

THE PENNSYLVANIA STATE UNIVERSITY  
SCHREYER HONORS COLLEGE

DEPARTMENT OF PHYSICS

THEORY OF THE DIELECTRIC CONSTANT OF POLAR LIQUIDS

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SPRING 2014

A thesis  
submitted in partial fulfillment  
of the requirements  
for baccalaureate degrees  
in Physics and Mathematics  
with honors in Physics

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## **ABSTRACT**

I study the dielectric constant of highly polar liquids, such as ionic liquids (ILs) and polymerized ionic liquids (PILs). ILs and PILs have wide applications in fields like electrolytes in lithium ion batteries, fuel cell-membrane, electrode assemblies, supercapacitors, sensors and actuators. To understand the dielectric properties of ILs and PILs is of both scientific and practical importance. Nevertheless, Onsager's theory applicable to common polar systems is not applicable in IL and PIL systems with huge permanent dipole moments, for which an additional correlation g factor, originally introduced by Kirkwood should be incorporated, which specifies the short range interaction among dipoles. It is noted that in highly polar liquids the g factor decreases rapidly as the density of strong dipoles increases, making the dielectric constant also decrease as the dipole density increases. This trend is opposite to the prediction of Onsager's theory which expects the dielectric constant to increase as the density of the polar content increases. This thesis reviews all the classical models about the dielectric constant and recognizes the assumptions and limits of those models. I will propose some possible theories to explain the deviation from Onsager's Theory in highly polar liquids.

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## **ACKNOWLEDGEMENTS**

I am indebted to my research advisor Professor Ralph Colby for his encouragement, guidance, help, and unstinting support. I am very grateful to Dr. Quan Chen, whose help and guidance made this project possible. I would like to also thank Josh Bartels for his help and advice on my Thesis.

## Chapter 1 Introduction

### 1.1. Macroscopic Maxwell's equations and the Dielectric Constant

Unlike the vacuum, there is charge distribution in materials. When the electric field  $E$  travels through a material, it interacts with that material to change from the electric field in vacuum space. The fundamental Microscopic Maxwell's equations still hold.

Microscopic Maxwell's equations

$$\nabla \cdot E = 4\pi\rho \quad (1.1)$$

$$\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t} \quad (1.2)$$

$\rho$  is the charge density and  $B$  is the magnetic field in the materials.

Since we are studying the electrostatic case with no applied magnetic field, the right hand side of eqn(1.2) equals to 0 to give

$$\nabla \times E = 0 \quad (1.3)$$

Equation (1.1) is a function of charge density. In the materials, the fundamental unit is the molecules, thus it is useful to derive a macroscopic version of equation (1.1) for the molecules.

As discussed, we can think of the molecules as clusters of charges. To denote the  $i$ -th charge in the  $k$ -th cluster, we use  $e_{ki}$ . Using the same idea, we denote the position of that charge as  $r_{ki}$  and the mass as  $m_{ki}$ . Then the position of the center of mass of the  $k$ -th cluster is denoted as  $r_k$

$$r_k \sum_i m_{ki} = \sum_i m_{ki} r_{ki} \quad (1.4)$$

And the relative position of the charge  $e_{ki}$  in the cluster, with respect with its center of mass is denoted as

$$l_{ki} = r_{ki} - r_k \quad (1.5)$$

Since the molecule is not a point charge, it may interact with other molecules even if they do not possess charge. So we not only need to consider the charge, but also the dipole, quadrupole and higher order electric moments of the molecule. The charge here is the charge one molecule possesses, and we call it the free charge. The free charge, the dipole moment and quadrupole moment of the molecule can be written as the following:

$$e_k = \sum_i e_{ki} \quad (1.6)$$

$$\mathbf{m}_k = \sum_i e_{ki} l_{ki} \quad (1.7)$$

$$\mathbf{Q}_k = \frac{1}{2} \sum_i e_{ki} l_{ki} l_{ki} \quad (1.8)$$

The total electrostatic energy of the system is given by

$$\phi(r) = \sum_k \sum_i \frac{e_{ki}}{|r_{ki} - r|} \quad (1.9)$$

For each cluster of charge, the denominator can be written as

$$|r_{ki} - r| = |(r_k - r) + l_{ki}| \quad (1.10)$$

We do Taylor expansion with respect to  $1/(|r_k - r|)$  and we get

$$\begin{aligned} \phi(r) &= \sum_k \sum_i \left\{ e_{ki} \frac{1}{|r_{ki} - r|} + l_{ki} \cdot \nabla_{r_k} \frac{1}{|r_k - r|} + \frac{1}{2} l_{ki} l_{ki} : \nabla_{r_k} \nabla_{r_k} \frac{1}{|r_k - r|} + \dots \right\} \\ &= \sum_k \left\{ \frac{e_k}{|r_k - r|} + m_k \cdot \nabla_{r_k} \frac{1}{|r_k - r|} + Q_k : \nabla_{r_k} \nabla_{r_k} \frac{1}{|r_k - r|} + \dots \right\} \end{aligned} \quad (1.11)$$

By applying (1.1), we find:



$$\nabla \cdot E = \Delta \phi \quad (1.12)$$

And we know that

$$-\Delta \frac{1}{|r_k - r|} = 4\pi \delta(r_k - r) \quad (1.13)$$

From this we get,

$$-\Delta \phi(r) = \text{div} E(r) = 4\pi \left\{ \sum_k e_k \delta(r_k - r) + \nabla_{rk} \cdot \sum_k m_k \delta(r_k - r) + \nabla_r \nabla_r \sum_k Q_k \delta(r_k - r) \right\} \quad (1.14)$$

Since the quantity times the delta function at its location gives the density function at that position, we get

$$\sum_k e_k \delta(r_k - r) = \rho_f(r) \quad (1.15)$$

$$\sum_k m_k \delta(r_k - r) = P(r) \quad (1.16)$$

$$\sum_k e_k \delta(r_k - r) = \zeta(r) \quad (1.17)$$

They are free charge density, dipole moment density and quadrupole moment density.

Then we can get the macroscopic Maxwell's equation for divergence of the electric field:

$$\nabla \cdot E(r) = 4\pi(\rho_f - \nabla \cdot P + \nabla \nabla : \zeta) \quad (1.18)$$

We usually think that the quadrupole term can be neglected. So we have

$$\nabla \cdot (E - 4\pi P) = 4\pi \rho_f \quad (1.19)$$

And thus the displacement field, D is

$$D = E - 4\pi P \quad (1.20)$$

In eqn(1.20), we write a relation between D and E. The dielectric constant,  $\varepsilon$  describes the proportionality between the displacement field D and the electric field E.

$$\varepsilon = D / E \quad (1.21)$$

We are using the cgs unit here and the vacuum permittivity  $\epsilon_0$  is unity.

$$\epsilon_0=1 \quad (1.22)$$

With the displacement field  $D$ , we can also rewrite the macroscopic Maxwell Formula:

$$\nabla \cdot D = 4\pi\rho_f \quad (1.23)$$

In some systems, the molecules are all electrically neutral, so the free charge density is zero everywhere. In such system, (1.23) becomes

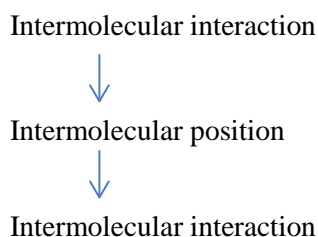
$$\nabla \cdot D = 0 \quad (1.24)$$

## Chapter 2 Dielectric Constant Model for Polar Liquids

### 2.1. Idea of Dielectric Constant Model

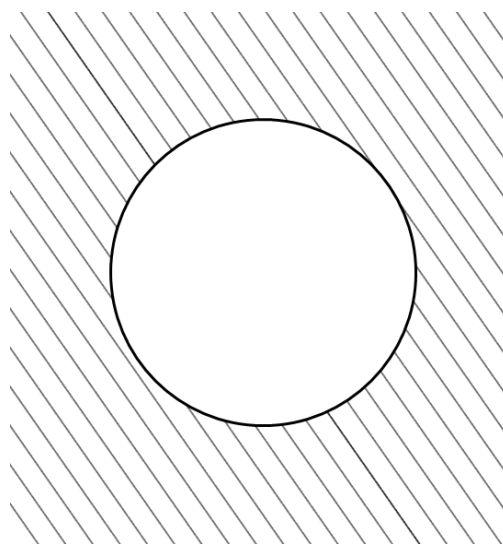
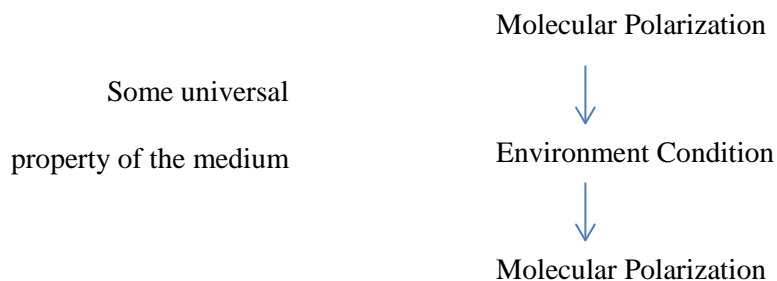
The dielectric constant of the material is a topic that has been studied for a long time. The difficulty of this problem is that we not only need to consider the kinetics of the molecules in the electric field and its contribution to the total polarization of the material, but also need to consider the interaction between the molecules. It is usually easy to study the kinetics and contribution of the atoms, so the major difficulty falls into studying the interaction between the atoms.

In crystals, atoms tend to stay on the crystal lattice, so the intermolecular positions are known and interactions are easier to study. However, molecules are constantly moving in the liquid phase, and intermolecular interactions are harder to study. At the same time, the intermolecular position in the liquids is strongly dependent on the intermolecular interactions. Thus this question becomes a loop question:



So how could we attack this problem? In the Clausius-Mossotti Model and the Onsager Model, they both assume a spherical cavity with a polarized point dipole in the center as the nucleus in the atom and the outside medium with some universal properties.

Then they study the interaction between one molecule and its environment. In the Clausius-Mossotti Model, a homogeneous polarization density outside the molecule is assumed. And in Onsager's Model, the outside medium is assumed to have a homogeneous dielectric constant.

