SERG Summer Seminar Series #12

Theory and Applications of Dielectric Materials

– Classical Theories of Dielectrics

Tzuyang Yu

Associate Professor, Ph.D.
Structural Engineering Research Group (SERG)
Department of Civil and Environmental Engineering
UMass Lowell, U.S.A.

August 8, 2014

Outline

- **Types of Polarizations**

- **The Theories of Static Permittivity**
  - **Debye's Theory**
  - **Onsager's Theory**

- **The Statistical Theories of Static Permittivity**
  - **Kirkwood's Theory**
  - **Frohlich's Theory**

Types of Polarization

- Interfacial polarization (Maxwell-Wagner) – From static to very low frequencies ($10^{exchRA_{D}avid_{P}erloff3}$Hz)

- Dipolar polarization – Orientational polarization for polar molecules; distortional polarization for non-polar molecules; in the frequency range of 10^{9} 10^{11} Hz

- Ionic polarization – In the frequency range of 10^{13} Hz

- Electronic polarization – In the frequency range of 10^{15} Hz or higher

Debye's Theory

- Assume that the permanent electric moments of an assembly of dipolar molecules are distributed about an externally-applied field in accordance with Boltzmann's law. If there is no directional forces due to the structure of the dielectric, a dipole moment μ (Note that this is not the magnetic permeability) at an angle θ to an electric field F has potential energy U in the following expression.

$$U = -\mu F \cos\theta \tag{1}$$

Boltzmann's law states that, the probability of the dipole axis lying within an element of solid angle $d\omega$ at an average angle θ to the direction of the field F is

$$\frac{\exp\{\frac{\mu F \cos\theta}{kT}\} d\omega}{\int \exp\{\frac{\mu F \cos\theta}{kT}\} d\omega} \tag{2}$$

Debye's Theory

where k is Boltzmann's constant ($k = 1.3806488\times 10^{-23}-$ $m^2 kg - s^{-2} - K^{-1}$). The element of solid angle can be taken as the value between cones of semi-angle θ and $\theta + d\theta$ having the field F along the axis. This means

$$d\omega = 2\pi \sin\theta d\theta \tag{3}$$

The average component of the dipole moment in the direction of F is

$$\mu < \cos\theta >= \frac{\int_0^\pi \mu \cos\theta \exp\{\frac{\mu F \cos\theta}{kT}\} \sin\theta d\theta}{\int_0^\pi \exp\{\frac{\mu F \cos\theta}{kT}\} \sin\theta d\theta} \tag{4}$$

$$= \frac{\int_{+1}^{-1} \mu x \exp\{\frac{\mu F x}{kT}\} dx}{\int_{+1}^{-1} \exp\{\frac{\mu F x}{kT}\} dx} \tag{5}$$

Debye's Theory

where $< \cos\theta >$ is the average value of $\cos\theta$ and $x = \cos\theta$. Applying integration by parts leads to

$$< \cos\theta >= \frac{x\left[\frac{kT}{\mu F}\exp\{\frac{\mu F x}{kT}\}\right]_{-1}^{+1} - \left[\left(\frac{kT}{\mu F}\right)^2\exp\{\frac{\mu F x}{kT}\}\right]_{-1}^{+1}}{\left[\left(\frac{kT}{\mu F}\right)\exp\{\frac{\mu F x}{kT}\}\right]_{-1}^{+1}} \quad (6)$$

$$= \coth\left(\frac{\mu F x}{kT}\right) - \left(\frac{kT}{\mu F x}\right) \quad (7)$$

$$= L\left(\frac{\mu F x}{kT}\right) \quad (8)$$

where $L(y) = \coth(y) - \frac{1}{y}$ is called Langevin's function.

