Abstract

Point polarizable molecules at fixed spatial positions have solvable electrostatic properties in classical approximation, the most familiar being the Clausius-Mossotti (CM) formula. This paper generalizes the model and imagines various applications to nanosystems. The behavior is worked out for a sequence of octahedral fragments of simple cubic crystals, and the crossover to the bulk CM law is found. Some relations to fixed moment systems are discussed and exploited. The one-dimensional dipole stack is introduced as an important model system. The energy of interaction of parallel stacks is worked out, and clarifies the diverse behavior found in different crystal structures. It also suggests patterns of self-organization which polar molecules in solution might adopt. A sum rule on the stack interaction is found and tested. Stability of polarized states under thermal fluctuations is discussed, using the one-dimensional domain wall as an example. Possible structures for polar hard ellipsoids are considered. An idea is formulated for enhancing polarity of nanosystems by intentionally adding metallic coatings.

1 Introduction

Electrical polarity (neutral charge distributions with positive and negative charge centers separated in space), and in particular dipole moments, are ubiquitous in asymmetric molecules, and therefore no doubt very common in nanocrystals [1]. Systematic studies of polarity of nanocrystals are rare. Two primitive questions arise. (1) When can a nanosystem develop a spontaneous polarity, analogous to a bulk ferroelectric, i.e. reversible in a strong applied field, and how can this polarity be controlled [2]? A particularly fascinating example is the recent discovery [3] of spontaneous polarization in small clusters of Nb atoms at low temperature \( T \). (2) What “permanent” moments occur, how stable are they in time, and how much fluctuation occurs within an ensemble of similarly prepared nanocrystals?

The venerable “Clausius-Mossotti model” (CM model, or CMM) [4, 5, 6], provides a simple solvable picture of spontaneous polarity. Most of this paper consists of imagining possible applications of the CMM and working out some consequences in nanosystems. I define the CMM to mean a system of fixed points \( \vec{r}_i \), each of which has a polarizability \( \alpha_i \). When an electric field \( \vec{F}_{i,tot} \) appears at point \( i \), it induces an electric dipole moment \( \vec{\mu}_i = \alpha_i \vec{F}_{i,tot} \). Each such moment creates a dipole field. The sum of all such dipole fields is the induced field

\[
\vec{F}_{i,ind} = \sum_j \frac{3 \vec{R}_{ij} (\vec{R}_{ij} \cdot \vec{\mu}_j) - \vec{R}_{ij}^2 \vec{\mu}_j}{R_{ij}^5}
\]

and the total field is the sum of these plus the external field \( \vec{F}_{i,tot} = \vec{F}_{i,ext} + \vec{F}_{i,ind} \). This problem requires self-consistency to find the answer for \( \vec{\mu}_i \).

The limitation to induced moments and dipole-dipole interactions inhibits application of the CMM to real systems. However, by focusing on the dipole-dipole interaction, this model clarifies a difficult aspect of real polar systems, including systems with fixed moments.

There is a large chemical literature developing and using model interactions between molecules, in which some or all of the quantum electron behavior can be represented approximately as classical charges.
and dipoles which interact electrostatically [7, 8, 9, 10, 11] Ideas of this kind are particularly appropriate for interacting organic molecules (e.g. molecular crystals [12, 13, 14]). Interactions alter their electronic properties from values found in isolated molecules; the effect is large, but not so large as to destroy the identity of the molecule as happens in covalent, ionic, or metallic interactions. The alterations arise from the polarization of surrounding molecules and can be modelled by classical electrostatics. The present paper is motivated by more primitive questions; the methods developed here can be found in related but more sophisticated contexts elsewhere.

2 The “Generalized Clausius-Mossotti Law” (CML)

The textbook version of the CML considers an infinite periodic medium with polarizable molecules sitting on equivalent sites of cubic symmetry. The result is that the total field \( \vec{F} \) at any molecular site is enhanced from the value \( \vec{F}_{\text{ext}} \) of the homogeneous applied field by an enhancement factor \( f = (1 - 4\pi n\alpha/3)^{-1} \), where \( n \) is the number density of the molecules. Equivalently, \( \alpha \) is enhanced to the value \( f\alpha \) by the fields of the other dipoles. A general derivation from microscopic response theory was given by Maksimov and Mazin [15].

A good example is crystalline C\(_{60}\) which has weakly-coupled molecules of known [16, 17] polarizability \( \alpha = 85\text{Å}^3 \) sitting on a face-centered cubic (fcc) lattice of density \( n = 0.001406 \text{molecules/Å}^3 \). The enhancement factor is \( f = 2.00 \) and the dielectric constant [18] is \( \epsilon_{\infty} = 1 + 4\pi n\alpha = 4.0 \). These independently measured values of the the vapor-phase property [16] \( \alpha \), and bulk-solid property [18] \( \epsilon_{\infty} \), provide an excellent confirmation of the CML. Metallic screening by intermolecular charge transfer, while needed in a complete theory, is small enough in C\(_{60}\) that the Clausius-Mossotti approach works well.

The microscopic calculation of Pederson and Quong [17] shows that, for C\(_{60}\), the theoretical free-molecule polarizability (83.5Å\(^3\)) is strongly affected by intramolecular screening. Even within a single molecule the local field is reduced by a factor of three by intramolecular charge rearrangement. But when assembled into the fcc solid, the details of local charge are successfully ignored by the CMM which places all the polarity at a single point of cubic symmetry. There is no guarantee that this would be equally successful for less symmetric molecules. Schemes for representing the quantum electrostatics of molecules by interacting “submolecules” have been developed [12, 13, 14].

Note that the CM enhancement factor \( f \) diverges to infinity when the polarizability increases to \( \alpha_{\text{max}} = 3/4\pi n \), or alternately, the density increases to \( n_{\text{max}} = 3/4\pi \alpha \). There is no known molecular crystal where this limit is reached, but C\(_{60}\) comes within a factor of 2. If the limit were reached, the material would enter a phase of spontaneous polarization. Actual solids which do polarize spontaneously [19, 20] are more complicated, but the CMM provides a useful simple system with the same property.