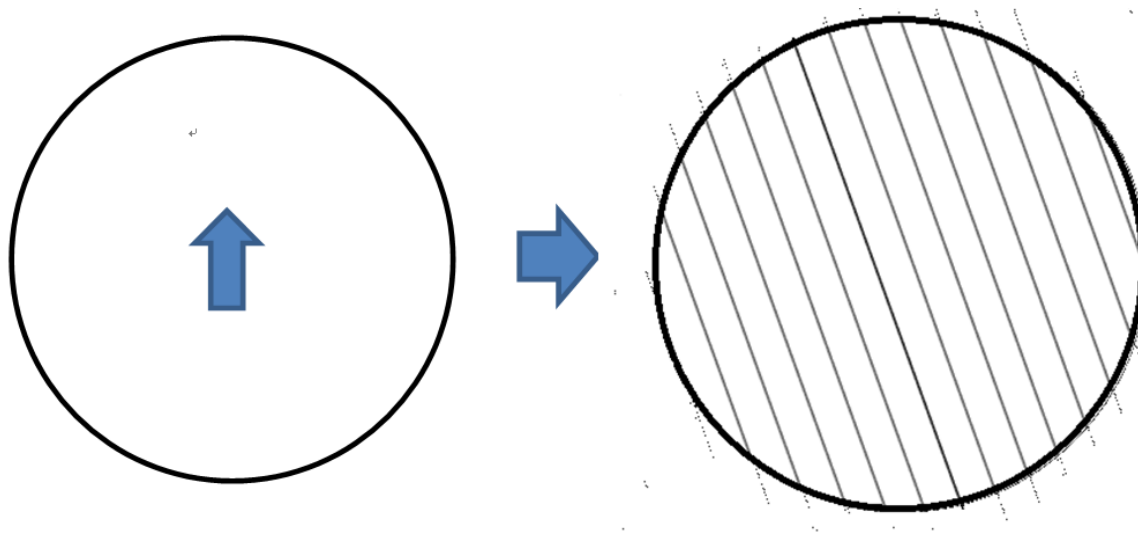


**Figure 1 a spherical cavity and the surrounding medium to model the field that the point dipole in the center of the cavity experiences. In the Clausius-Mossotti Model, the medium has uniform polarization density. In the Onsager Model, the medium has uniform dielectric constant.**

In addition, since the medium is made up of molecules, the total polarization of the medium equals the total polarization of all molecules. With the relationship between the surrounding medium and the center molecule, we can find the equilibrium of the polarization by solving a single variable equation and calculate the dielectric constant from that. This method is called the self-consistent field method. As we see, the self-consistent

field model is a very crude model based on strict constraints. The alternative way is to calculate the exact statistical mechanics equation. However, in order to give the analytic solution to the statistical mechanics equation, we also need to give some crude assumptions, from which it gives us the similar results.

Actually, the self-consistent field model can be viewed as a simplified version of the statistical mechanics equation. As we argue that since the polarization is in the center of the molecule, the polarization is discretized in space. However, its electric property is similar to the electric property of some continuous medium. By studying the electric interaction of one molecule, we can find its equivalent continuous description. And since the molecules are usually equally probable in the space, the outside medium would have some kind of homogeneity due to that.



**Figure 2 Left: the molecule in the cavity. Right: the continuous dielectric medium. The electric properties in the left picture is equivalent to the electric properties in the right picture (Onsager, 1936)**

The microscopic field inside the cavity is called the internal field and the macroscopic field in the continuous medium is called the Maxwell field.

The polarization in the dielectric continuum can be calculated by combining (1.20) and (1.21),

$$P = \frac{\varepsilon - 1}{4\pi} E \quad (2.1)$$

On the other hand, the polarization can be calculated by the polarization contributed by the molecules under the internal field.

$$\frac{\varepsilon - 1}{4\pi} E = \sum_k N_k m_k \quad (2.2)$$

$N_k$  is the number density of dipoles with dipole moment  $m_k$ .

## 2.2. Electric Properties of the Cavity

Since the free charge density is zero everywhere, we have two fundamental Macroscopic Maxwell relations

$$\nabla \cdot D = 0 \quad (2.3)$$

$$\nabla \times E = 0 \quad (2.4)$$

For the self-consistent model, we are interested in the boundary condition of the cavity. If we denote the direction perpendicular to the boundary surface to be the z-axis, then from (2.3), we get

$$\frac{\partial D_x}{\partial x} + \frac{\partial D_y}{\partial y} + \frac{\partial D_z}{\partial z} = 0 \quad (2.5)$$

Since the x-axis and y-axis are parallel to the surface and the dielectric constant is continuous, the displacement field should be continuous and its derivative should be finite. At the same time, the sum in eqn 2.5 is zero, so the derivative on the z-axis is finite and the D field on the z-axis is continuous. Thus the z-component of the displacement field is the same on the both sides of the surface.

$$D_{1z} = D_{2z} \quad (2.6)$$

The subscripts 1 and 2 denote two different dielectric mediums.

From (2.4), we get

$$\frac{\partial E_y}{\partial z} - \frac{\partial E_z}{\partial y} = 0 \quad (2.7)$$

With the same argument as for the displacement field, since  $\frac{\partial E_z}{\partial y}$  changes in the same medium, it gives a finite number. Thus we have

$$E_{1y} = E_{2y} \quad (2.8)$$

From these boundary conditions, we are able to write down the differential equations and solve for the electric field.

Another important property with respect to the surface between two dielectric media is the surface charge density. As shown before, the potential from the dipole moment is

$$\begin{aligned} V(r) &= \int_{\nu} P \cdot \nabla \left( \frac{1}{r} \right) d\tau \\ &= \int_{\nu} \frac{P \cdot \hat{r}}{r^2} d\tau \end{aligned} \quad (2.9)$$

We take  $\nu$  as the space that contains the dipole and we integrate over the space.

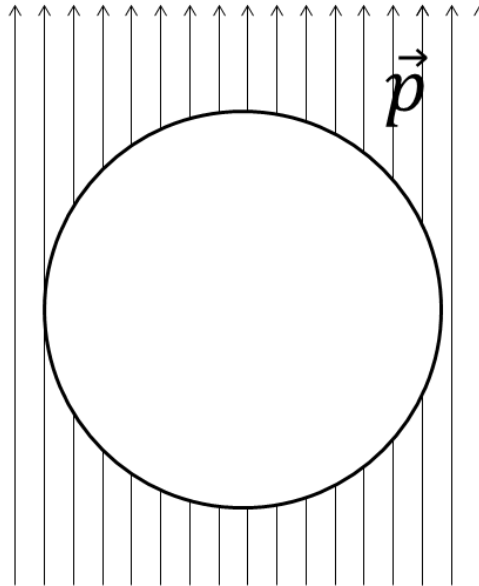
Since polarization is the dipole moment per unit volume, in an infinitesimally small volume  $d\tau$  the dipole moment will be  $Pd\tau$ . The potential of the dielectrics will be:

$$\begin{aligned} V(r) &= \int_{\nu} P \cdot \nabla \left( \frac{1}{r} \right) d\tau \\ &= \int_{\nu} \nabla \cdot \left( \frac{P}{r} \right) d\tau - \int_{\nu} \frac{1}{r} (\nabla \cdot P) d\tau \\ &= \oint_s \frac{1}{r} P \cdot da - \int_{\nu} \frac{1}{r} (\nabla \cdot P) d\tau \end{aligned} \quad (2.10)$$

From (1.30), we can see that the potential due to the term  $\nabla \cdot \mathbf{P}$  is similar to the potential due to the free charge. The other term is acting like charge on the surface, so we call  $\sigma_b = \mathbf{P} \cdot \hat{\mathbf{n}}$  the surface charge density and  $\rho_b = -\nabla \cdot \mathbf{P}$  the bound charge density.

### 2.3. Clausius-Mossotti Model

The first successful model is the Clausius-Mossotti Model. It studies the pure solution with only atomic polarization. In this model, since we can view the solution as homogeneous, we have the same polarization density everywhere.



**Figure 3 the Clausius-Mossotti Model Diagram. The polarization and the electric field are both homogeneous outside the cavity.**

As we discussed earlier, the polarization on the boundary between two media would induce the surface charge and the surface charge would create a field at the center. We call this field the sphere field,  $E_{sph}$ , since this field is generated by the outside sphere. The



internal field consists of two parts: the Maxwell field and the sphere field. This field was first calculated by Lorentz, so it is also called Lorentz field. We first calculate the sphere field, using polar coordinates with the origin at the center of the cavity and the z-axis pointing in the direction of the electric field.

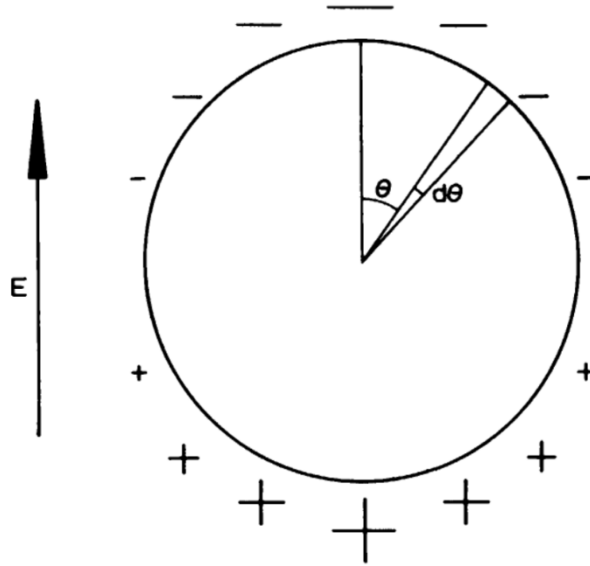


Figure 4 the Lorentz Field Diagram (Bottcher, 1973)

The surface charge density is the projection of the polarization on the normal vector of the surface,  $\sigma_b = P \cdot \hat{n}$ . And the surface charge is obtained by the surface charge density times the surface area.

$$de = -2\pi r^2 \sin \theta d\theta P \cos \theta \quad (2.11)$$

Since the overall electric field will only have a component in the z-direction, we calculate the z-direction component of the electric field contributed by the charge on the surface:

$$dE = \frac{de}{r^2} \cos \theta \quad (2.12)$$

$E_{sph}$  is obtained by integrating the contribution over the whole surface:

$$E_{sph} = P \int_0^{\pi} 2\pi \sin \theta \cos^2 \theta d\theta = \frac{4\pi}{3} P \quad (2.13)$$

Thus the Lorentz field equals to

$$E_L = \frac{\varepsilon + 2}{3} E \quad (2.14)$$

Since the Lorentz field is the internal field, the polarization is the field times the atomic polarization. From (2.1), we get an equation for the dielectric constant

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha \quad (2.15)$$

This is the Clausius-Mossotti equation.

### 2.3. Onsager's Model

The Clausius-Mossotti model was a great success. However, it did not explain the dielectric behavior of a dipolar liquid well. In 1936, Dr. Lars Onsager came up with the famous Onsager's model which gives a very good prediction for the dielectric constant of dipolar liquids. We will present the derivation based on Onsager's paper in 1936 (Onsager, 1936).

Onsager's model also considers a vacuum cavity inside some homogeneous dielectric medium. However, there are two differences between Onsager's Model and the Clausius-Mossotti Model:

1. Onsager's Model assumes a homogeneous dielectric medium outside the cavity instead of a homogeneous polarization medium. At the surface of the cavity, the polarization adjusts itself due to the existence of the cavity.