- Under the condition $\left(\frac{\mu F x}{kT}\right) \ll 1$, the polarization (electric

Debye's Theory

moment per unit volume) due to the dipoles is

$$P_{\text{dipole}} = N_1 < \cos\theta >= N_1 \frac{\mu^2 F}{3kT} \tag{9}$$

where N_1 is the number of dipoles per unit volume. If we add this polarization to the distortional polarization $N_1 \alpha F$, the total polarization becomes

$$P = N_1 \left(\alpha + \frac{\mu^2}{3kT} \right) F \tag{10}$$

The local field F needs to be determined by the applied field E.

- Debye considered the Lorentz equation for the internal field by considering a parallel plate condenser model. In

Debye's Theory

this model, the potential difference between two plates is

$$E = \frac{V}{t} = \frac{4\pi Q}{\epsilon'} \tag{11}$$

where Q is the charge per surface area on the plates of the empty condenser when a potential difference V is applied to the the condenser. The internal field at the center of the spherical dielectric inclusion inside a homogeneous dielectric matrix is due to three parts.

1. The field due to the charges on the condenser plates and the dielectric surface adjacent to them, $F_1 = \frac{4\pi Q}{\epsilon}$;
2. the field due to the polarization charges on the spherical surface, F_2; and

Debye's Theory

3. the field due to the molecules in the spherical region, F_3,

in which we have two terms to determine; F_2 and F_3.

- The field due to the surface polarization charges − The surface of this spherical dielectric inclusion is $2\pi r^2 \sin\theta d\theta$ between the angles θ and $\theta + d\theta$. By symmetry, it produces no field at the center of the dielectric sphere, perpendicular to the direction of P, while in the direction parallel to P it produces a field in the following expression

$$\frac{2\pi r^2 \sin\theta d\theta P \cos\theta \cos\theta}{\epsilon r^2} \tag{12}$$

Debye's Theory

After integrating both sides over θ, we have

$$F_2 = \frac{2\pi}{\epsilon'} \int_0^{\pi} P \cos^2 \theta \sin \theta d\theta = \frac{4\pi P}{3\epsilon} \tag{13}$$

- The field due to the molecules in the spherical region – F_3 can only be determined if the distribution of individual molecules in space is known. Consider a special case in which the molecules ar distributed on a cubic lattice and when the molecules form an ideal gas, F_3 becomes zero. In this case,

  $$F = F_1 + F_2 = E + \frac{4\pi P}{3\epsilon} \tag{14}$$

  Since

  $$4\pi P = (\epsilon_0 - 1)\epsilon E \tag{15}$$

Debye's Theory

it provides

$$F = \frac{(\epsilon_0 + 2)E}{3} \tag{16}$$

Considering Eq.(10), it leads to

$$P = N_1 \left(\alpha + \frac{\mu^2}{3kT}\right) \frac{(\epsilon_0 + 2)E}{3} \tag{17}$$

Now we have

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = 4\pi N_1 \frac{\left(\alpha + \frac{\mu^2}{3kT}\right)}{3\epsilon} \tag{18}$$

which is Debye's equation for the static permittivity. It

Debye's Theory

can also be written as

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \cdot \frac{M}{\rho} = 4\pi N \frac{\left(\alpha + \frac{\mu^2}{3kT}\right)}{3\epsilon} \tag{19}$$

where N is the Avogadro's number. The quantity

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \cdot \frac{M}{\rho} \tag{20}$$

is called the molar polarization.

- Assumptions in Debye's theory –

1. No local directional forces due to neighboring molecules act on the dipole, such that they are distributed according to Langevin's law.

Onsager's Theory

2. The component F_3 of the local field is zero.

- Conclusions drawn from Debye's theory –

  1. For a non-polar material the molar polarizability should be a constant, independent of temperature and pressure.

  2. For a polar material the molar polarizability will fall within the increasing temperature, since the thermal agitation decreases the dipolar polarization.

