$
Why? $\theta = 90^\circ$ is an equipotential line:
no work creating extra dipole moment,
but $U(\theta)$ is then -ve in range $0<\theta<90^\circ$
Write $U(\theta) = U(90^\circ)$ - (energy lost in rotating $90^\circ \rightarrow \theta$)
$= 0$ - (horiz. force by dist.)

$$U = -QEs\cos\theta = -pE\cos\theta$$

$$U = -p\cdot E$$

(of course, $E$ should be $E_{loc}$ - later!)
Number Distribution function

Molecular density: $N$

Distribution function: $N(\theta)$

density of dipoles oriented between $\theta$ and $\theta + d\theta$ : $N(\theta)d\theta$

density of dipoles oriented between $\theta_1$ and $\theta_2$?

Define $\theta = 0$ axis along $E$

Note width of annulus between $\theta$ and $\theta + d\theta$ : $rd\theta$

$$\int_{\theta_1}^{\theta_2} N(\theta)d\theta$$

$$\int_{all \ \theta} N(\theta)d\theta = N$$
Random \((E=0)\) Distribution

No field: prop. to solid angle

\[ N(\theta)d\theta = Cd\Omega \]

\[ \frac{d\Omega}{4\pi} \text{ area annulus} \quad = \quad \frac{2\pi(r \sin \theta)(rd\theta)}{4\pi r^2} \quad = \quad \frac{\sin \theta d\theta}{2} \]

\[ d\Omega = 2\pi \sin \theta d\theta \quad \Rightarrow \quad N(\theta)d\theta = C2\pi \sin \theta d\theta \]

Find \(C\) by integrating \(N(\theta)d\theta\) between \(0\) and \(\pi\):

\[ N = \int_{0}^{\pi} N(\theta)d\theta = 2\pi C \int_{0}^{\pi} \sin \theta d\theta = 2\pi C \left[-\cos \theta\right]^{\pi}_{0} \]

\[ C = \frac{N}{4\pi} \quad \Rightarrow \quad N(\theta)d\theta = \frac{N}{2} \sin \theta d\theta \quad \text{(random)} \]
Distribution in presence of Field

Include Boltzmann term:

\[ N(\theta)d\theta = A \exp\left(-\frac{U}{kT}\right) d\Omega \]

\[ = 2\pi A \exp\left(-\frac{U}{kT}\right) \sin \theta d\theta \]

Find A by integrating \( N(\theta)d\theta \) between 0 and \( \pi \), as before?

Complex integral, simplifies when \( U/kT \) is small:

\[ \exp\left(-\frac{U}{kT}\right) \approx 1 - \frac{U}{kT} = 1 + \frac{pE \cos \theta}{kT} \]

This is a “low E, high T” approximation……..
Low $E$, high $T$ approximation

\[ N = \int_0^\pi N(\theta)\,d\theta = 2\pi A \int_0^\pi \sin\theta \left(1 + \frac{pE \cos\theta}{kT}\right) \,d\theta \]

\[ = 2\pi A \left[-\cos \theta + \frac{pE}{2kT} \sin^2 \theta\right]_0^\pi \]

\[ A = \frac{N}{4\pi} \quad (\text{as for random!}) \]

\[ \Rightarrow N(\theta)\,d\theta = \frac{N}{2} \sin\theta \left(1 + \frac{pE}{kT} \cos\theta\right) \,d\theta \]

Now Polarisation distribution:
(component of $p$ along $E$)

\[ P(\theta) = N(\theta)\,p \cos\theta \]
Net Polarisation

\[ P = \int_{0}^{\pi} P(\theta)d\theta = \frac{N}{2} \int_{0}^{\pi} \sin \theta \left( 1 + \frac{pE \cos \theta}{kT} \right) p \cos \theta d\theta \]

\[ = \frac{Np^2E}{3kT} \quad \Rightarrow \quad P = \frac{Np^2}{3kT} E \]

Recall \( P = \chi e \varepsilon_o E \) \( \Rightarrow \) \([\chi_e]_{\text{polar}} = \frac{Np^2}{3\varepsilon_o kT} \)

But all molecules acquire induced dipole moment:
Assuming \( E_{loc} = E \) :

\([\chi_e]_{\text{non-polar}} = N\alpha \)

\([\chi_e]_{\text{general}} = N \left( \alpha + \frac{p^2}{3\varepsilon_o kT} \right) \)
Plotting $\chi_e$ vs $1/T$

Works well for gases where $E_{loc} = E$ is a good approximation; Otherwise, must use

$$P = \frac{Np^2}{3\varepsilon_o kT} E_{loc}$$

Unfortunately, there is no simple expression, as for non-polar:

(partly because $E_{loc}$ rotates with the dipole!)
The Langevin Equation

When $U/kT$ is not small, integration of $N(\theta)d\theta$ yields:

$$P = Np \left[ \coth \left( \frac{pE}{kT} \right) - \frac{kT}{pE} \right]$$

Plotting $P$ vs $pE/kT$
shows two distinct regimes:

1. High $E$, low $T$: all dipoles aligned:
   $$P = Np$$

2. Low $E$, high $T$: small $U/kT$ approximation:
   (strictly $E_{loc}$)
   $$P = \frac{Np^2}{3kT} E$$