2. Onsager's Model also considers the interaction between the external field and the dipole, which will eventually apply a field called reaction field back on the dipoles.

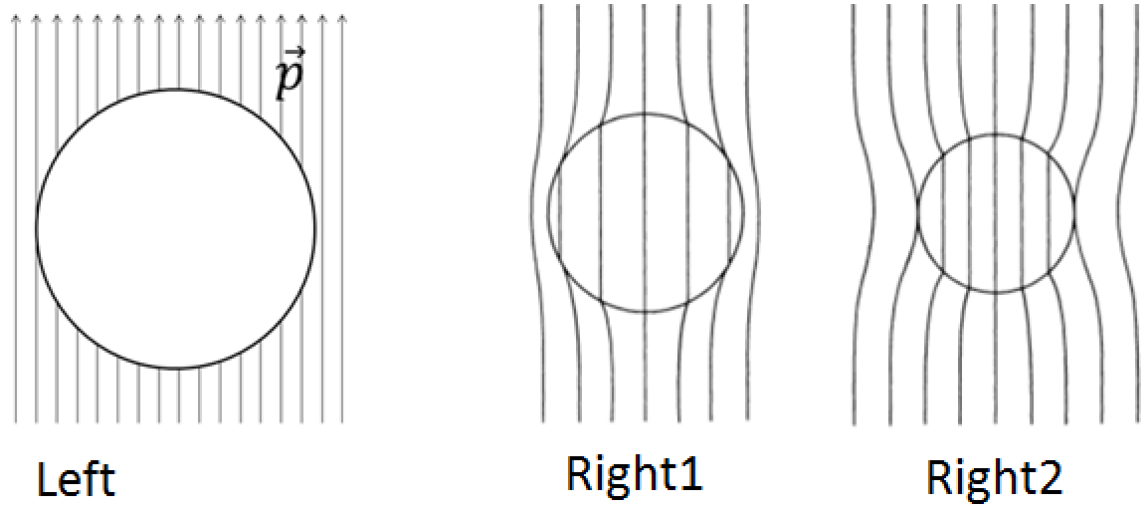


Figure 5 Left: Clausius-Mossotti Model, both electric field and polarization are homogeneous Right 1,2(Bottcher, 1973): lines of displacement field in Onsager's Model. Inside the cavities are vacuum with the dielectric constant equal to 1. 1, dielectric constant is 1.8. 2, the dielectric is 3. The polarization will adjust itself due to the existence of the cavity. Both electric field and polarization are affected.

This model considers a homogeneous medium of dielectric constant,  $\epsilon$  around a vacuum cavity of radius  $a$ . Onsager then introduces a rigid dipole of moment  $m$  into the cavity. For simplicity, he assumed the dipole to be ideal and placed in the center of the cavity. There is no charge density anywhere in the model, so we can use Laplace's Equation.

### 2.3.1 Laplace's Equation

From Maxwell's equations, the laplacian of the potential  $\phi$  is the charge density. If we have no charge density, then the laplacian of potential energy is 0.

$$\Delta\phi = \left(\frac{\partial}{\partial r} + \frac{2}{r}\right)\frac{\partial\phi}{\partial r} + \frac{1}{r^2}\left(\frac{\partial}{\partial\theta} + \cot\theta\right)\frac{\partial\phi}{\partial\theta} = 0 \quad (2.16)$$

We assume that we can solve this equation by separation of variables.

$$\phi(r, \theta) = U(r)V(\theta) \quad (2.17)$$

Applying the laplacian of polar coordinates, and we get:

$$\frac{r^2}{U(r)} \left( \frac{\partial}{\partial r} + \frac{2}{r} \right) \frac{\partial U(r)}{\partial r} + \frac{1}{V(\theta)} \left( \frac{\partial}{\partial \theta} + \cot \theta \right) \frac{\partial V(\theta)}{\partial \theta} = 0 \quad (2.18)$$

Because the first part only depends on r, and the second part only depends on  $\theta$ , so to have their sum vanish the only possibility is that they are both equal to some constant.

$$\frac{r^2}{U(r)} \left( \frac{\partial}{\partial r} + \frac{2}{r} \right) \frac{\partial U(r)}{\partial r} = - \frac{r^2}{U(r)} \left( \frac{\partial}{\partial r} + \frac{2}{r} \right) \frac{\partial U(r)}{\partial r} = C \quad (2.19)$$

Solving this ordinary equation set, we get our general solution below:

$$\phi(r, \theta) = \sum_{n=0}^{\infty} (a_n r^n + b_n r^{-(n+1)}) P_n(\cos \theta) \quad (2.20)$$

With the general solution of the Laplace equation, we can solve for the homogeneous field and the reaction field under different boundary conditions.

Boundary conditions for reaction field

$$\psi_{out}(\infty) < \infty \quad (2.21)$$

$$(\psi_{in})_{r \rightarrow 0} - \frac{m \cos \theta}{r^2} < \infty \quad (2.22)$$

$$(\psi_{out})_{r=a} = (\psi_{in})_{r=a} \quad (2.23)$$

$$\mathcal{E} \left( \frac{\partial \psi_{out}}{\partial r} \right)_{r=a} = \left( \frac{\partial \psi_{in}}{\partial r} \right)_{r=a} \quad (2.24)$$

This boundary condition considers the interaction between the dipole and its environment under no external electric field. It can be seen as the surrounding medium reacts to the existence of the dipole and then applies an electric field on the dipole. So the field applied is called the reaction field.

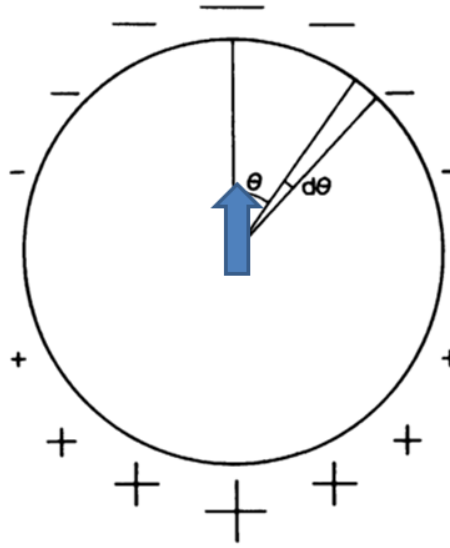


Figure 6 the Visualization of the Reaction Field. The dipole induces the charge on the surface. And the induced surface charge then applies the electric field on the dipole

From (2.21), we get

$$\psi_{out}(r, \theta) = \sum_{n=0}^{\infty} a_n r^{-(n+1)} P_n(\cos \theta) \quad (2.25)$$

From (2.22), we get

$$\psi_{in}(r, \theta) = \sum_{n=0}^{\infty} b_n r^n P_n(\cos \theta) + \frac{m \cos \theta}{r^2} \quad (2.26)$$

From (2.23), (2.25), (2.26) we get:

$$\forall n \neq 1, a_n = 0, b_n = 0 \quad (2.27)$$

When  $n=1$ ,

$$\frac{m}{a^2} + b_1 a = \frac{a_1}{a^2} \quad (2.28)$$

$$-2 \frac{m}{a^3} + b_1 = -2\varepsilon \frac{a_1}{a^3} \quad (2.29)$$

Solving the equation set (2.28), (2.29), we get:

$$b_1 = -\frac{2(\varepsilon - 1)}{2\varepsilon + 1} \frac{m}{a^3} := R \quad (2.30)$$

$$a_1 = \frac{3m}{2\varepsilon + 1} := \frac{m^*}{\varepsilon} \quad (2.31)$$

After arrangement, the solution is

$$\psi_{out}(r, \theta) = \frac{m^* \cos \theta}{\varepsilon r^2} \quad (2.32)$$

$$\psi_{in}(r, \theta) = \frac{m \cos \theta}{r^2} - R r \cos \theta \quad (2.33)$$

$$R = \frac{2(\varepsilon - 1) m}{2\varepsilon + 1 a^3} \quad (2.34)$$

$$m^* = \frac{3\varepsilon}{2\varepsilon + 1} m \quad (2.35)$$

$$E_{in, r=0} = -\frac{\partial \psi_{in}}{\partial r}(0) = R \quad (2.36)$$

Onsager's reaction field is a result of the induced dipole moment of the medium, caused by the electric field of the rigid dipole.

Onsager's Homogeneous field E

Next Onsager considers the cavity in an electric field, and applies the Laplace's equation again.

Boundary Conditions

$$(\psi_{out})_{r \rightarrow \infty} = -Er \cos \theta \quad (2.37)$$

$$\psi_{in}(0) < \infty \quad (2.38)$$

$$(\psi_1)_{r=a} = (\psi_2)_{r=a} \quad (2.39)$$

$$\varepsilon \left( \frac{\partial \psi_{out}}{\partial r} \right)_{r=a} = \left( \frac{\partial \psi_{in}}{\partial r} \right)_{r=a} \quad (2.40)$$

By (2.37), we get:

$$\psi_{out}(r, \theta) = \sum \frac{a_n}{r^{n+1}} P_n(\cos \theta) - Er \cos \theta \quad (2.41)$$

By (2.38), we get:

$$\psi_{in}(r, \theta) = \sum b_n r^n P_n(\cos \theta) \quad (2.42)$$

when  $n \neq 1$ , from (2.39), (2.40), (2.41) and (2.42), we get

$$\frac{a_n}{a^{n+1}} = b_n r^n \quad (2.43)$$

$$-\varepsilon(n+1) \frac{a_n}{a^{n+2}} = n b_n a^{n-1} \quad (2.44)$$

And we find when  $n \neq 1$ ,  $a_n = b_n = 0$ .