  3. The left-hand side of Eq.(19) tends to $\frac{M}{\rho}$ as ϵ_0 approaches infinity.

Onsager's Theory

- In order to calculate the internal filed inside a molecule, Onsager considered a polarizable point dipole at the center of a spherical cavity inside a homogeneous dielectric matrix with ϵ_0. The radius of this spherical cavity is assumed to meet the following condition.

$$\frac{4\pi N_1 a^3}{3} = 1 \tag{21}$$

$$\Rightarrow a = \left[\frac{3}{4\pi N_1}\right]^{1/3} \tag{22}$$

suggesting the volume of the spherical cavity equals to the total volume of the material. This assumption is only applicable when there is no strong local fields inside the materials.

Onsager's Theory

- To calculate the total internal field, Onsager considered two parts in his calculation:

  1. The cavity field G produced by the external applied field E, and

  2. the reaction field R built up inside the cavity by the polarization which the dipole induces in its surroundings.

  Two potentials can be calculated by these two parts; V_1 for the internal field (inside the spherical region) and V_2 for the external field (outside the spherical region).

- The potential <u>outside</u> the spherical region V_2 is assumed

Onsager's Theory

to be in the form:

$$V_2 = -Er\cos\theta + \frac{A\cos\theta}{r^2} \tag{23}$$

where A is the constant determined by the boundary conditions.

- The potential <u>inside</u> the spherical region V_1 is assumed to be in the form:

$$V_1 = Br\cos\theta + \frac{B'\cos\theta}{r^2} \tag{24}$$

where B and B' are the constants determined by the boundary conditions. As we can see, B' must be zero

Onsager's Theory

to avoid the onset of singularity when $r = 0$. To determine these constants, we apply the potential boundary conditions in the normal and tangential directions.

$$-\epsilon_2 \frac{\partial V_2}{\partial r} = -\epsilon_1 \frac{\partial V_1}{\partial r} \tag{25}$$

at $r = a$ to preserve field continuity at the interface in the normal direction. In the tangential direction, we have

$$-\frac{1}{r} \cdot \frac{\partial V_2}{\partial \theta} = -\frac{1}{r} \cdot \frac{\partial V_1}{\partial \theta} \tag{26}$$

at $r = a$. These two boundary conditions lead to

$$\epsilon_2 \left(E \cos\theta + 2A \frac{\cos\theta}{a^3} \right) = \epsilon_1 \left(-B \cos\theta \right) \tag{27}$$

$$-E \sin\theta + A \frac{\sin\theta}{a^3} = B \sin\theta \tag{28}$$

Onsager's Theory

With these equations, we obtain the conditions to solve the constants.

$$\frac{A}{a^3} = -\frac{\epsilon_2 - \epsilon_1}{2\epsilon_2 + \epsilon_1} E \tag{29}$$

$$B = -\frac{3\epsilon_2}{2\epsilon_2 + \epsilon_1} E \tag{30}$$

Therefore, the potentials are

$$V_1 = -\frac{3\epsilon_2}{2\epsilon_2 + \epsilon_1} E r \cos\theta \tag{31}$$

$$V_2 = -E r \cos\theta - \frac{\epsilon_2 - \epsilon_1}{2\epsilon_2 + \epsilon_1} \cdot \frac{E \cos\theta}{r^2} a^3 \tag{32}$$

such that the field inside the spherical region is

$$F_1 = \frac{3\epsilon_2}{2\epsilon_2 + \epsilon_1} E \tag{33}$$

Onsager's Theory

In Onsager's model, $\epsilon_1 = 1$ and $\epsilon_2 = \epsilon_0$, the cavity field is

$$G = \frac{3\epsilon_0}{2\epsilon_0 + 1} E \qquad (34)$$

- Reaction field – To calculate the reaction field in Onsager's model, a point dipole moment m needs to be considered at the center of the spherical region, with its axis in the direction of $\theta = 0$, in the absence of an external field. Onsager assumed the following potentials.

$$V_2 = \frac{A\cos\theta}{r^2} V_1 = Br\cos\theta + \frac{B'\cos\theta}{r^2} \qquad (35)$$