To derive a more general result, note that the dipole moments \( \{\vec{\mu}_i\} \) or their Cartesian components \( \{\mu_{i\alpha}\} \), obey a minimum principle. That is, they minimize the energy expression

\[
E_{\text{dip}} (\{\vec{\mu}_i\}) = \sum_i \left( \frac{\mu_i^2}{2\alpha} - \vec{\mu}_i \cdot \left( \frac{1}{2} \vec{F}_{i,\text{ind}} + \vec{F}_{i,\text{ext}} \right) \right).
\] (2)

The first term expresses the fact that it costs less to polarize a molecule when its polarizability is large. The factor of 1/2 in the second term avoids double counting the dipole-dipole interaction. The energy formula is a quadratic form, amenable to methods of linear algebra. It is helpful to use a vector space notation,

\[
E_{\text{dip}} (\{\vec{\mu}_i\}) = \frac{1}{2} < \vec{\mu}, \frac{1}{\alpha} \Gamma |\mu > - < \mu | F_{\text{ext}} > ,
\] (3)

where the 3N-dimensional column vectors have been introduced:

\[
|\mu > = \begin{pmatrix}
\mu_{1x} \\
\mu_{1y} \\
\vdots \\
\mu_{Nz}
\end{pmatrix} \quad |F > = \begin{pmatrix}
F_{1x} \\
F_{1y} \\
\vdots \\
F_{Nz}
\end{pmatrix}.
\] (4)
The $3N \times 3N$-dimensional matrix $\Gamma$ is the dipole-dipole interaction, defined by Eq. (1), i.e. $|F_{\text{ind}} \rangle = \Gamma |\mu \rangle$, and has elements

$$\Gamma_{\alpha\beta,j\beta} = \frac{3R_{ij\alpha}R_{ij\beta} - \delta_{\alpha\beta}R_{ij}^5}{R_{ij}^3},$$

(5)

where $R_{ij\alpha}$ is the $\alpha$ Cartesian component of the vector $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$. The solution for the dipoles $\vec{\mu}_i$ which minimize the energy is

$$\vec{\mu}_i = \sum_j \left( \frac{1}{\alpha - \gamma} \right)^{-1} \vec{F}_{\text{ext},ij}^\gamma,$$

(6)

This is the generalized Clausius-Mossotti law (CML), valid for arbitrary collections of polarizable neutral molecules [21]. For simplicity it is assumed that all molecules have the same polarizability. The generalization to multiple species is straightforward. The structure $\mu \approx f\alpha F_{\text{ext}}$ is evident. In sec. 4 it will be shown how the usual textbook CML follows from this formula in the appropriate limit.

It is interesting and useful to consider the eigenvalues $\gamma$ and eigenvectors $|\gamma \rangle$ of the dipole-dipole interaction $\Gamma$:

$$\Gamma = \sum_\gamma |\gamma \rangle \langle \gamma |.$$

(7)

In terms of these eigenstates, the generalized CML for the induced dipoles is

$$\vec{\mu}_i = \sum_\gamma <i| \left( \frac{1}{\alpha - \gamma} \right)^{-1} |\gamma \rangle \langle \gamma | F_{\text{ext}},$$

(8)

In the usual case, the factors $(1/\alpha - \gamma)^{-1}$ are all positive finite numbers. The largest eigenvalue $\gamma$ is less than the resistance $1/\alpha$ to polarization. Because the interaction Eq.(5) scales as $1/R^3$, the eigenvalues $\gamma$ scale linearly with density $n$. If one imagines increasing the density of the system, leaving everything else fixed, eventually the largest eigenvalue $\gamma_{\text{max}}$ exceeds $1/\alpha$ and the response is divergent. This signifies that a spontaneous polarization now occurs, with a pattern of polarization given by the corresponding eigenvector $|\gamma_{\text{max}} \rangle$.

3 Octahedral Fragments

How does the CMM describes the evolution from nanocrystal to bulk ferroelectric? Consider the sequence of octahedral fragments of a simple cubic lattice. The simplest fragment with a central molecule and six octahedral neighbors is shown in Fig. 1. Larger fragments have $N=25$, 63, ... molecules and retain the full cubic point symmetry. The largest eigenvalues of the dipole-dipole matrix have been computed numerically for these cases and are shown plotted versus a convenient reciprocal power of $N$ in Fig. 1.

The $N=\infty$ bulk limit is nearly achieved for 200-molecule clusters. For the infinite simple cubic crystal, the CML tells us that a ferroelectric instability occurs when $1/\alpha$ diminishes to $4\pi/3$. For fragments of the crystal, the critical value of $1/\alpha$ should surely be less than $4\pi/3$, increasing to this value as $N \to \infty$. Fig. 1 shows that there is a monotonic increase with $N$ but that already by $N=25$ the largest eigenvalue exceeds the bulk CML value $4\pi/3$.

The reason for this unexpected result is that the sc structure prefers antiferro rather than ferro ordering when only dipole-dipole interactions are present. This was discovered by Luttinger and Tisza [22]. The next section elaborates, and Sec. 7 gives a simple way to calculate the preferred dipole ordering on a lattice. To confirm the antiferro preference, Fig. 2 shows how the polarization directions evolve as the octahedral fragment enlarges toward the bulk limit.

A recent report by Fu and Bellaiche [23] considers dipoles on larger cubic fragments of a simple cubic lattice. They find a surprising spiral pattern to be stable, with no net moment. They are solving a somewhat different model.
Figure 1: Largest eigenvalue of dipole-dipole matrix for octahedral fragments of a simple cubic lattice. Units are used where the density $n=1$. The smallest octahedral fragment with 7 molecules is shown. The horizontal line is the CM eigenvalue $4\pi/3$.

4 Bulk Clausius-Mossotti Law

Infinite periodic crystals have translational symmetry that permits computation of the eigenvalues and eigenvectors of the dipole-dipole matrix $\Gamma$. Specifically, the Floquet theorem says that eigenstates $|\gamma\rangle$ can be chosen to have the Bloch form $|\vec{k}\lambda\rangle$

$$<\alpha|\vec{k}\lambda\rangle = e^{i\vec{k}\cdot\vec{R}_{\alpha}}/\sqrt{N},$$

where (for a one-atom cell) the eigenvector $\vec{\epsilon}(\vec{k}\lambda)$ is a 3-d unit vector, labeled by wavenumber $\vec{k}$ and branch index $\lambda$. This eigenvector corresponds to eigenvalue $\gamma(\vec{k}\lambda)$ and satisfies

$$\Gamma_{\alpha\beta}(\vec{k})\epsilon_{\beta}(\vec{k}\lambda) = \gamma(\vec{k}\lambda)\epsilon_{\alpha}(\vec{k}\lambda),$$

where the $3 \times 3$ dipole-dipole matrix $\Gamma$ is now in Fourier space,

$$\Gamma_{\alpha\beta}(\vec{k}) = \frac{1}{N} \sum_{i \neq j} e^{i\vec{k} \cdot \vec{R}_i - \vec{R}_j} \left( \nabla_{\alpha}\frac{1}{r} \nabla_{\beta}\frac{1}{r} \right)_{\vec{r} = \vec{R}_i - \vec{R}_j}.$$

For the $sc$ structure, the eigenvalues $\gamma(\vec{k}\lambda)$ are shown in Fig.3. The numerical calculation used the Ewald method to converge the sums [24]. The sum of the three eigenvalues (trace of the matrix $\Gamma_{\alpha\beta}(\vec{k})$) is 0, independent of $\vec{k}$. This is because $\nabla^2(1/r)$ is 0 everywhere except at $r = 0$ and the $\vec{R}_i = \vec{R}_j$ term is omitted from Eq.(11). The same dispersion curve shown in Fig.3 has a different interpretation in phonon physics. By a change the sign and an additive constant $4\pi/3$, these become the curves of squared frequencies of vibration of the Coulomb lattice of unit point charges. These are the “bare phonons” encountered in older approaches to the theory of phonons in metals [25]. The fact that the eigenvalue at the $\Gamma$ point ($\vec{k} = 0$) is not the extreme eigenvalue in $sc$ structure corresponds to a linear instability (imaginary eigenfrequencies) of the Coulomb lattice in $sc$ structure. Conversely, the fact that the $\vec{k} = 0$ eigenvalue $\gamma$ is maximal in $fcc$ and $bcc$ structures corresponds to linear stability of the Coulomb lattice in these structures.