When  $n = 1$ , we get

$$\frac{a_1}{a^2} - Ea = b_1 a \quad (2.45)$$

$$\varepsilon \left( \frac{2a_1}{a^3} + E \right) = -b_1 \quad (2.46)$$

Solving (2.45) and (2.46), we get

$$a_1 = -\frac{\varepsilon - 1}{2\varepsilon + 1} a^3 E := -M \quad (2.47)$$

$$b_1 = -\frac{3\varepsilon}{2\varepsilon + 1} E := -G \quad (2.48)$$

So after arrangement we get,

$$\psi_{out}(r, \theta) = -Er \cos \theta - \frac{M \cos \theta}{r^2} \quad (2.49)$$

$$\psi_{in}(r, \theta) = -Gr \cos \theta \quad (2.50)$$

$$M = \frac{\varepsilon - 1}{2\varepsilon + 1} E a^3 \quad (2.51)$$

$$G = \frac{3\varepsilon}{2\varepsilon + 1}E \quad (2.52)$$

$$E_{in,r=0} = -\frac{\partial\psi_{in}}{\partial r}(0) = G \quad (2.53)$$

### 2.3.2 Internal field

The total field acting inside the cavity will be

$$F = G + R = \frac{3\varepsilon}{2\varepsilon + 1}E + \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)a^3}m \quad (2.54)$$

And the dipole moment is the sum of the induced and the permanent dipole:

$$m = \mu_0 u + \alpha F \quad (2.55)$$

Together with “internal refractive index”  $n$  as follows

$$\alpha = \frac{n^2 - 1}{n^2 + 2}a^3 \quad (2.56)$$

Combine (2.54), (2.55) and (2.56), we get:

$$\begin{aligned} m &= \frac{(n^2 + 2)(2\varepsilon + 1)}{3(2\varepsilon + n^2)}\mu_0 u + \frac{\varepsilon(n^2 - 1)}{(2\varepsilon + n^2)}\alpha^3 E \\ &= \mu u + \frac{\varepsilon(n^2 + 2)}{(2\varepsilon + n^2)}\alpha E \end{aligned} \quad (2.57)$$

So, when  $\alpha=0$ ,

$$I = F - E = \frac{\varepsilon - 1}{2\varepsilon + n^2}En^2 \quad (2.58)$$

which is similar to Clausius's result:

$$I = E(\varepsilon - 1) / 3 \quad (2.59)$$

For the non-polar liquids  $\varepsilon=n^2$ , and the two results then become identical.



### 2.3.3 Orientation of the Dipole Moment

The force-couple equals

$$M = F \times m = G \times m = \frac{3\varepsilon}{2\varepsilon + 1} E \times m = \frac{3\varepsilon}{2\varepsilon + 1} \mu E \times u = \mu^* E \sin \theta \quad (2.60)$$

where  $\theta$  is the angle between the electric field and the permanent dipole moment and  $\mu^*$  is

$$\mu^* = \frac{\varepsilon(n^2 + 2)}{(2\varepsilon + n^2)} \mu \quad (2.61)$$

Where  $\mu^*$  stands for “external” characteristic moment of the molecules, while the actual electric moment  $\mu$  will depend on the dielectric constant of the environment according to (2.57).

$$\begin{aligned} \mu &= \frac{(n^2 + 2)(2\varepsilon + 1)}{3(2\varepsilon + n^2)} \mu_0 \\ \mu^* &= \frac{\varepsilon(n^2 + 2)}{2\varepsilon + n^2} \mu_0 \end{aligned} \quad (2.62)$$

So the electric potential energy of the particle is:

$$w = \int M d\theta = -\mu^* E \cos \theta \quad (2.63)$$

The distribution of  $w$  will follow the Boltzmann distribution:

$$P(w) = \frac{e^{-w/kt}}{\int e^{-w/kt} dw} \quad (2.64)$$

$$dw = \mu^* E \sin \theta d\theta \quad (2.65)$$

$$\begin{aligned} \overline{\cos \theta} &= \frac{\int \cos \theta e^{-w/kt} \mu^* E \sin \theta d\theta}{\int e^{-w/kt} \mu^* E \sin \theta d\theta} = L(\mu^* E / 3kT) \\ &= \coth(\mu^* E / 3kT) - (kT / \mu^* E) \\ &= \mu^* E / 3kT - O(E^3) \end{aligned} \quad (2.66)$$

And we get the polarization per unit volume by combining with (2.57)

$$P = N\bar{m} = N(\mu \cos \theta + \alpha F) = N\left(\frac{\mu\mu^*}{3kT} + \frac{\varepsilon(n^2 + 2)}{(2\varepsilon + n^2)}\alpha\right)E \quad (2.67)$$

### 2.3.4 Dielectric Constants of Pure Polar Liquids

In the paper (Onsager, 1936), Onsager first considers a pure solution and assumes the volume of the liquid is mainly made up by the volume of the molecules. So accordingly,

$$N \times 4\pi a^3 / 3 = 1 \quad (2.68)$$

Together with equation (2.62), we get

$$4\pi N(n^2 + 2)\alpha = 4\pi N(n^2 - 1)a^3 = 3(n^2 - 1) \quad (2.69)$$

Now using the fundamental electrostatic formula (2.2), we get

$$(\varepsilon - 1)E = 4\pi P \quad (2.70)$$

Combine (2.67) and (2.70),

$$\varepsilon - 1 = 4\pi N \frac{\mu\mu^*}{3kT} + \frac{3\varepsilon(n^2 - 1)}{2\varepsilon + n^2} \quad (2.71)$$

So we can rewrite this as

$$\frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} = \frac{4\pi N\mu_0^2}{9kT} \quad (2.72)$$

This is Onsager's equation. For the non-polarizable molecules, we can redo the derivation by only considering the homogeneous field and the statistical mechanics of the dipole orientation and get:

$$\frac{(\varepsilon - 1)(\varepsilon + 2)}{3\varepsilon} = \frac{4\pi N\mu^2}{3kT} \quad (\text{only permanent dipole}) \quad (2.73)$$

## 2.4 Landau and Lifshitz 1/3 Mixing Rule

Compared to Clausius-Mossotti Model, Onsager's model made the improvement that the Maxwell field will adjust due to the existence of the cavity. However, as we see in Fig. 5, the electric field will be distorted due to the existence of the cavity. While the Onsager Model simplified the cavity into the continuum model, the variation in the local field is overlooked. If the dielectric constant and the dipole density are large enough, the local field would be different from the Maxwell field. And the local dielectric constant would have some perturbation away from the averaged value. Thus we would like to build a model based on this.

Landau and Lifshitz (Landau & Lifshitz) derived a mixing law to calculate the dielectric constant of mixtures. This mixing model considers the variations in the local field and local dielectric constant. The derivation is shown below.

The total polarization of space can no longer be extended from the polarizability of one single particle and the uniform electric field. The dielectric constant will be

$$\epsilon_{mix} = \overline{D} / \overline{E} \quad (2.74)$$

The only identity we know now is  $\text{div } D=0$ , since there are no free charges. So we examine

$$\overline{D} = \overline{\epsilon E} = \overline{(\epsilon + \delta\epsilon)(\overline{E} + \delta E)} = \overline{\epsilon E} + \overline{\delta\epsilon \delta E} \quad (2.75)$$

since  $\text{div } D=0$ , we get:

$$\nabla \cdot [(\overline{\epsilon} + \delta\epsilon)(\overline{E} + \delta E)] = \overline{\epsilon} \nabla \cdot \delta E + \overline{E} \cdot \nabla \delta\epsilon = 0 \quad (2.76)$$

In the low applied electric field limit, the averaged difference in electric field and dielectric constant should each be isotropic.

$$\frac{\partial}{\partial x} \overline{\delta E_x} = \frac{\partial}{\partial y} \overline{\delta E_y} = \frac{\partial}{\partial z} \overline{\delta E_z} = \frac{1}{3} \nabla \cdot \overline{\delta E} \quad (2.77)$$

$$\frac{\partial \delta \varepsilon}{\partial x} = \frac{\partial \delta \varepsilon}{\partial y} = \frac{\partial \delta \varepsilon}{\partial z} \quad (2.78)$$

If we take the average for (2.76) and assume the liquid is isotropic, we get

$$3\bar{\varepsilon} \frac{\partial}{\partial x} \overline{\delta E_x} = -\bar{E}_x \frac{\partial \delta \varepsilon}{\partial x} \quad (2.79)$$

$$\overline{\delta E_x} = -(\bar{E}_x / 3\bar{\varepsilon}) \partial \delta \varepsilon \quad (2.80)$$

Since the direction of the x-axis is arbitrary, we can ignore the subscript x. Substitute (2.80) to (2.81),

$$\varepsilon_{mix} = \bar{\varepsilon} - (1/3\bar{\varepsilon}) \overline{(\delta \varepsilon)^2} \quad (2.81)$$

Now we want to find the relation between the mixture dielectric constant and the microscopic dielectric constants of the components in the mixture. We take the 1/3 power of the mixture dielectric constant and Taylor expand it over  $(1/3\bar{\varepsilon}) \overline{(\delta \varepsilon)^2}$ :

$$\varepsilon_{mix}^{1/3} = \left( \bar{\varepsilon} - (1/3\bar{\varepsilon}) \overline{(\delta \varepsilon)^2} \right)^{1/3} = \bar{\varepsilon}^{1/3} \left( 1 - \frac{\overline{(\delta \varepsilon)^2}}{9\bar{\varepsilon}^2} \right) \quad (2.82)$$

where for the 1/3 power of the microscopic dielectric constant, we can also Taylor expand it over  $\delta \varepsilon$

$$\bar{\varepsilon}^{1/3} = \left( \bar{\varepsilon} + \delta \varepsilon \right)^{1/3} = \bar{\varepsilon}^{1/3} \left( 1 + \frac{\delta \varepsilon}{\bar{\varepsilon}} \right)^{1/3} \quad (2.83)$$

Thus to the second order term, the following equation holds:

$$\varepsilon_{mix}^{1/3} = \bar{\varepsilon}^{1/3} \quad (2.84)$$

This mixing law is called one third mixing law, since it has the one third power.

We can now compare Landau and Lifshitz's 1/3 mixing rule (2.84) with experimental data. We first notice that this rule works perfectly for the copolymer plasticizers.