Onsager's Theory

in which B' cannot be set to be zero (due to singularity). After applying the boundary conditions,

$$A = -\frac{3\epsilon_1}{2\epsilon_2 + \epsilon_1} B' \tag{36}$$

$$B = -\frac{2(\epsilon_2 - \epsilon_1)}{2\epsilon_2 + \epsilon_1} \cdot \frac{B'}{a^3} \tag{37}$$

It follows that the potentials are

$$V_1 = -\frac{2(\epsilon_2 - \epsilon_1)}{2\epsilon_2 + \epsilon_1} \cdot \frac{B' r \cos\theta}{a^3} + \frac{B' \cos\theta}{r^2} \tag{38}$$

$$V_2 = \frac{3\epsilon_1}{2\epsilon_2 + \epsilon_1} \cdot \frac{B' \cos\theta}{r^2} \tag{39}$$

- An isolated dipole in a medium of permittivity of ϵ_1 – If we set the radius of the spherical region to approach

Onsager's Theory

infinity , we have

$$V_1 = \frac{m\cos\theta}{\epsilon\epsilon_1 r^2} \tag{40}$$

from which we found

$$B' = \frac{m}{\epsilon\epsilon_1} \tag{41}$$

In summary,

$$V_1 = -\frac{2(\epsilon_2 - \epsilon_1)}{2\epsilon_2 + \epsilon_1} \cdot \frac{mr\cos\theta}{\epsilon\epsilon_1 a^3} + \frac{m\cos\theta}{\epsilon\epsilon_1 r^2} \tag{42}$$

$$V_2 = \frac{3\epsilon_1}{2\epsilon_2 + \epsilon_1} \cdot \frac{m\cos\theta}{\epsilon\epsilon_1 r^2} \tag{43}$$

- Total internal field – The total internal field on the molecule

Onsager's Theory

is

$$F = G + R = gE + \frac{rm}{a^3} \tag{44}$$

where

$$g = \frac{3\epsilon_0}{2\epsilon_0 + 1} \tag{45}$$

$$r = \frac{2(\epsilon_0 - 1)}{(2\epsilon_0 + 1)\epsilon} \tag{46}$$

It is noteworthy to point out that, when ϵ_0 approach infinity, Onsager's internal field tends to approach a finite value, while Debye's internal field tends to infinity.

- Total moment and polarization – The total moment, m of the molecule is the vector sum of its permanent moment,

Onsager's Theory

μ, and the moment αF induced in it by the local field

$$\begin{aligned} m &= \mu + \alpha F && (47) \\ &= \mu + \alpha g E + \frac{r\alpha m}{a^3} && (48) \\ &= \frac{\mu + \alpha g E}{1 - \frac{r\alpha}{a^3}} && (49) \end{aligned}$$

The couple moment acting on the molecule is

$$\begin{aligned} C &= m \times F && (50) \\ &= \frac{(\mu + \alpha g E) \times \left(gE + \frac{r\mu}{a^3}\right)}{\left(1 - \frac{r\alpha}{a^3}\right)^2} && (51) \end{aligned}$$

Onsager's Theory

$$= \frac{\left(g - \frac{rg\alpha}{a^3}\right)}{\left(1 - \frac{r\alpha}{a^3}\right)^2} \times E \tag{52}$$

$$= \frac{g}{\left(1 - \frac{r\alpha}{a^3}\right)} \mu \times E \tag{53}$$

We can also calculate the energy of the dipole induced at an angle θ to the applied field.

$$U = -\frac{g}{\left(1 - \frac{r\alpha}{a^3}\right)} \mu E \cos\theta \tag{54}$$

The average value of $\cos\theta$, $< \cos\theta >$, can be found using

Onsager's Theory

Boltzmann's equation.

$$< \cos\theta >= \frac{g}{\left(1-\frac{r\alpha}{a^3}\right)}\cdot\frac{\mu E}{3kT} \tag{55}$$

The mean moment parallel to the field is

$$\frac{\mu < \cos\theta > + \alpha g E}{\left(1-\frac{r\alpha}{a^3}\right)} = \frac{g}{\left(1-\frac{r\alpha}{a^3}\right)^2}\cdot\frac{\mu^2 E}{3kT} + \frac{\alpha g E}{\left(1-\frac{r\alpha}{a^3}\right)} \tag{56}$$