The Clausius-Mossotti formula ($\mu_i = f\alpha F_{ext}^i$ with $1/f = 1 - 4\pi n\alpha/3$) can be obtained from these results. The external field is homogeneous, so only eigenvectors $|\gamma\rangle$ corresponding to $\vec{k} = 0$ can couple
in Eq.(8). Then from Eq.(8) we get

$$
\mu_i = \sum_{\lambda=1}^{3} \left( \frac{1}{\alpha} - \gamma(\vec{k} = 0, \lambda) \right)^{-1} (\hat{\epsilon}(\vec{k} = 0, \lambda) \cdot \vec{F}_{\text{ext}}) \hat{\epsilon}(\vec{k} = 0, \lambda).
$$

(12)

Thus it is needed that all three eigenvalues $\gamma(\vec{k} = 0, \lambda)$ should be $4\pi n/3$. Two eigenvalues indeed agree with this, but consistent with summing to zero, the third eigenvalue is $-8\pi n/3$. The corresponding eigenvector $\hat{\epsilon}(\vec{k} = 0, \lambda)$ is “longitudinal,” that is, it pointed along $\vec{k}$ before the $\vec{k} \to 0$ limit was taken. Longitudinal fields suffer depolarization which transverse fields avoid. A longitudinal field is created by a parallel plate capacitor applied to a block of dielectric. The “external” field is related to the classical macroscopic field $\vec{F}$ by $\vec{F}_{\text{ext}} = \vec{F} + 4\pi \vec{P}$ and the polarization density $\vec{P}$ is $n\vec{\mu}$. Thus for a longitudinal field, Eq.(12) is the same as

$$
\vec{\mu} = \left( \frac{1}{\alpha} + \frac{8\pi n}{3} \right)^{-1} (\vec{F} + 4\pi n\vec{\mu}).
$$

(13)

This is equivalent to $\vec{\mu} = f_0 \vec{F}$, which is the correct Clausius-Mossotti law for a macroscopic sample.

5 Fixed rather than Induced Moments

The CMM refers to a system of polarizable molecules whose induced dipoles $\vec{\mu}_i$ minimize the energy Eq.(3). If spontaneous moments are just barely stable in no applied field, the solution is $\mu_{i\alpha} \propto \langle \mu_{i\alpha} \rangle_{\gamma_{\text{max}}}$, where $\langle \gamma_{\text{max}} \rangle$ is the eigenvector of $\Gamma$ with largest eigenvalue. The proportionality constant is determined by higher order terms.

Another model, more in touch with chemical reality, has molecules with moments $\vec{\mu}_i$ fixed in magnitude ($|\vec{\mu}_i| = \mu_0$) but free to choose their spatial orientation. The ground-state moment configuration then minimizes Eq.(3), except with the resistance $1/\alpha$ to polarization set to zero, and with the $N$ constraints $|\vec{\mu}_i| = \mu_0$. In general, this is a difficult algebraic problem. However, suppose the eigenvector $\gamma_{\text{max}}$ has the property that $|\gamma_{\text{max}}| = \mu_0$ where $\mu_{i\alpha} \propto \langle \mu_{i\alpha} \rangle_{\gamma_{\text{max}}}$. For example, an infinite system with perfect ferroelectricity or simple antiferroelectricity has this property (each moment has the same magnitude.) Then this also must provide the ground state of the fixed moment problem. As a magnetic example
(magnetic and electric fixed moments obey the same dipole-dipole laws), White et al. [26] studied crystals of hydrated rare-earth phosphomolybdates. The magnetic moments of the rare-earth ions (located on a diamond-structure sublattice) are fixed by Hund’s rules but sufficiently separated from each other that interatomic exchange is ignorable. Then the magnetic order (seen below an ordering temperatures ≤ 50 mK) is determined by dipole-dipole interactions, and has been measured. The magnetic order is antiferromagnetic, much like the result of Sec. 3 for sc structure, except the order is more interesting in diamond structure. As explanation, the authors computed the largest antiferromagnetic eigenvalue of the matrix \( \Gamma \) and showed that for diamond structure (and also for bcc or fcc) this eigenvalue exceeds the ferromagnetic (CM) eigenvalue \( 4\pi n/3 \). Their calculation is the \( N \rightarrow \infty \) limit of Fig.(1).

In general, as illustrated in Fig. 2, but unlike the bulk examples just discussed, the vector \( |\gamma_{\text{max}}| \) with largest eigenvalue of \( \Gamma \) does not have all moments \( \mu_i \propto <i|\gamma_{\text{max}}> \) equal in magnitude, and thus does not solve the problem of finding the most favorable alignment of fixed dipole moments. In what sense is the solution of the fixed dipole problem \( \{\hat{\mu}_i\} \) “close” to the unconstrained solution given by \( |\gamma_{\text{max}}| \)? It is required to minimize the dipole energy \( -\mu|\Gamma|\mu>/2 \) plus constraint terms \( \lambda_i\mu_i^2/2 \). The solution depends on the Lagrange multipliers (LM) \( \lambda_i \) which are then varied until the constants \( \mu_i^2 = \text{const} \) are satisfied. There are \( N \) moments \( \hat{\mu}_i \), but only \( N - 1 \) constraints, because the constant value of \( \mu_i^2 \) is arbitrary since the problem is linear. The minimization can be formulated as a “generalized Hermitean eigenvalue problem.” The N LM’s define a vector \( \hat{\lambda} \) in the \( N \)-dimensional LM space. Write this as \( \hat{\lambda} = \lambda \hat{c} \) where the components \( c_i \) of \( \hat{c} \) are normalized by \( \sum c_i^2 = N \). Also write \( \mu_i^2 = <\mu_i|P_i|\mu_i> \) where \( P_i \) is a projection operator onto the 3-vector space of the \( i \)-th moment \( \hat{\mu}_i \). Then the formal solution of the minimization problem is

\[
\Gamma|\mu> - \lambda P(\hat{c})|\mu> = 0
\]

where the Hermitean operator \( P(\hat{c}) \equiv \sum c_i P_i \) is the sum of projection operators. The normalized vector \( \hat{c} \) defines a “ray” in LM space. There is one special ray \( \hat{c}_0 \), where \( c_i = 1 \) for all \( i \), so that \( P(\hat{c}_0) \) is the unit operator. For this special case, Eq.(14) is the ordinary eigenvalue equation for \( \Gamma \). For other rays, as long as no component \( c_i \) is zero, \( P \) is invertible and Eq.(14) is a generalized Hermitean eigenvalue equation. The \( N \) eigenvalues \( \lambda_\kappa \) depend on the direction \( \hat{c} \) of the ray, and define \( N \) surfaces \( \hat{\lambda} = \lambda_\kappa(\hat{c}) \hat{c} \) in LM space. Each surface \( \kappa \) intersects the special ray at distance \( \gamma_\kappa \), where \( \gamma_\kappa \) is an ordinary eigenvalue of \( \Gamma \).