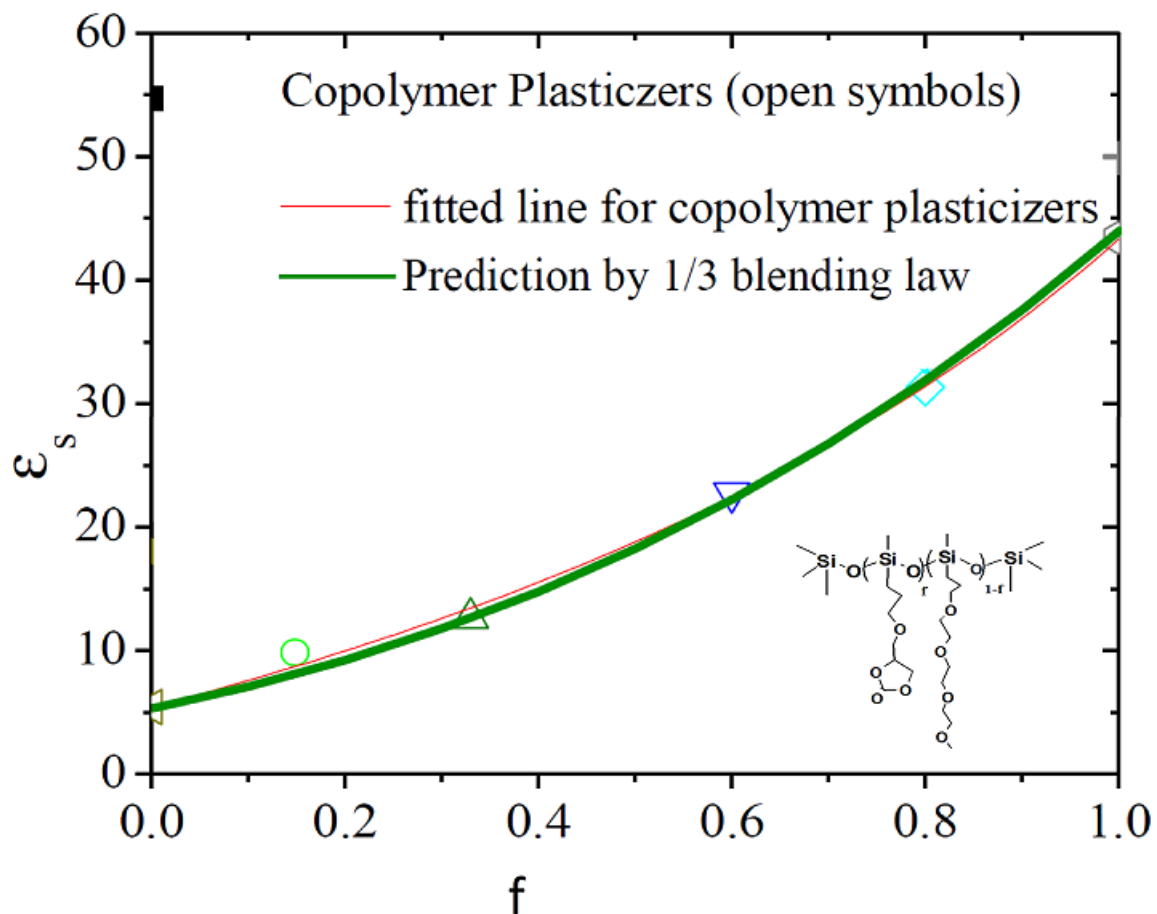


Figure 7 dielectric constant of the random copolymer plasticizers and the prediction from 1/3 mixing rule. The chemical structure of the copolymer is at the right bottom corner of the plot;  $f$  is the fraction of the more polar carbonate monomer.

However, experimentalist widely used the linear mixing rules, which is

$$\epsilon_{mix} = \bar{\epsilon} \quad (2.85)$$

Note that (2.85) would be a straight line in Fig. 7.

We want to compare the data of the small molecules mixture and the mixing rules.

Decroocq reported a table of the dielectric constant of the mixture changing with composition (see appendix B).

We can make a universal comparison by rewriting the 1/3 mixture rule (2.84).

$$\epsilon_{mix}^{1/3} = \phi_{\beta} \epsilon_{\beta}^{1/3} + (1 - \phi_{\beta}) \epsilon_{\alpha}^{1/3} \quad (2.86)$$

$$\phi_{\beta} = \frac{\left(\frac{\varepsilon}{\varepsilon_{\alpha}}\right)^{1/3} - 1}{\left(\frac{\varepsilon_{\beta}}{\varepsilon_{\alpha}}\right)^{1/3} - 1} = \frac{\varepsilon^{1/3} - \varepsilon_{\alpha}^{1/3}}{\varepsilon_{\beta}^{1/3} - \varepsilon_{\alpha}^{1/3}} \quad (2.87)$$

In the same method, we can get

$$\phi_{\beta} = \frac{\frac{\varepsilon}{\varepsilon_{\alpha}} - 1}{\frac{\varepsilon_{\beta}}{\varepsilon_{\alpha}} - 1} = \frac{\varepsilon - \varepsilon_{\alpha}}{\varepsilon_{\beta} - \varepsilon_{\alpha}} \quad (2.88)$$

for the linear mixing rule. By comparing the variance of the prediction from the predicted values, we found that some curves fit the 1/3 curves and some fit the linear mixing rule.

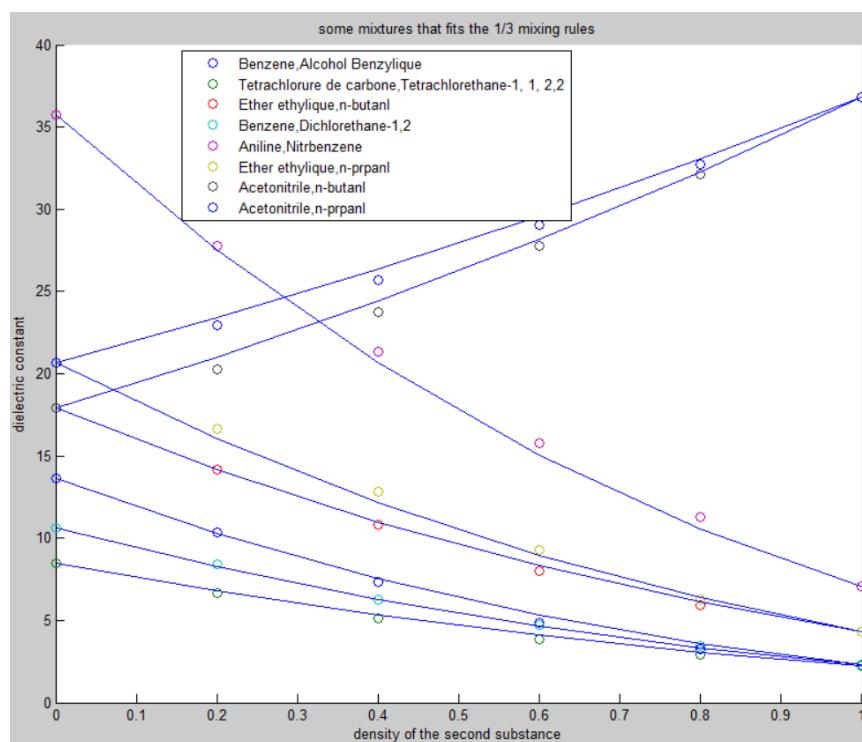


Figure 8 the mixtures that fit the 1/3 mixing law. The dielectric constant and the 1/3 prediction

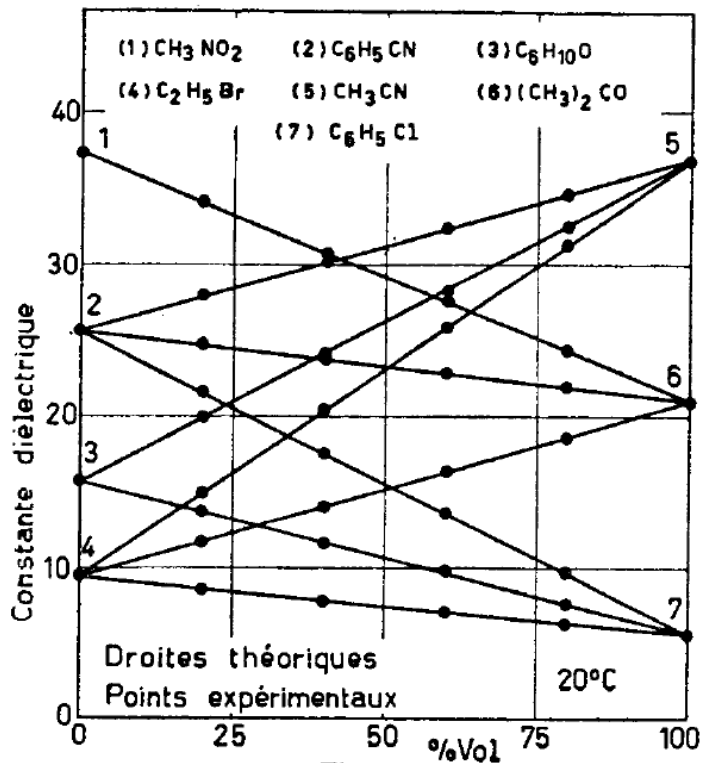


Figure 9 the dielectric constant that fits the linear mixing laws (Decroocq, 1964)

We then calculate the variance between the predicted density and the real density. We set the threshold variance as 0.005.

Table 1 number of small molecules mixtures which prefer linear mixing rule or prefer 1/3 mixing rule

# of mixtures have variance between the density and	Linear Mixing Prediction <0.005	Linear Mixing Prediction >0.005
One Third Mixing <0.005	30	22 Prefer one third mixing
One Third Mixing >0.005	58 Prefer linear mixing	Below 1/3: 56 Above linear: 33

As we see for small molecules, still more mixtures prefer the linear mixing. However, as we see in the derivation, the  $1/3$  factor comes from randomness of the local field direction and the variation of local dielectric constant and electric field. If this condition is not met, it will obey a linear mixing rule.

Also the original paper of Decroocq 1964 advocates the linear mixing rule as the function of volume fraction. In the table, one column lists the type of the mixture: L means that mixture fits the ideal linear mixture curve, M means above the ideal curve, m means below the ideal curve, and s means cutting the ideal curve. There are 204 kinds of mixtures: 108 of them are below the ideal curve and 44 of them are on the curve. Thus, many small molecules mixtures still bend downward and some of them just do not bend to the extent of  $1/3$ .

By reviewing the derivation, we suspect two conditions that need to be met for the one third mixing principle rule to apply to a given mixture:

1. Since the local dielectric constant has some variation from the averaged dielectric constant of all space, the dielectric constant should have heterogeneity locally and homogeneity macroscopically. This means the mixture should be single-phase with components of different dielectric constants.
2. The local field should be in the random direction, meaning that the polarization of focus is from orientation of dipoles but not from electronic, atomic, or space charge (interfacial).





As we can see in Fig. 10, the dielectric constant of polymer solution increases as the molecular volume increases. Since we add nonpolar content to the side chains, the polar content gets diluted in the ionic liquid as molecular volume is increased. Thus the dielectric constant increases, as the polar content per unit volume decreases. In contrast, Onsager's Model suggests that the dielectric constant should increase as the polar content per unit volume increases. The dielectric constant calculated using Onsager's equation is also larger than the dielectric constant measured. The ionic liquids typically have large dipole moments but exhibit lower dielectric constant. Obviously Onsager's equation being continuously verified in varied systems is not obeyed in ionic liquids having larger permanent dipoles. This experimental result shows that for high polarity liquids, the dielectric constant should be affected by other factor.

This interesting phenomenon has been noted in a simulation on the dielectric constant of polar liquid (Johnson, Barnes, Draxler, Eichinger, & Robinson, 2010). The paper used the Stockmayer fluid model. The Stockmayer fluid model considers the molecules as the Lennard-Jones spheres containing a single point dipole in the center. Thus the interactions between the molecules are the Lennard-Jones interaction and electrostatic interaction. This paper also considers the dipoles are nonpolarizable. The Stockmayer fluid is placed inside a large sphere and the outside medium has dielectric constant  $\epsilon_s$ .  $\epsilon_s$  has different values under different boundary condition:  $\epsilon_s = 1$  (spherical cutoff/SC),  $\epsilon_s = \epsilon$  (self-consistent reaction field/SCRF), and  $\epsilon_s = \infty$  (conductive boundary/CB). Like Onsager's Model, the outside medium would also have the reaction field effect. The field is given by

$$E = \frac{2\epsilon_s + \epsilon}{2\epsilon_s + 1} E_{ex} \quad (3.2)$$

The dielectric constant of the simulation is plotted in Fig. 11.