The polarization is

$$\frac{\epsilon}{4\pi}(\epsilon_0 - 1)E = P \tag{57}$$

$$= \frac{N_1 g}{\left(-\frac{r\alpha}{a^3}\right)}\left(\alpha + \frac{1}{1-\frac{r\alpha}{a^3}}\cdot\frac{\mu^2}{3kT}\right)E \tag{58}$$

Onsager's Theory

- Internal refraction index – Onsager defined an internal refraction index in the following.

$$\frac{n^2-1}{n^2+2}=\frac{\alpha}{\epsilon a^3} \tag{59}$$

as well as other relationships:

$$1-\frac{r\alpha}{a^3}=\frac{3(2\epsilon_0+n^2)}{(2\epsilon_0+1)(n^2+2)} \tag{60}$$

$$\frac{4\pi N_1\alpha}{\epsilon}=\frac{3(n^2-1)}{(n^2+2)} \tag{61}$$

With these relationships, we obtain Onsager's equation for the static permittivity.

$$\frac{(\epsilon_0-n^2)(2\epsilon_0+n^2)}{\epsilon_0(n^2+2)^2}=\frac{4\pi N_1\mu^2}{9kT\epsilon} \tag{62}$$

Onsager's Theory

- Comparison between Debye's model and Onsager's model
  –

  1. Internal field – In Debye's model,

     $$F = \frac{(\epsilon_0 + 2)E}{3} \tag{63}$$

     while in Onsager's model,

     $$F = \frac{2(\epsilon_0 - 1)}{((2\epsilon_0 + 1))\epsilon} \cdot \frac{m}{a^3} \tag{64}$$

  2. Polarization – In Debye's model,

     $$4\pi P = \epsilon(\epsilon_0 - 1)E = 4\pi N_1 \left(\alpha + \frac{\mu^2}{3kT}\right) F \tag{65}$$

Onsager's Theory

while in Onsager's model,

$$4\pi P = \epsilon(\epsilon_0 - 1)E = 4\pi N_1 \left(\alpha + \frac{A\mu^2}{3kT}\right) AgE \tag{66}$$

where

$$g = \frac{3\epsilon_0}{2\epsilon_0 + 1} \tag{67}$$

$$A = \frac{1}{1 - \frac{r\alpha}{a^3}} = \frac{(2\epsilon_0 + 1)(n^2 + 2)}{3(2\epsilon_0 + n^2)} \tag{68}$$

Kirkwood's Theory

- Kirkwood considered a specimen containing N dipoles of moment μ confined in a spherical volume V and situated in a constant, uniform external field E_0. The orientation of all dipoles is described by a set of coordinate vector X. The potential energy of the specimen in the configuration X in the presence of E_0 is denoted by $U(X, E_0)$. According to classical statistical theory, the probability that the specimen will have a configuration between X and $X + dX$ is $p(X, E_0)$ which is determined by

  $$p(X, E_0) = \frac{\exp\{-\frac{U(X,E_0)}{kT}\}dX}{\int \exp\{-\frac{U(X,E_0)}{kT}\}dX} \tag{69}$$

  where dX is the infinitesimal change of configurations. The average component of the moment of the ith molecule

Kirkwood's Theory

in the direction, e, of the applied field is found by averaging all possible states of the system.

$$< \mu_i, e >= \frac{\int (\mu_i, e) \exp\{-\frac{U(X, E_0)}{kT}\} dX}{\int \exp\{-\frac{U(X, E_0)}{kT}\} dX} \tag{70}$$

The energy of the specimen in the configuration X with the application of external field can be expressed in terms of the energy of the same configuration without the application of external field.