All that has been accomplished so far is that the eigenvalue problem for \( \Gamma \) has been generalized to an infinite family of eigenvalue problems, one for each ray \( \hat{c} \) in LM space. Now we have to find the optimal solution \( |\mu> \) which minimizes dipole energy with fixed components \( \mu_i = \mu \). The \( N - 1 \) constraints \( \mu_i^2 = \text{const} \) will be satisfied along 1-dimensional lines in LM space. These lines will puncture each surface \( \kappa \) at isolated points. The optimal solution occurs at such a point on the surface of maximum eigenvalues.
That is, it lies on the surface which passes through $\gamma_{\text{max}}\hat{c}_0$, i.e., the surface which evolves from the solution of the unconstrained problem. This suggests an algorithm. First find the optimal solution $|\gamma_{\text{max}}>$ of the unconstrained problem. Then find the nearby eigenvalue $\lambda_{\text{max}} \approx \gamma_{\text{max}}$ and corresponding eigenvector $|\lambda_{\text{max}}>$ of the generalized problem for rays $\hat{c}$ near the special ray $\hat{c}_0$. Wander stepwise through nearby rays guided by the demand that the components $\hat{\mu}_i = P_i|\lambda_{\text{max}}>$ of the maximal eigenvector should evolve toward equal lengths. This should provide an efficient iterative solution of the fixed moment problem.

6 1-Dimensional Dipole Stack

Polar molecules in solution [27] may tend to self-organize into structures which optimize dipole-dipole interactions. The “Stockmayer fluid” [28] is a simplified model for such a system, which keeps hard core repulsion and long-range dipole-dipole interactions for spherical molecules with point dipoles. Such models may show linear arrangements of dipoles [29]. Such arrangements have also been directly visualized for magnetic nanoparticles in solution [30], and even for Au nanoparticles [31] which are presumed to acquire their polarity from interactions with species on their surface or in solution. This section considers ordered one-dimensional arrays, and the subsequent two sections considers the interactions between different ordered linear arrays.

Consider a one-dimensional stack of dipoles, with repeat distance $b$. For simplicity, think of them as permanent rather than induced moments, with identical magnitudes. Let each moment $\vec{\mu}$ point along the stack axis, chosen as the $z$ axis. The total interaction energy is

$$U_{\text{tot}} = \frac{\mu^2}{2} \sum_{i \neq j} \frac{-2}{|z_{ij}|^3} = -2\frac{\mu^2}{b^3} \left[ \frac{N - 1}{1^3} + \frac{N - 2}{2^3} + \frac{N - 3}{3^3} + \cdots + \frac{1}{(N - 1)^3} \right] = -2\frac{\mu^2}{b^3} \left[ N\zeta(3) - \zeta(2) + \frac{1}{N - 1/2} + \cdots \right]$$

Thus adding a molecule to the stack gains energy $2\zeta(3)\mu^2/b^3$ where $\zeta$ is the Riemann $\zeta$-function and $\zeta(3)$ has the numerical value 1.202057... Breaking a stack into two smaller stacks creates two new surface points, each costing energy $(\mu^2/b^3)\zeta(2)$ where $\zeta(2) = \pi^2/6 = 1.6449 \ldots$.

If the molecules are instead polarizable (with zero fixed moment) then the stack will spontaneously polarize when the energy gain exceeds the cost $\mu^2/2\alpha$, that is, when $1/\alpha$ is less than $4\zeta(3)/b^3$. One should ask if this situation is thermodynamically stable. For example, how much does it cost to rotate the direction of $\vec{\mu}$ away from the stack axis? How much does it cost to create a defect, for example, a stacking fault where the direction of $\vec{\mu}$ changes at the fault?

For the octahedral fragments considered in Sec. 3, cubic point symmetry has the consequence that terms of higher order are considered, there is no preference for any particular direction of $\vec{\mu}$. There is no anisotropy energy, so the ordered moment lacks a permanent direction in space. A collection of such nanoparticles would be called a “superparaelectric,” the analog of a “superparamagnet.” For the 1-d stack, this is no longer the case. Cubic symmetry is maximally broken, and it costs $3\zeta(3)\sin^2(\theta)\mu^2/b^3$ per molecule to rotate all dipoles. The anisotropy energy is very large.

On the other hand, it is a well-known property of ordered states in one dimension that domain wall defects destroy long-range order. We can estimate the cost of a domain wall as follows. An absolutely abrupt boundary, where induced moments have their full positive value on one side of the boundary between two molecules, and their full negative value on the other side, costs energy $4\zeta(2)\mu^2/b^3$ in lost dipole-dipole attraction. A more gradual case is an abrupt boundary on the site of a molecule. This loses the same amount of dipole-dipole attraction but there is a savings $\mu^2/2\alpha$ since one molecule is unpolarized, making this domain wall structure more favorable. More gradual boundaries become lower in energy when the polarizability is diminished.

Domain-wall defects will always be thermally excited except in shorter chains at lower temperature. The number of thermally excited domain walls is $Np$ where $p = \exp(-\Delta/k_BT)$ and $\Delta$ is the energy to create a domain wall. Suppose molecules in solution interact by dipolar forces. It is argued in Sec. 8...
that for oblate ellipsoidal molecules with dipoles along the short axis, chains are favored and only weakly attract neighboring chains. Then the statistical distribution of chain lengths $n$ may be given by the Flory-Schulz [32] distribution $P_n = p(1-p)^{n-1}$. The mean chain length would be $1/p$ but the most probable chain length would be 1. The derivation of this distribution assumes that $\Delta$ and thus $p$ do not depend on length, whereas actually $\Delta$ becomes smaller for short chains, which will enhance $P_n$ at small $n$. The Flory-Schulz distribution is usually written in terms of a variable $p' = 1 - p$ which measures the “completion” of the “reaction.” For prolate ellipsoids, there will be greater organization of chains into bundles. Domain walls then become correspondingly larger in area and harder to excite thermally, and the system evolves into a ferroelectric.

7 Interacting Parallel Stacks

There is an interesting and important interaction between two parallel stacks of fixed dipoles. Consider the case of infinite stacks (vertical separation of moments is $b$), where each moment is vertical (along the stack) and the two stacks are identical and parallel. Then it is obvious that the interaction is a periodic function of the vertical offset $y$ with period $b$. It turns out that the interaction is strictly oscillatory with no constant component (in powers of $\exp(i2\pi y/b)$) and decays exponentially (as $\exp(-2\pi x/b)$) with horizontal separation $x$.