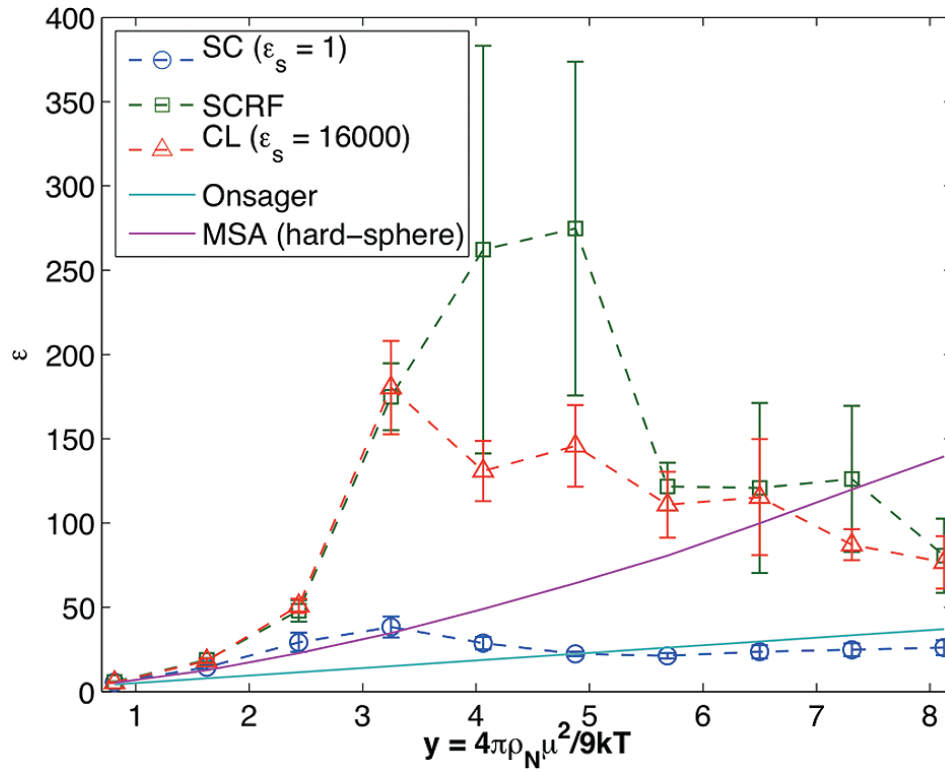


Figure 11 dielectric constant from the Stockmayer fluid simulation versus dielectric constant calculated using Onsager formula. Different curves correspond to different boundary conditions of the solution.

By converting  $y$  to  $V_p/V_m$ ,

$$y = \frac{4\pi\mu^2}{V_m 9kT} = \frac{4\pi}{3} \frac{V_p}{V_m} \quad (3.3)$$

we compare Figure 10 and Figure 11.

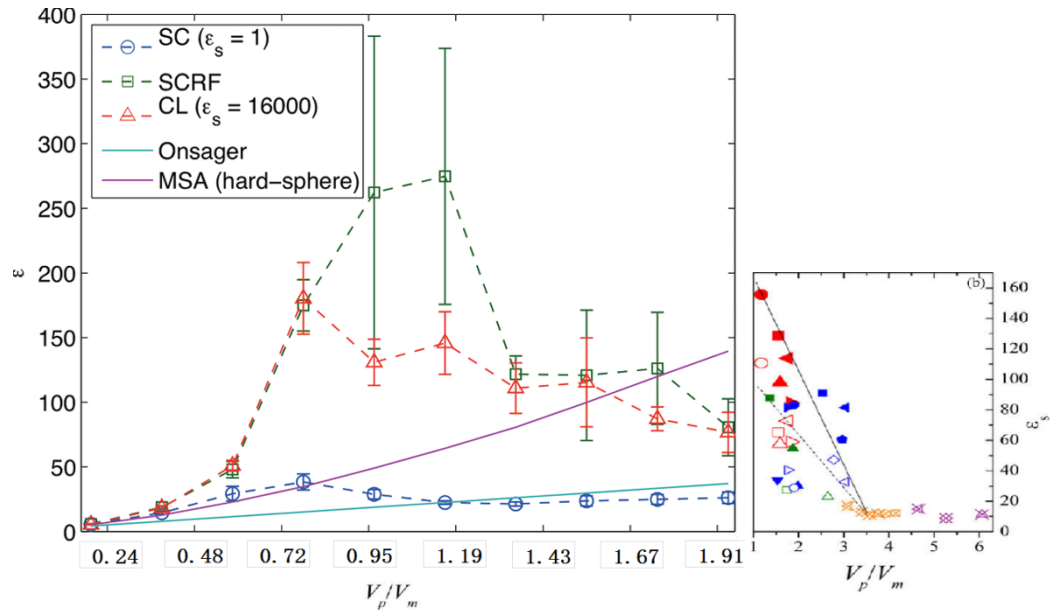


Figure 12 the dielectric constant versus  $V_p/V_m$  combining the simulation result (Johnson, Barnes, Draxler, Eichinger, & Robinson, 2010) and the experimental result (Choi, Mittal, Price Jr, Gibson, Runt, & Colby, 2013).

As we see for all three boundary conditions, the dielectric constant decreases as the solution becomes more polar. Under the SC boundary condition, the dielectric constant is even smaller than the dielectric constant predicted by Onsager's model. The paper uses the Kirkwood  $g$  factor to explain this phenomenon. Onsager's derivation only considers the interaction between the dipole and its environment, but fails to consider the dipole-dipole interaction between the dipoles. Kirkwood re-derived Onsager's equation using statistical mechanics equations, but got one more factor to correct the correlation between the dipole with the surrounding dipole (Kirkwood, 1939):

$$g = 1 + z \langle \cos \gamma \rangle \quad (3.4)$$

$\gamma$  is the angle between the two dipoles.  $\langle \cos \gamma \rangle$  means the average projection of the surrounding dipoles on the center dipole.  $z$  is the number of surrounding dipoles we consider. The bigger  $z$  is chosen, the better precision we get.  $g$  is the Kirkwood correlation factor. Thus the dielectric constant becomes

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{3\varepsilon} = \frac{4\pi N\mu^2}{3kT} g \quad (3.5)$$

The total dipole moment can be calculated using a fluctuation expansion of the dipole moment per unit volume  $M$ . The fluctuation expansion is (Adam, 1987)

$$\langle M \rangle_{E_0} \approx \langle M \rangle_{E_0=0} + \frac{E_0}{3kT} \left( \langle M^2 \rangle_0 - \langle M \rangle_0^2 \right) \quad (3.6)$$

Then the Kirkwood correlation factor from this method is

$$g = \frac{\langle M^2 \rangle_0 - \langle M \rangle_0^2}{N\mu^2} \quad (3.7)$$

$\langle M \rangle_0^2$  is considered very small in the usual sense, since we believe the dipoles locally do not have strong correlation. (Johnson, Barnes, Draxler, Eichinger, & Robinson, 2010) called  $g$  in (3.7)  $g(\text{Var}(M))$ . Then we define the correlation factor ignoring  $\langle M \rangle_0^2$  as  $g(\langle M_0^2 \rangle)$

$$g(\text{Var}(M)) = \frac{\langle M^2 \rangle_0 - \langle M \rangle_0^2}{N\mu^2} \approx \frac{\langle M^2 \rangle_0}{N\mu^2} = g(\langle M_0^2 \rangle) \quad (3.8)$$

The paper examines the correlation factor in the Stockmayer fluid simulation under self-consistent reaction field boundary condition (Johnson, Barnes, Draxler, Eichinger, & Robinson, 2010).

Table 2 Self-Consistent Reaction Field Kirkwood correlation factor (Johnson, Barnes, Draxler, Eichinger, & Robinson, 2010)

$y$	$\mu$ (D)	$g_K$ (Var(M))	$g_K$ ( $\langle M^2 \rangle_0$ )	Var(M)/ $\langle M^2 \rangle_0$
0.81	1.43	1.44 ± 0.06	1.47 ± 0.06	0.97
1.62	2.02	2.54 ± 0.14	2.66 ± 0.15	0.96
2.44	2.48	4.53 ± 0.54	5.05 ± 0.54	0.90
3.25	2.86	13.72 ± 1.31	19.76 ± 2.02	0.69
4.06	3.20	21.07 ± 6.61	414.5 ± 19.2	0.051
4.87	3.50	18.57 ± 4.51	761.9 ± 9.4	0.024
5.69	3.78	7.06 ± 0.55	935.0 ± 4.4	0.0075
6.50	4.04	6.13 ± 1.72	1065 ± 9	0.0058
7.31	4.29	5.70 ± 1.31	1099 ± 41	0.0052
8.12	4.52	3.26 ± 1.19	1189 ± 11	0.0027

As we see from Table 2 and (3.7),  $\langle M_0 \rangle^2$  increases as the dipole moment increases and the correlation factor decreases respectively. This seems contradicts our sense, since if the local correlation is strong, the local polarization should increase. So why is this case? We can find some clues from our discussion about the one third mixing. As we discussed, when the local homogeneity and macroscopic heterogeneity is reached, the linear mixing rule is not applicable anymore. The local dielectric constant then will be different from the dielectric constant. By (2.81)

$$\epsilon_{mix} = \bar{\epsilon} - \left(1/3\bar{\epsilon}\right) \overline{(\delta\epsilon)^2} \quad (3.9)$$

If the local variation from the averaged dielectric constant is large, the macroscopic dielectric constant is then small.

## **Chapter 4**

### **Conclusion**

As we discussed, since Onsager derives the dielectric constant by modeling the interaction between the dipole and the homogeneous field from the homogeneous dielectric medium and the outside field, he fails to consider the perturbation from the local dipole field. As the local homogeneity increases, the macroscopic field will be dominated by the local orientation. Thus in any highly polar liquid, the macroscopic heterogeneity plays an important role to lower the dielectric constant. However, the analysis of the mechanics of the perturbation in the local field and the dielectric constant is not fully developed. Further study about this needs be done.