Assume a moment $M(X)$ to represent the energy state $U(X, 0)$. When the external field is applied, the difference in the energy states can be determined by

$$U(X, E_0) - U(X, 0) = -M(X)E_0 \tag{71}$$

Kirkwood's Theory

The Boltzmann factor in Eq.(71) can be expressed by

$$\text{exp}\{-\frac{U(X,E_0)}{kT}\} = \text{exp}\{-\frac{U(X,0)}{kT}\}\,\text{exp}\{\frac{M(X)E_0}{kT}\} \quad (72)$$

If we restrict our discussion in the case when

$$\frac{M(X)E_0}{kT} \ll 1 \quad (73)$$

suggesting that the measurement is taken under ordinary temperature condition. $\text{exp}\{-\frac{U(X,0)}{kT}\}$ can be approximated by

$$\text{exp}\{-\frac{U(X,0)}{kT}\} \approx 1 + \frac{U(X,0)}{kT} + \text{H.O.T.} \quad (74)$$

where H.O.T. denotes higher order terms. Then the average moment of the ith molecule in the direction of the

Kirkwood's Theory

field becomes

$$< \mu_i, e >= \frac{\int (\mu_i, e) \left[1 + \frac{U(X,0)}{kT} \right] \text{exp}\{-\frac{U(X,E_0)}{kT}\} dX}{\int \left[1 + \frac{U(X,0)}{kT} \right] \text{exp}\{-\frac{U(X,E_0)}{kT}\} dX} \tag{75}$$

Since Eq.(73), the second term in denominator can be neglected, define the denominator by

$$J^{-1} = \int \text{exp}\{-\frac{U(X,E_0)}{kT}\} dX \tag{76}$$

But the second term in the numerator cannot be neglected since the first term in the numerator is zero. Therefore, the first term of $< \mu_i, e >$ is

$$J \int (\mu_i, e) \, \text{exp}\{-\frac{U(X,E_0)}{kT}\} dX \tag{77}$$

Kirkwood's Theory

Since this is the average moment in the absence of applied field, it must be zero. Thus, we obtain

$$< \mu_i, e >= J \int (\mu_i, e) \left[\frac{M(X)E_0}{kT}\right] \text{exp}\{-\frac{U(X, E_0)}{kT}\} dX \quad (78)$$

$$=< (\mu_i, e)(M(X)e) > \frac{E_0}{kT} \quad (79)$$

In the absence of external field, the direction of e is arbitrary. Therefore,

$$< (\mu_i, e)(M(X)e) >=< \mu_i, M(X) > \quad (80)$$

Kirkwood calculated the average moment in two steps.

1. Allow all molecules (except the ith to randomly con-

Kirkwood's Theory

figured, giving

$$< \mu_i, e >=< \mu_i, \bar{M}_i > \frac{E_0}{3kT} \tag{81}$$

where $\bar{M}_i$ is the average moment of the entire specimen when only the ith molecule is fixed.

2. Average over all configurations of the ith molecule, giving

$$< \mu_i, M >=< \mu_i, \bar{M}_i >=< \mu, M > \tag{82}$$

- Dipole moment of small sphere under extreme conditions
  – Kirkwood defined

$$\bar{\mu} = \lim_{r_0 \to \infty} \bar{M}(R, r_0) \tag{83}$$

Kirkwood's Theory

where R is the radius of the specimen and r_0 the radius of a sphere whose radius is large enough to preserve homogeneity assumption and small enough when compared to R. Kirkwood further determined the expression of $\bar{M}$ in the limits $r_0 \to \infty$ and $R/r_0 \to \infty$.

$$\bar{M} = \frac{9\epsilon_0}{(\epsilon_0 + 2)(2\epsilon_0 + 1)}\bar{\mu} \tag{84}$$

In general, we have

$$\bar{\mu} = g\mu \tag{85}$$

where g is a measure of the local ordering. Then,

$$< \mu_i, e > = < \mu, \bar{M} > \frac{E_0}{3kT} \tag{86}$$

$$= \frac{9\epsilon_0}{(\epsilon_0 + 2)(2\epsilon_0 + 1)} \cdot \frac{g\mu^2}{3kT} E_0 \tag{87}$$