The stack-stack interaction (per molecule) is

$$U_{ss} = \frac{\mu^2}{b^3} \sum_{n=-\infty}^{\infty} \frac{1}{[x^2 + (nb - y)^2]^{3/2}} \left[ 1 - \frac{3(nb - y)^2}{x^2 + (nb - y)^2} \right]. \quad (15)$$

This is also the interaction energy between a single infinite stack and a single $z$-oriented dipole at $(x, y)$. At large separations $x$ we can use the continuum approximation of a constant linear dipole density $\mu/b$ along the stack. Then the stack is electrostatically equivalent to charges $\pm \mu/b$ on the ends of the stacks which are infinitely removed from the observation point. Therefore at large separations the electric field and the interaction are zero. Any non-zero remainder (contained in Eq.(15) derives from the graininess of the dipole density.

To derive an asymptotic formula for the interaction, use the Poisson sum formula

$$\sum_{n=-\infty}^{\infty} f(in) = \frac{1}{2i} \int_C dz \coth(\pi z) f(z). \quad (16)$$

The contour in the complex $z$-plane surrounds the imaginary axis where $\coth(\pi z)$ has poles at $z = in$. Rewrite the summand of Eq.(15) as $-d^2/dy^2[x^2 + (nb - y)^2]^{-1/2}$. After bending the contour around suitable branch cuts, the dimensionless interaction is

$$\frac{U_{ss}}{\mu^2/b^3} = u_{ss}(x, y/b) = -2d^2/d(y/b)^2 \int_{x/b}^{\infty} du \frac{\sinh(2\pi u)}{\sqrt{u^2 - (x/b)^2} \cosh(2\pi u) - \cos(2\pi y/b)} \quad (17)$$

From this exact representation, extract the leading term in the asymptotic expansion in powers $\exp(2\pi nx/b)$ and $(x/b)^{-m-1/2},$

$$u_{ss}(x/b, y/b) \approx 8\pi^2 \cos(2\pi y/b) e^{-2\pi x/b} \sqrt{x/b}. \quad (18)$$

An understanding of formulas like this dates back to Madelung [33]. Because of $y$-periodicity, the electrostatic potential $\phi(x, y)$ can be expanded as $\sum C_i f_i(x) \exp(2\pi i y/b)$. Madelung points out that Poisson’s equation demands that $f_i(x)$ be the Hankel function $K_0(2\pi \ell x/b)$. The absence of the constant ($\ell = 0$) term from the sum follows from the charge neutrality of the stack. The asymptotic behavior of $K_0(t)$ is $\exp(-t)\sqrt{\pi/2t}$. In Figs.4 and 5, the exact and the asymptotic version of the interaction are compared. They agree to within $\pm 15\%$ for $(x/b) = 0.5$ and to within $\pm 2\%$ at $(x/b) = 1$. A plot of the electric field near the stack is shown in a separate paper [35].

The oscillation in $u_{ss}$ as a function of $y/b$ shown in Fig.5 has interesting consequences. When adjacent stacks have zero offset (as happens in the sc crystal structure), their moments $\mu$ prefer to be antiparallel,
Figure 4: Stack-stack interaction between two identical stacks of fixed dipoles \( \mu \) separated along the stack by distance \( b \). The stacks are separated horizontally by distance \( x \) shown horizontally in units of \( b \). The vertical offset \( y \) is zero. The interaction is in units \( \mu^2 / b^3 \). The solid line is computed numerically from Eq.(15) and the circles are the first term, Eq.(18) in the asymptotic expansion.

as was already seen for the octahedral fragments in Sec. 3. When adjacent stacks have a full offset \( y/b = 0.5 \), their moments prefer to be parallel, which is known to be the preference in the bcc and fcc crystal structures. Triangular packing of adjacent stacks has “frustrated” interactions. If the offset is zero, then some nearest neighbor interactions are necessarily repulsive no matter what orientations of \( \vec{\mu} \) are chosen. This problem is discussed further later in this section and in the next.

For cubic structures, an interesting sum-rule on stack-stack interactions is implied by the CM formula. This formula is equivalent to the statement that the dipole-dipole interaction energy for a cubic arrangement of dipoles, all oriented in the same direction, is \(-\gamma_{CM} \mu^2 / 2\) per molecule, and the CM eigenvalue \( \gamma_{CM} \) is \( 4\pi n / 3 \). Crystal structures can be viewed (in multiple ways) as parallel lines of stacked molecules. If the dipoles line up along the stacks, the total dipole-dipole energy can be computed as the energy per molecule in a stack, plus the energy per molecule of stack-stack interactions. Set these two versions of the total energy equal to each other, divide out \( \mu^2 \), and multiply by the volume of a cube whose edge length is the periodicity \( b \) on the stack. Define \( \nu = nb^3 \). Then the dimensionless energy equation is the sum rule

\[
-\frac{2\pi \nu}{3} = -2\zeta(3) + \frac{1}{2} \sum_{j \neq 0}^{\text{stacks}} u_{ss}(\frac{x_j}{b}, \frac{y_j}{b}) \quad \text{(cubic structures)}
\]  

(19)

Because the stack-stack interaction decays rapidly with separation, the dipole-dipole energy comes from the single stack energy \(-2\zeta(3) = -2.4041\) plus near neighbor stack interactions (the last term in Eq. 19, with a factor of 1/2 to avoid double counting.) This is demonstrated to be true in tables 1–3. For each crystal structure, there is more than one simple axis which can be chosen as a stack axis. In bcc structure (111)-oriented stacks are a favorable choice relative to (100) orientation because the spacing of molecules is closer \((b = \sqrt{3}a/2\) instead of \(a\); (110) stacks are best for both diamond and fcc structures, while (100) stacks are best in sc structure. The sum rule applies for any consistent choice of stacks. First-neighbor interactions converge the sum rule to better than 1% for sc (100) and bcc (111) stacks, and fcc requires only second-neighbor interactions in either (100) or (110) orientations. It is easily seen how the sc structure lowers its dipole energy by switching orientation of first-neighbor (100) stacks. For diamond, although (110) stacks give only a small improvement in convergence, they allow a better understanding of the antiferroelectric solution which gives the largest eigenvalue \( \gamma \). Each (110) stack has one very close neighbor with offset \( y/b = 1/2 \) which makes a strong ferroelectric bond, and two quite close next neighbors with zero offset, which therefore prefer to be antiferroelectrically oriented.
Figure 5: Stack-stack interaction between two identical stacks of fixed dipoles $\mu$ separated along the stack by distance $b$. The stacks are separated horizontally by distance $x/b = 0.5$ (solid line and filled circles) or by distance $x/b = 1.0$ (dashed line and open circles). The vertical offset $y/b$ is shown horizontally. The interaction is in units $\mu^2/b^3$. Note that the $x = b$ interaction is shown after multiplication by 20.