## Appendix A

### NOTATION

$a$	Radius of spherical cavity
$\alpha$	Atomic polarization
B	Magnetic Field
c	Speed of Light
D	Displacement Field
$\mu_0$	Permanent dipole moment
$\mu$	The dipole moment under effect of reaction field
$\mu^*$	The effective dipole moment in the Maxwell field
m	Dipole moment of the molecule
$\mu_0$	Permanent dipole moment
M	Dipole moment per unit volume
e	Elementary charge
E	Electric field
$E_{ex}$	External field
$E_0$	Homogeneous part of the Maxwell field in the dielectric
$E_L$	Lorentz field



$E_i$	Internal field
$\epsilon$	Dielectric constant
$\epsilon_s$	Dielectric constant of surrounding medium
$g$	Kirkwood g factor
$G$	Homogeneous field
$R$	Reaction field
$\phi$	Potential
$\psi_{in}$	Potential inside the cavity
$\psi_{out}$	Potential outside the cavity
$\rho$	Microscopic Charge Density
$\rho_{free}$	Free Charge Density (the total charge enclosed in some space)

## Appendix B

## Dielectric Constant of Common Mixtures (Decroocq, 1964)

A	% Vol. B						B	Type
	0	20	40	60	80	100		
<i>n</i> -hexane .....	1,90	5,85	10,61	15,60	20,68	25,65	Benzonitrile	m
	1,90	6,24	12,22	19,39	27,30	35,75	Nitrobenzène	m
Cyclohexane .....	1,90	5,67	10,30	15,37	21,10	26,80	<i>m</i> -nitrotoluène	m
	2,02	4,68	8,16	12,18	16,48	21,07	Acétone	m
Benzène .....	2,02	4,28	7,26	10,72	14,44	18,35	Butanone-2	m
	2,02	4,17	6,78	9,67	12,67	15,70	Cyclohexanone	m
Benzène .....	2,02	6,37	12,25	19,30	27,10	35,75	Nitrobenzène	m
	2,28	2,69	3,12	3,56	4,11	4,80	Chloroforme	m
Benzène .....	2,28	3,43	4,70	6,28	8,44	10,65	Dichloréthane-1,2	m
	2,28	3,04	3,94	4,94	6,38	8,50	Tétrachloréthane-1,1,2,2	m
Benzène .....	2,28	2,92	3,57	4,25	4,96	5,70	Monochlorobenzène	m
	2,28	3,12	3,96	4,83	5,77	6,75	Trichlorobenzène-1,2,4	m
Benzène .....	2,28	2,63	2,98	3,38	3,84	4,35	Éther éthylique	m
	2,28	2,66	3,05	3,45	3,85	4,25	Phénétole	L
Benzène .....	2,28	4,77	7,60	10,71	14,17	17,85	Benzaldéhyde	m
	2,28	5,06	8,40	12,20	16,35	21,07	Acétone	m
Benzène .....	2,28	4,67	7,22	9,83	12,72	15,70	Cyclohexanone	m
	2,28	5,36	9,00	13,10	17,50	22,45	Anhydride acétique	m
Benzène .....	2,28	8,08	14,50	21,55	29,20	36,80	Acétonitrile	m
	2,28	6,52	10,95	15,65	20,50	25,65	Benzonitrile	m
Benzène .....	2,28	5,21	8,47	11,83	15,27	18,95	Cyanure de Benzyle	m
	2,28	2,69	3,14	3,66	4,20	4,78	<i>n</i> -butylamine	m
Benzène .....	2,28	3,06	3,94	4,94	5,96	7,06	Aniline	m
	2,28	7,22	13,17	20,10	28,45	37,45	Nitrométhane	m
Benzène .....	2,28	6,73	12,15	18,35	26,15	35,75	Nitrobenzène	m
	2,28	6,38	10,80	15,45	20,80	26,80	<i>m</i> -nitrotoluène	m
Benzène .....	2,28	6,35	12,75	19,90	26,95	33,60	Méthanol	m
	2,28	4,66	9,30	14,70	20,00	25,07	Éthanol	m
Benzène .....	2,28	3,88	7,30	11,80	16,45	20,65	<i>n</i> -propanol	m
	2,28	3,32	5,80	9,70	13,90	17,90	<i>n</i> -butanol	m
Benzène .....	2,28	3,25	4,87	7,35	10,37	13,62	Alcool Benzyle	m
	2,27	6,68	12,22	18,80	26,65	35,75	Nitrobenzène	m
<i>p</i> -xylène .....	4,80	4,20	3,64	3,13	2,66	2,24	Tétrachlorure de Carbone	m
	4,80	5,68	6,72	7,90	9,20	10,65	Dichloréthane-1,2	m
Chloroforme .....	4,80	5,37	5,98	6,72	7,52	8,50	Tétrachloréthane-1,1,2,2	m
	4,80	5,02	5,20	5,38	5,54	5,70	Monochlorobenzène	m
Chloroforme .....	4,80	5,56	5,98	5,94	5,36	4,35	Éther Éthylique	M
	4,80	4,80	4,73	4,61	4,45	4,25	Phénétole	M
Chloroforme .....	4,80	4,08	3,58	3,16	2,72	2,22	Dioxane-1,4	S
	4,80	9,52	13,00	15,80	18,40	21,07	Acétone	M
Chloroforme .....	4,80	8,75	11,62	13,35	14,62	15,70	Cyclohexanone	M
	4,80	10,20	14,73	18,65	22,30	25,65	Benzonitrile	M
Chloroforme .....	4,80	5,16	5,31	5,05	4,10	2,64	Triéthylamine	M
	4,80	6,12	7,04	7,31	6,89	6,29	<i>n</i> -propylamine	M
Chloroforme .....	4,80	5,25	5,46	5,34	4,59	3,24	Di <i>n</i> -propylamine	M
	4,80	5,68	6,27	6,44	5,84	4,78	<i>n</i> -butylamine	M
Chloroforme .....	4,80	5,04	5,38	5,83	6,38	7,06	Aniline	m
	4,80	9,45	15,85	22,35	28,20	33,60	Méthanol	S
Tétrachlorure de carbone	2,24	3,05	4,26	5,96	8,08	10,65	Dichloréthane-1,2	m
	2,24	2,94	3,88	5,10	6,66	8,50	Tétrachloréthane-1,1,2,2	m
Tétrachlorure de carbone	2,24	2,88	3,56	4,28	4,96	5,70	Monochlorobenzène	m
	2,24	3,07	3,95	4,87	5,82	6,75	Trichlorobenzène-1,2,4	m
Tétrachlorure de carbone	2,24	2,64	3,04	3,46	3,90	4,35	Éther Éthylique	m
	2,24	2,62	3,02	3,43	3,84	4,25	Phénétole	L
Tétrachlorure de carbone	2,24	5,13	8,63	12,47	16,56	21,07	Acétone	m
	2,24	5,18	8,95	13,25	17,67	22,45	Anhydride acétique	m
Tétrachlorure de carbone	2,24	7,65	14,32	21,70	29,30	36,80	Acétonitrile	m
	2,24	7,05	13,30	20,80	29,00	37,45	Nitrométhane	m
Tétrachlorure de carbone	2,24	6,87	12,60	19,25	26,94	35,75	Nitrobenzène	m
	2,24	6,26	13,20	20,25	27,05	33,60	Méthanol	m
Bromure d'éthyle .....	9,50	8,72	7,93	7,15	6,39	5,70	Monochlorobenzène	L
	9,50	8,36	7,25	6,18	5,20	4,25	Phénétole	m
Bromure d'éthyle .....	9,50	7,88	6,35	4,86	3,47	2,22	Dioxane-1,4	m
	9,50	11,45	12,80	14,48	16,16	17,85	Benzaldéhyde	L
Bromure d'éthyle .....	9,50	11,80	14,11	16,43	18,75	21,07	Acétone	L
	9,50	12,10	14,70	17,28	19,88	22,45	Anhydride acétique	L
Bromure d'éthyle .....	9,50	8,89	8,27	7,65	7,01	6,19	Acétate d'éthyle	M
	9,50	14,96	20,37	25,90	31,45	36,80	Acétonitrile	L
Bromure d'éthyle .....	9,50	12,95	16,32	19,51	22,67	25,65	Benzonitrile	M
	9,50	13,70	18,32	23,57	29,47	35,75	Nitrobenzène	L
Dichloréthane-1,2 .....	10,65	10,22	9,78	9,36	8,93	8,50	Tétrachloréthane-1,1,2,2	L
	10,65	9,20	8,04	7,10	6,31	5,70	Monochlorobenzène	m
Dichloréthane-1,2 .....	10,65	9,24	7,94	6,70	5,53	4,35	Éther Éthylique	m
	10,65	13,50	16,05	18,12	19,80	21,07	Acétone	M