Kirkwood’s Theory

Since the equation defining the permittivity is

$$\epsilon(\epsilon_0 - 1) = \frac{4\pi M}{VE} = \frac{4\pi(\epsilon_0 + 2)M}{3VE_0} \tag{88}$$

Then,

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{4\pi M}{3V\epsilon E_0} = \frac{4\pi N < \mu_i, e >}{3V\epsilon E_0} \tag{89}$$

Finally,

$$\underline{\frac{(\epsilon_0 - 1)(2\epsilon_0 + 2)}{3\epsilon_0} = \frac{4\pi N}{V\epsilon} \cdot \frac{g\mu^2}{3kT}} \tag{90}$$

which is Kirkwood’s equation for the static permittivity of non-polarizable dipoles.

Frohlich’s Theory

- Similar to Debye’s model, but the considered model region does not have to be an exact sphere (to avoid cutting through molecules).

- The ”spherical” region contains charges e_i whose positions are denoted by a set of displacement vector r_i. The state of the all displacement vectors is denoted by X.

- The potential energy of the charges in the state X in the presence of an applied field E is denoted by $U(X, E)$.

- The spherical region has a dipole moment $M(X)$. The

Frohlich's Theory

mean moment in the direction of E is

$$< M, e >= \frac{\int (M(X)e) \exp\{-\frac{U(X,E)}{kT}\} dX}{\int \exp\{-\frac{U(X,E)}{kT}\} dX} \tag{91}$$

Frohlish considered the potential energy difference due to the polarization of surrounding continuous medium to be

$$U(X,E) - U(X,0) = -M(X)G \tag{92}$$

such that the Boltzmann's factor becomes

$$\exp\{-\frac{U(X,E_0)}{kT}\} = \left[1 + \frac{M(X)G}{kT}\right] \exp\{-\frac{U(X,0)}{kT}\} \tag{93}$$

The average/mean moment of the spherical region in the

Frohlich's Theory

direction of E is

$$< M,e >= \frac{\int (M(X),e)\left[1+\frac{M(X)G}{kT}\right]\text{exp}\{-\frac{U(X,0)}{kT}\}dX}{\int\left[1+\frac{M(X)G}{kT}\right]\text{exp}\{-\frac{U(X,0)}{kT}\}dX} \tag{94}$$

With previous definition (Eq.(76)), it simplifies to

$$< M,e >= J\left[M(X)e\right]^2\left(\frac{G}{kT}\right)\text{exp}\{-\frac{U(X,0)}{kT}\}dX \tag{95}$$

$$= \frac{JG}{3kT}\int M^2(X)\,\text{exp}\{-\frac{U(X,0)}{kT}\}dX \tag{96}$$

$$= \frac{G}{3kT} < M^2 > \tag{97}$$

where $< M^2 >$ represents the mean squared moment of the spherical region in the absence of an applied field.

Frohlich's Theory

- Suppose the spherical region is made up of N similar "units" (can be atoms, molecules or unit cells of a crystal) and let $x_i = (r_1, r_2, ...)$ represent the configuration of the jth unit and $m_j(r_j)$ the electric moment of the jth unit in the configuration x_j. The total moment becomes

$$M(X) = \Sigma_{j=1}^{N} m_j(x_j) \tag{98}$$

$$M^2(X) = \Sigma_{j=1}^{N} M(X) m_j(x_j) \tag{99}$$

After averaging over all configurations by considering their probabilities, it gives

$$< M^2 >= J \int \left[\Sigma_{j=1}^{N} M(X) m_j(x_j) \right] \text{exp}\{ -\frac{U(X,0)}{kT} \} dX \tag{100}$$

which is solved by two parts. The first part is to integrate

Frohlich's Theory

all the spherical region except the jth unit. The second part is to integrate the jth unit.