Solutions of polar molecules of ellipsoidal shape may self-organize into arrays of stacks. For cylindrically shaped molecules, the stacks may organize in a 2-d triangular lattice. Therefore it is interesting to look at the cubic structures from this point of view. Diamond is the only cubic structure that does not work, because (111) stacks are dimerized (alternate spacings of $\sqrt{3}a/4$ and $3\sqrt{3}a/4$ occur). The other cubic structures are triangular arrays of (111) stacks. The “frustration” problem is solved by alternating offsets of $\pm 1/3$ for the six first-neighbor stacks surrounding a central stack. At this offset, ferroelectric alignment is preferred by all first-neighbor pairs. Consider the rhombohedral translation vectors $\vec{R}_i = \vec{R}(\theta_i) = r \cos \theta_i \hat{x} + r \sin \theta_i \hat{y} + (b/3) \hat{z}$, where $\theta_i = 0^\circ, 120^\circ$, and $240^\circ$. The sum of these three primitive translations is $b\hat{z}$, the period of the stack, and the distance $r$ is the transverse separation of stacks. The rhombohedral angle $\alpha$ is defined by $R^2 \cos \alpha = \vec{R}_i \cdot \vec{R}_j$ which gives $\cos \alpha = [(b/3)^2 - r^2/2]/[(b/3)^2 + r^2]$. The three special values of $\cos \alpha$ are $-1/3$ (bcc), 0 (sc), and 1/2 (fcc), which correspond to ratios $r/b$ of spacing to period of $r_1 = \sqrt{8/9}$ (bcc), $r_1/2$ (sc), and $r_1/4$ (fcc). For bcc, the period and separation are nearly the same, so stacks interact only weakly. The sc structure is intermediate, while fcc structure has a small transverse separation relative to periodicity, leading to very strong stack-stack interactions. For both fcc and bcc structures, the ferroelectric alignment is optimal. However, for the intermediate case of sc structure, a lower energy solution tilts the axis of polarization of molecules along (111) stacks alternately to $\pm (100)$. Structures like sc and fcc should not necessarily be considered as arrays of (111) stacks even though it may be mathematically interesting to do so.
\[ \nu \frac{2 \pi \nu}{3} + 2 \zeta(3) \quad x_j \quad y_j \quad M_j \quad \frac{1}{j} M_{ju}(x_j, y_j) \]

| structure | \( \nu \) | \( \frac{2 \pi \nu}{3} + 2 \zeta(3) \) | \( x_j \) | \( y_j \) | \( M_j \) | \( \frac{1}{j} M_{ju}(x_j, y_j) \) |
|-----------|-----------|-----------------|-------|-------|------|-----------------|
| sc        | 1         | 0.3097          | \( \frac{1}{\sqrt{2}} \) | \( \frac{1}{2} \) | 4    | -0.2910         |
| bcc       | 2         | -1.7847         | \( \frac{1}{\sqrt{2}} \) | \( \frac{1}{2} \) | 4    | -2.0822         |
| fcc       | 4         | -5.9735         | \( \frac{1}{\sqrt{2}} \) | \( \frac{1}{2} \) | 4    | -8.2484         |
| diamond   | 8         | -14.3510        | \( \frac{1}{\sqrt{2}} \) | \( \frac{1}{2} \) | 4    | -8.3287         |

\[ \sum = -14.3683 \]

Table 1: Sum rule satisfaction for cubic crystals where the stacks have period \( b = a \) along a cube axis, and dipoles are oriented along the same axis. \( \nu \) is the number of molecules in a cube of edge \( b \). \( M_j \) is the multiplicity of the \( j \)-th set of neighboring stacks.

| structure | \( \nu \) | \( \frac{2 \pi \nu}{3} + 2 \zeta(3) \) | \( x_j \) | \( y_j \) | \( M_j \) | \( \frac{1}{j} M_{ju}(x_j, y_j) \) |
|-----------|-----------|-----------------|-------|-------|------|-----------------|
| fcc       | \( \sqrt{2} \) | -0.5578         | \( \frac{1}{\sqrt{3}} \) | \( \frac{1}{2} \) | 4    | -0.7110         |
| diamond   | \( 2\sqrt{2} \) | -3.5196         | \( \frac{1}{\sqrt{3}} \) | \( \frac{1}{2} \) | 4    | -0.7710         |

\[ \sum = -3.5249 \]

Table 2: Sum rule satisfaction for cubic crystals where the stacks have period \( b = a/\sqrt{2} \) along a cube face diagonal. \( \nu \) is the number of molecules in a cube of edge \( b \).

| structure | \( \nu \) | \( \frac{2 \pi \nu}{3} + 2 \zeta(3) \) | \( x_j \) | \( y_j \) | \( M_j \) | \( \frac{1}{j} M_{ju}(x_j, y_j) \) |
|-----------|-----------|-----------------|-------|-------|------|-----------------|
| bcc       | \( 3\sqrt{3} \) | -0.3166         | \( \frac{\sqrt{3}}{2} \) | \( \frac{1}{3} \) | 6    | -0.3224         |
| sc        | \( 3\sqrt{3} \) | -8.4787         | \( \frac{\sqrt{3}}{2} \) | \( \frac{1}{3} \) | 6    | -9.6448         |

\[ \sum = -8.5075 \]

Table 3: Sum rule satisfaction for cubic crystals where the stacks have period \( b = \sqrt{3}a/2 \) (bcc) and \( b = \sqrt{3}a \) (sc) along a cube body diagonal. \( \nu \) is the number of molecules in a cube of edge \( b \). The sum rule is satisfied to similar accuracy for fcc structure with (111) stacks only when stacks out to 12th neighbors are summed.
8 Close Packed Ellipsoidal Dipoles

Here is a mathematical puzzle of possible chemical interest. It is a relative of a popular statistical mechanics model, the dipolar liquid [27]. Consider an infinite set of hard ellipsoids of revolution (radius of revolution $a/2$, axial half-length $b/2$. Let there be a permanent moment $\mu$ along the unique axis. What is the ground state structure and energy? This section only states and does not pretend to solve the problem, but makes a conjecture about the answer for the special case $a = b$ of hard-sphere dipoles. This puzzle would be relevant to liquid phase self-assembly of ellipsoidal shaped molecules, if no other interactions were important besides hard-core repulsion and electrostatic interactions.

One possible family of structures is arrays of “chains,” where the term “chain” will be used to denote a stack of touching ellipsoids with the axis of revolution the same as the axis of the chain. Dipole-dipole interactions will favor ferro alignment along the chain. What transverse arrangement of chains is favored? Close packing will require at least an approximate triangular pattern of chain axes. In the “simple hexagonal” structure of perfect triangular symmetry and zero longitudinal offsets, first neighbor chains all wish to have antiparallel moments. This is geometrically impossible, so the pattern is frustrated. Various anti-ferroelectric (e.g. alternating rows of up and down oriented chains) or ferrielectric (e.g. one out of three anti-aligned chains in a hexagonal pattern) give two out of three neighbors favorably anti-aligned and one out of three unfavorably aligned.