A	% Vol. B						B	Type
	0	20	40	60	80	100		
Dichloréthane-1,2 .....	10,65	17,40	23,15	28,20	32,60	36,80	Acétonitrile	M
	10,65	14,40	17,80	20,85	23,52	25,65	Benzonitrile	M
	10,65	16,65	22,13	27,60	32,43	37,45	Nitrométhane	M
	10,65	14,00	18,70	24,20	29,06	33,60	Méthanol	S
	10,65	12,10	14,73	18,30	21,85	25,07	Éthanol	m
Tétrachloréthane-1,1,2,2 .....	8,50	7,95	7,55	7,20	6,95	6,75	Trichlorobenzène-1,2,4	m
	8,50	8,40	8,01	7,21	5,96	4,35	Éther éthylique	M
	8,50	13,10	16,60	18,95	20,30	21,07	Acétone	M
	8,50	13,90	17,55	19,83	21,25	22,45	Anhydride acétique	M
	8,50	13,70	17,90	21,25	23,80	25,65	Benzonitrile	M
	8,50	7,34	6,80	6,70	6,81	7,06	Aniline	m
	8,50	15,35	21,20	26,65	31,95	37,45	Nitrométhane	M
	8,50	14,52	20,05	25,50	30,65	35,75	Nitrobenzène	M
	8,50	13,08	18,67	24,54	29,20	33,60	Méthanol	S
	8,50	5,52	5,30	5,06	4,72	4,35	Éther éthylique	M
Monochlorobenzène .....	5,70	8,45	11,35	14,37	17,55	21,07	Acétone	m
	5,70	7,75	9,75	11,73	13,71	15,90	Cyclohexanone	L
	5,70	11,63	17,54	23,90	30,35	36,80	Acétonitrile	m
	5,70	9,73	13,70	17,60	21,55	25,65	Benzonitrile	L
	5,70	10,24	15,20	21,10	28,08	35,75	Nitrobenzène	m
	5,70	7,90	11,95	16,42	20,72	25,07	Éthanol	m
	5,70	10,00	15,39	21,43	28,15	35,75	Nitrobenzène	M
	5,70	6,46	6,06	5,60	5,03	4,35	Éther éthylique	M
	5,70	10,55	14,30	18,00	21,75	25,65	Benzonitrile	L
	5,70	6,68	6,68	6,74	6,90	7,06	Aniline	m
Éther éthylique .....	4,35	7,10	9,81	12,49	15,20	17,85	Benzaldéhyde	L
	4,35	7,60	10,92	14,28	17,68	21,07	Acétone	L
	4,35	7,87	11,50	15,25	18,85	22,45	Anhydride acétique	L
	4,35	4,78	5,11	5,48	5,84	6,19	Acétate d'éthyle	L
	4,35	10,95	17,53	24,34	30,55	36,80	Acétonitrile	M
	4,35	8,85	13,35	17,58	21,65	25,65	Benzonitrile	M
	4,35	4,43	4,51	4,60	4,69	4,78	n-butylamine	L
	4,35	4,42	4,50	4,57	4,65	4,72	Cyclohexylamine	L
	4,35	5,57	6,42	6,76	7,00	7,06	Aniline	M
	4,35	10,07	17,05	23,65	30,60	37,45	Nitrométhane	m
Phénétole .....	4,35	9,70	15,40	21,85	28,60	35,75	Nitrobenzène	M
	4,35	9,45	15,25	21,60	27,75	33,60	Méthanol	S
	4,35	7,42	11,42	15,76	20,43	25,07	Éthanol	m
	4,35	6,26	9,30	12,80	16,65	20,65	n-propanol	m
	4,35	5,92	8,00	10,85	14,15	17,90	n-butanol	m
	4,35	5,01	5,61	6,06	6,34	6,22	Acide acétique	M
	4,35	8,93	12,82	14,51	13,45	8,70	Acide Dichloracétique	M
	4,35	6,71	9,40	12,11	14,95	17,85	Benzaldéhyde	M
	4,35	7,11	10,25	13,55	17,10	21,07	Acétone	m
	4,35	6,51	8,80	11,10	13,38	15,70	Cyclohexanone	L
Dioxanne-1,4 .....	4,25	6,36	8,80	11,43	14,28	17,65	Acétophénone	m
	4,25	8,52	12,80	17,03	21,29	25,65	Benzonitrile	L
	2,22	5,05	8,52	12,25	16,33	21,07	Acétone	m
	2,22	4,60	7,21	9,92	12,75	15,70	Cyclohexanone	m
	2,22	8,54	15,19	22,23	29,49	36,80	Acétonitrile	m
	2,22	4,69	7,34	9,70	11,31	8,70	Acide dichloracétique	M
	2,22	12,40	26,80	43,90	61,80	80,37	Eau	m
	17,85	18,54	19,22	19,87	20,47	21,07	Acétone	L
	17,85	17,40	17,00	16,55	16,12	15,70	Cyclohexanone	L
	17,85	18,75	19,68	20,61	21,52	22,45	Anhydride acétique	L
Benzaldéhyde .....	17,85	19,38	20,93	22,51	24,10	25,65	Benzonitrile	L
	17,85	14,90	11,89	8,72	5,73	3,24	Di n-propylamine	m
	17,85	15,40	11,85	8,28	5,05	2,49	Tri n-butylamine	m
	17,85	21,62	25,57	29,55	33,50	37,45	Nitrométhane	L
	17,85	20,82	24,20	27,80	31,63	35,75	Nitrobenzène	m
	21,07	20,50	19,95	19,40	18,88	18,35	Butanone-2	L
	21,07	19,94	18,80	17,72	16,69	15,70	Cyclohexanone	L
	21,07	21,47	21,82	22,12	22,30	22,45	Acétone	M
	21,07	17,90	14,25	11,45	8,85	6,19	Acétate d'éthyle	m
	21,07	24,55	27,65	30,72	33,75	36,80	Acétonitrile	M
Acétone .....	21,07	21,95	22,90	23,80	24,70	25,65	Benzonitrile	M
	21,07	17,70	14,60	11,55	8,45	5,38	Isopropylamine	L
	21,07	17,65	14,27	10,95	7,78	4,72	Cyclohexylamine	m
	21,07	18,50	16,05	13,35	10,37	7,06	Aniline	M
	21,07	24,25	27,45	30,70	34,05	37,45	Nitrométhane	L
	21,07	23,80	26,60	29,45	32,45	35,75	Nitrobenzène	m
	21,07	23,60	25,80	28,37	31,04	33,60	Méthanol	m
	21,07	20,85	21,30	22,13	23,40	25,07	Éthanol	m
	21,07	18,25	15,82	13,25	10,30	6,22	Acide Acétique	M

A	% Vol. B						B	Type
	0	20	40	60	80	100		
Acétone .....	21,07	21,65	22,92	22,90	18,10	8,70	Acide dichloracétique	M
	21,07	34,55	47,60	59,90	70,40	80,37	Eau	M
Cyclohexanone .....	15,70	13,68	11,74	9,82	8,01	6,19	Acétate d'éthyle	L
	15,70	19,95	24,15	28,40	32,60	36,80	Acétonitrile	L
Anhydride acétique .....	15,70	17,70	19,65	21,65	23,62	25,65	Benzonitrile	L
	22,45	25,45	28,44	31,30	34,07	36,80	Acétonitrile	M
	22,45	23,10	23,75	24,40	25,05	25,65	Benzonitrile	L
	22,45	25,30	28,25	31,25	34,35	37,45	Nitrométhane	L
	22,45	24,67	27,00	29,45	32,40	35,75	Nitrobenzène	m
	22,45	24,40	26,55	28,95	31,27	33,60	Méthanol	m
	22,45	22,15	22,30	22,95	23,90	25,07	Éthanol	m
	22,45	20,80	19,87	19,55	19,75	20,65	n-propanol	m
	22,45	20,10	18,60	17,75	17,33	17,90	n-butanol	m
Acétate d'éthyle .....	6,19	11,90	17,70	23,85	30,25	36,80	Acétonitrile	m
	6,19	10,05	13,91	17,83	21,75	25,65	Benzonitrile	L
Acétonitrile .....	36,80	34,60	32,45	30,27	28,00	25,65	Benzonitrile	L
	36,80	33,25	29,65	26,07	22,48	18,95	Cyanure de Benzyle	L
	36,80	29,55	22,25	15,15	8,60	2,64	Triéthylamine	L
	36,80	30,10	22,90	16,05	9,72	3,24	n-propylamine	m
	36,80	37,08	37,20	37,32	37,41	37,45	Nitrométhane	M
	36,80	36,73	36,63	36,48	36,23	35,75	Nitrobenzène	M
	36,80	36,15	35,50	34,85	34,20	33,60	Méthanol	L
	36,80	33,90	31,40	29,20	27,18	25,07	Éthanol	m
	36,80	32,73	29,05	25,70	22,92	20,65	n-propanol	m
	36,80	32,15	27,75	23,72	20,25	17,90	n-butanol	m
	36,80	45,55	54,60	64,75	73,20	80,37	Eau	M
Benzonitrile .....	25,65	24,29	22,93	21,57	20,26	18,95	Cyanure de Benzyle	L
	25,65	21,05	16,45	11,80	7,20	2,64	Triéthylamine	L
	25,65	21,70	17,75	13,95	10,05	6,29	n-propylamine	L
	25,65	21,45	17,30	13,15	8,98	4,72	Cyclohexylamine	L
	25,65	22,33	18,90	15,17	11,28	7,06	Aniline	M
	25,65	27,50	29,70	32,05	34,63	37,45	Nitrométhane	m
	25,65	27,00	28,75	30,75	33,00	35,75	Nitrobenzène	m
	25,65	27,45	29,30	31,05	32,45	33,60	Méthanol	M
	25,65	25,05	24,95	24,98	25,02	25,07	Éthanol	m
n-butylamine .....	4,78	6,05	6,90	7,26	7,34	7,06	Aniline	M
Aniline .....	7,06	11,30	15,78	21,35	27,75	35,75	Nitrobenzène	m
	7,06	11,06	16,45	22,17	27,75	33,60	Méthanol	m
	7,06	9,61	12,70	16,50	20,65	25,07	Éthanol	m
Nitrométhane .....	37,45	36,86	36,45	36,08	35,85	35,75	Nitrobenzène	m
	37,45	35,30	34,20	33,55	33,45	33,60	Méthanol	m
	37,45	33,05	30,00	27,70	25,15	25,07	Éthanol	m
	37,45	31,95	27,65	24,30	21,90	20,65	n-propanol	m
Nitrobenzène .....	35,75	34,04	32,33	30,63	28,92	27,20	o-nitrotoluène	L
	35,75	33,90	33,23	33,05	33,17	33,60	Méthanol	m
	35,75	31,60	29,02	27,22	25,95	25,07	Éthanol	m
	35,75	29,85	25,25	21,70	19,20	17,90	n-butanol	m
Méthanol .....	33,60	31,85	30,10	28,50	26,70	25,07	Éthanol	L
	33,60	30,95	28,20	25,45	23,00	20,65	n-propanol	m
	33,60	30,80	28,00	25,15	22,50	19,90	Isopropanol	m
	33,60	30,30	27,05	23,65	20,60	17,90	n-butanol	m
	33,60	28,60	23,70	18,85	14,50	9,95	n-octanol	m
	33,60	44,90	55,20	64,70	73,00	80,37	Eau	M
Éthanol .....	25,07	35,80	47,30	60,00	70,90	80,37	Eau	S
n-propanol .....	20,65	28,80	40,60	54,50	68,70	80,37	Eau	S
Acide acétique .....	6,22	9,12	10,76	11,35	10,75	8,70	Acide dichloracétique	M

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### EDUCATION

The Pennsylvania State University, University Park, PA  
Schreyer Honors College  
B.S. in Physics  
B.S. in Mathematics

Jan, 2011 - May, 2014

### HONORS and AWARDS

*PMASS Program*, PMASS Scholarship  
Penn State University, Department of Mathematics  
<http://www.math.psu.edu/mass/pmass/2014/>

Spring 2011

*The University Physics Competition*, Bronze Medal

Fall 2010

*Sigma Pi Sigma Physics Honor Society member*

May 2013 - Present

### RESEARCH EXPERIENCE

*Senior Thesis Research*  
The Pennsylvania State University Materials Science Department

Spring 2013 -Present

- Studied the Dielectric Constant Theory of the Polar Systems and focused on giving theoretical explanation of low dielectric phenomena at high density (advised by Dr Ralph Colby)
- Studied the Dielectric Saturation Problem and reproduced the  $g$  factor from the experiment by considering only the first-cell interaction and the high directing field limit
- Studied the Ferroelectric Transition of the Polar Liquids and find the relation between the Ferroelectric transition point from the simulation and the Dielectric Saturation Threshold from the experiment
- Studying the Cluster Expansion Method of Dipolar HardSphere (DHS) Liquids
- *Penn State Summer Research Experiences for Undergraduates (REU) Program with NSF Grant* Summer 2013
- "*Dielectric Constant of ionic liquid (IL) and polymerized ionic liquid (PIL) with strong local dipole-dipole interaction*". Presentation and Poster offered at Penn State REU Research Symposium August 2013

### CLASS PROJECTS

*The Mathematical Analysis of the Percolation Problem*. Final Project and Oral Exam of the Honors Brownian Motion Math Class May 2013  
Computed and proved the 2D Percolation Threshold Density. Studied the properties of the 3D Percolation Problem.

### SKILLS

*Languages & Software*: Mathematica, MATLAB, Latex, C++, MD Simulation with GROMACS code