- In the first part, consider

$$dX = dX_j dx_j \tag{101}$$

where dX_j is the product of all the configuration vectors except the jth unit. Thus,

$$< M^2 >= J\Sigma_{j=1}^{N} \int m_j(x_j) \left[\int M(X) \exp\{-\frac{U(X,0)}{kT}\} dX_j \right] dx_j \tag{102}$$

$$= \Sigma_{j=1}^{N} \int m_j(x_j) \bar{m}_j(x_j) p(x_j) dx_j \tag{103}$$

Frohlich's Theory

where

$$\bar{m}_j(x_j) = \frac{\int M(X)\,\mathrm{exp}\{-\frac{U(X,0)}{kT}\}dX_j}{\int \mathrm{exp}\{-\frac{U(X,0)}{kT}\}dX_j} \qquad (104)$$

is the average moment of the whole spherical region (including the jth unit) when the jth unit is held in the configuration x_j when all other units are free to take up all possible configurations and

$$p_j(x_j) = \frac{\int \mathrm{exp}\{-\frac{U(X,0)}{kT}\}dX_j}{\int \mathrm{exp}\{-\frac{U(X,0)}{kT}\}dX} \qquad (105)$$

is the probability of the jth unit in configuration x_j when

Frohlich's Theory

all other units are allowed to take up possible configurations. The integral becomes

$$\int m_j(x_j)\bar{m}_j(x_j)p(x_j)dx_j \tag{106}$$

is the weighted average of the product $m_j(x_j)\bar{m}_j(x_j)$ for all possible configurations of the jth unit. Therefore,

$$< M^2 >= \Sigma_{j=1}^{N} < m_j(x_j)\bar{m}_j(x_j) > \tag{107}$$

The N units are all similar, and $< m_j\bar{m}_j >$ should be the same for the majority of them. The value of $\bar{m}_j(x_j)$ depends on the short-range forces acting on the jth unit, and it may be different from average for units near the surface of the sphere. Since this difference should be small, we may write

$$< M^2 >= N < m\bar{m} > \tag{108}$$

Frohlich's Theory

Substituting this expression into $< Me >$ provides

$$< Me > = \frac{3\epsilon_0}{2\epsilon_0 + 1} \cdot \frac{< M^2 >}{3kT} E = \frac{3\epsilon_0}{2\epsilon_0 + 1} \cdot \frac{N < m\bar{m} >}{3kT} E \tag{109}$$

Since the polarization is defined as the electric moment per unit volume,

$$\frac{4\pi P}{E} = \epsilon(\epsilon_0 - 1) = \frac{3\epsilon_0}{2\epsilon_0 + 1} \cdot \frac{4\pi N < m\bar{m} >}{3kT} \tag{110}$$

where $N_1 = \frac{N}{V}$ is the number of atoms, molecules or units of cells per unit volume. Finally,

$$\underline{\frac{(\epsilon_0 - 1)(2\epsilon_0 + 1)}{3\epsilon_0} = \frac{4\pi N}{V\epsilon} \cdot \frac{< m\bar{m} >}{3kT}} \tag{111}$$

This is the Frohlich's equation for the static permittivity of non-polarizable dipoles.

Frohlich's Theory

- Comparison between Kirkwood's model and Frohlich's model –

  1. Potential energy due to polarization – In Kirkwood's model,

     $$U(X,E) - U(X,0) = -M(X)E_0 \tag{112}$$

     while in Frohlish's model,

     $$U(X,E) - U(X,0) = -M(X)G \tag{113}$$

     where $G = \dfrac{3\epsilon_0 E}{2\epsilon_0 + 1}$.

  2. Total moment of an molecule/unit – By definition, the

Frohlich's Theory

total moment of an molecule/unit is

$$m = \mu + \alpha F = \frac{\mu + \alpha g E}{1 - \frac{r\alpha}{a^3}} \tag{114}$$

In Kirkwood's model,

$$m = \mu \tag{115}$$

$$\bar{m} = g\mu \tag{116}$$

while in Frohlich's model, m and $\bar{m}$ must be evaluated.