The “offset” is defined as the distance along the chain axis separating centers of ellipsoids on two neighboring chains, measured in units of the period $b$ which is also the axial length of the ellipsoid. With offset zero touching ellipsoids have transverse separation $r = a$. With non-zero offset, the separation is $r = a\sqrt{1 - (\text{offset})^2}$. Introducing offsets allows two good things to happen. (1) The chains can pack more densely because the widest parts of adjacent ellipsoids are not touching. (2) For offsets roughly between $1/4$ and $1/2$, parallel moments are preferred. If all neighbors prefer to be parallel, there is no frustration problem. Of course, farther neighbors have other offsets, and if $b/a > 1$, farther interactions acquire more importance, reintroducing frustration.

From the discussion of the previous section, two symmetrical possibilities can be seen: (1) a triangular array with offsets $\pm 1/3$, which gives the rhombohedral family to which the primitive cubic structures belong; or (2) a body-centered orthorhombic (bco) family to which the fcc structure belongs. These structures are shown in Fig. 6. The bco structure minimizes the frustration problem by breaking triangular symmetry, giving the four closest neighbors the optimal offset $1/2$ for ferroelectric order, and having two slightly more distant neighbors with zero offset which are unhappily ferroelectric.

It is easy to see that bco is the preferred structure for dipolar hard spheres. Note that the density of ellipsoids ($1/v$ where $v$, the volume per ellipsoid, is $a^2 b/\sqrt{2}$ for bco and $\sqrt{16/27} a^2 b$ for rhombohedral) is higher for bco at all axial ratios $b/a$. For cubic structures (these structures are fcc and bcc respectively when $b = a$) the CM law tells us that the dipole energy $E = -(2\pi/3e)\mu^2$ depends only on the density. For other axial ratios, the CM law no longer works because the structure is not cubic. One might expect that bco would always win because of its higher density. However, numerical calculation shows that for axial ratios $b/a > 1.717$, the rhombohedral structure is better. This numerical test was done only in the range $0.5 < b/a < 2.5$. For larger $b/a$, the on-chain parallel alignment of dipoles is no longer a big part of the energy, so there is no reason to think that chains would form. For smaller $b/a$, the chain-chain interaction is no longer a big part of the energy, so it is not likely that dipole interactions would play the dominant role in determining how chains arrange themselves.

It seems reasonable to conjecture that the optimal solution for hard sphere dipoles is the bco=fcc structure with minimum volume. However, the complexity of dipolar interactions is such that it is not wise to be confident of this solution. For ellipsoids that are close to spherical, the same answer probably applies, but for $b/a = 1.717$ where bco loses to rhombohedral, there is no good argument preventing a totally different structure from doing even better.

9 Metallic Coatings

The CMM focusses on a single aspect of the physics of electrical polarity in nanosystems, namely dipole-dipole interactions of induced moments. In this final section the model is pushed a little further to model the effect of metallic screening from adjacent metallic regions. An interesting result was derived
Figure 6: Rhombohedral (left) and body-centered orthorhombic (bco, right) packing of hard ellipsoids. The axis of revolution is shown vertical. Rhombohedral packing achieves a greater 2-d density of ellipsoids, but lesser 3-d density, than bco.

by Maschhoff and Cowin [36]. They find that a neutral molecule with both a fixed point dipole moment $\mu_0$ and an isotropic polarizability $\alpha$, when favorably aligned perpendicular to a metal surface at distance $b/2$, has energy (attraction to the image dipole)

$$E = -\frac{\mu_0^2}{(b^3 - 2\alpha)}.$$  (20)

The induced dipole enhances the total dipole and increases the attractive interaction energy between the dipole and the surface. At a critical polarizability $\alpha_c = b^3/2$, the response is divergent. At this point, an induced dipole would spontaneously form even if the permanent moment $\mu_0$ were zero.

It is evident that coupling a polarizable medium to metallic electrodes or shielding devices may promote spontaneous polarization. As a specific model, we now investigate an array of $N$ fixed polarizable molecules (positions $\mathbf{R}_i$) which are coated, or otherwise mingled, with $N'$ fixed chargeable molecules (positions $\mathbf{R}_\ell$). The indices for polar sites are $i, j$ and for charge sites are $\ell, m$. Many models of this type can be found in the literature, for example [7, 8, 9, 10, 11, 17]. The energy of chargeable sites alone would be the classical electrostatic energy

$$E_{\text{ch}}(\{q\ell\}) = \frac{1}{2C} \sum_i q_i^2 + \frac{1}{2} \sum_{i \neq m} q_i q_m \frac{R_{\ell i}}{R_{\ell m}} + \sum_\ell q_\ell \phi_{\ell,\text{ext}}$$

$$= \frac{1}{2} < q|(1/C)1 + V|q > + < q|\phi_{\text{ext}} > .$$  (21)

The term $q_\ell^2/2C$ is the energy cost of putting charge $q_\ell$ at the $\ell$th site. Here $|q>$ is an $N'$-vector and 1 and $V$ are $N' \times N'$ matrices. The external potential $\phi_{\ell,\text{ext}} = \phi_{\text{ext}}(\mathbf{R}_\ell)$ is the external scalar potential, related to the external electric field by $\mathbf{E}_{\text{ext}} = -\nabla \phi_{\text{ext}}(\mathbf{r})$. The charges can adjust to minimize energy, subject to the constraint of charge conservation, $\sum_\ell q_\ell =$const, where the constant will normally be zero. Introducing a Lagrange multiplier $\lambda$, we find that for a system of charge sites in constant external potential,

$$[(1/C)1 + V]|q > + |\phi_{\text{ext}} > = \lambda|0 >$$  (22)

where $\langle \ell|q > = q_\ell$ is the charge at site $\ell$ and $\langle \ell|0 > = 1$ defines $|0 >$. The first term on the left hand side of Eq.(22) is the vector $|\phi_{\text{int}}>$ of internal electrostatic potentials at sites. The charges adjust to make a constant potential $\phi = \phi_{\text{int}} + \phi_{\text{ext}}$. A non-zero $\lambda$ just uniformly shifts the potential in order to adjust the total charge. The system of charges should be neutral when not driven. This requires the matrix $[(1/C)1 + V]$ to be positive. The Coulomb interaction $V$ by itself is not positive – two sites with charge $+Q$ and $-Q$ have negative energy – so a capacitance $C$ less than infinity is needed to keep charges
from spontaneously separating. In the resting state ($\phi_{ext} = 0$) we want a neutral system ($< 0 | q > = 0$) so $\lambda = 0$.

Now introduce electrostatic coupling between the charge sites and the polar sites,

$$\mathcal{E}_{int} \{\{q\ell\}, \{\mu_i\}\} = \sum_{\ell} \sum_i q_{\ell} \overrightarrow{R_{\ell i}} \cdot \overrightarrow{\mu_i} \overrightarrow{R_{\ell i}}^3$$

$$= < q | K | \mu >$$

(23)

where the matrix $K$ has dimension $N' \times 3N$. For simplicity, choose $\phi_{ext} = 0$, and find the charge distribution $|q>$ which minimizes the total energy, the sum of Eqs.(3, 21, 23), for an arbitrary fixed dipole distribution $|\mu>$. The answer is

$$|q> = - \left( \frac{1}{C} + V \right)^{-1} K |\mu>.$$  

(24)

When this answer is inserted into the total energy formula, the result is an effective dipole-dipole interaction $\Gamma_{eff}$,

$$\mathcal{E}_{tot} = \frac{1}{2} < \mu | [(1/\alpha)1 - \Gamma_{eff}] | \mu >$$

(25)

$$\Gamma_{eff} = \Gamma + K^\dagger [(1/C)1 + V]^{-1} K$$

(26)

where $K^\dagger$ is the transpose of the rectangular matrix $K$. The charge system effectively enhances the dipole-dipole interaction, driving the system closer to a ferroelectric instability.

As an illustration, consider a single polarizable molecule, with two chargeable sites, one to each side at a distance $r$. Assuming that charge responds instantly to polarization on the polarizable molecule, the energy to create a dipole is $\mu^2/2\alpha_{eff}$, where

$$\frac{1}{\alpha_{eff}} = \frac{1}{\alpha} - \frac{1/\mu^4}{2C - 1/4r}.$$  

(27)

The $1/r^4$ in the numerator is the two powers of the charge dipole interaction $K$, and $1/4r$ in the denominator is half the Coulomb attraction between the induced charges $\pm q$. When there is an external field (along the trimer axis) the total dipole $\mu_{tot} = \mu + 2qr$ has both a contribution from the polar molecule and from the metal, and the response is

$$\mu_{tot} = \alpha_{eff} \left[ 1 + \frac{1/\alpha - 2/\mu^3}{\frac{1}{2\mu^3} \left( \frac{1}{C} - \frac{1}{2} \right) r} \right] F_{ext}$$

(28)

This diverges at the same critical polarizability that makes $\alpha_{eff}$ diverge.

It is easy to produce an alternative theory in which charges are treated by quantum mechanics, and charge interactions are solved in random phase approximation. The simplest such model is to let the charge sites $\overrightarrow{R}_\ell$ be atoms which have only an $s$-orbital available near the Fermi level. The Hamiltonian is

$$\mathcal{H}_{el} = \sum_{\ell m} t_{\ell m} c_\ell^\dagger c_m + \frac{1}{2} \sum_{\ell \neq m} V_{\ell m} c_\ell^\dagger c_\ell c_m c_m$$

(29)

where $c_m$ destroys an electron from the orbital on site $\overrightarrow{R}_m$. The charge-dipole interaction is

$$\mathcal{H}_{el-dip} = \sum_{i\alpha m} K_{m,i\alpha} \mu_{i\alpha} c_m^\dagger c_m$$

(30)

Now the induced charge at site $\ell$ is related to the external potential at site $m$ by the density response function $\chi$,

$$\delta q_\ell = - \sum_m \chi_{\ell m} \delta V_{ext,m}.$$  

(31)
and the energy of the induced charge distribution (analog of Eq.(21) is

$$\mathcal{E}_{ch}\left(\{q\ell\}\right) = \frac{1}{2} < q | \chi^{-1} | q > \quad (32)$$

If we ignore the Coulomb interaction (second term in Eq.(29)), then the electrons are governed by the non-interacting Hamiltonian $\mathcal{H}^0_{el}$. This problem has the solutions $\mathcal{H}^0_{el}|n> = \epsilon_n|n>$, and the susceptibility can be computed from

$$\chi^0_{\ell m} = \frac{2}{\epsilon_n - \epsilon_{n'}} \sum_{n}^{\text{occ}} \sum_{n'}^{\text{empty}} <\ell|n'|<n'|m><m|n><n|\ell> \quad (33)$$

However, it is crucial to account for the Coulomb interaction between electrons, which means solving the electron many-body problem. This cannot be done exactly. The random-phase approximation (RPA, also known as the time-dependent Hartree approximation) provides good insight and not a bad numerical answer. The relevant equation is

$$\chi|\delta V_{\text{ext}} > = \chi^0(\delta V_{\text{ext}} > + |\delta V_{\text{Hartree}} > ) \quad (34)$$

Then Eq.(32) is replaced by

$$\mathcal{E}_{ch}\left(\{q\ell\}\right) \approx \frac{1}{2} < q | \chi^0_{0}^{-1} + V | q > \quad (35)$$

Note that the structure of the classical model Eq.(21) is closely followed, with the non-interacting susceptibility interpreted as a non-local capacitance. The result is an effective dipole-dipole coupling which replaces the classical Eq.(26),

$$\Gamma_{\text{eff}} = \Gamma + K^\dagger \left[1/\chi_0 + V\right]^{-1} K \quad (36)$$

As an illustration, consider the same problem of a single polarizable molecule, with two chargeable sites, one to each side at a distance $r$. This time the sites have $s$-orbitals coupled by hopping matrix element $t$ and Coulomb coupling $q^2/2r$. It is also sensible to include an on-site Hubbard repulsion $U$ which discourages deviation from charge neutrality. This system responds to external fields with the effective polarizability

$$\frac{1}{\alpha_{\text{eff}}} = \frac{1}{\alpha} - \frac{1}{t/e^2 + U/2e^2 - 1/r^4} \quad (37)$$

Halas et al. [37, 38] have discovered how to coat semiconducting nanoparticles with metal shells. It would be interesting to attempt this with nanoparticles of large polarizability, in order to engineer new superparaelectric or nanoferroelectric systems.

**Note added in proof, Nov. 15, 2003**

Concerning the possibility of ferroelectricity in fullerenes *via* the CM polarization catastrophe, R. L. Whetten had suggested to me endohedral fullerenes as a route to enhanced polarizability. It turns out the Clougherty [39, 40] has speculated about ferroelectricity in such systems, not from a CM point of view, but more correctly, from a Jahn-Teller point of view.

N. W. Ashcroft has reminded me that the CM polarization catastrophe was formulated by Goldhammer [41] and Herzfeld [42] as a criterion for metallization under pressure. As the macroscopic dielectric function diverges, we now understand that the frequency of some “ferroelectric soft mode” goes to zero. If this is not a lattice mode, but an electronic mode (plasmon), then the new phase as understood by Goldhammer and Herzfeld, should be a metal, not a ferroelectric. This criterion proved useful for guiding high pressure experiments [43], particularly for the metallization of Xe [44, 45], where there are no lattice modes internal to the “molecule” of Xe.

N. W. Ashcroft has also reminded me of an interesting extension of dipole ordering energy theory, namely the construction of harmonic polarization wave states, first done by Lundqvist and Sjolander [46]. Atwal and Ashcroft are applying this idea to superconducting interactions [47], following earlier work [48].

Finally G. Stell has introduced me to some of the literature on computer simulations of dipolar systems. Some of these papers [49, 50, 51, 52, 53, 54, 55, 56, 57] are particularly relevant to the discussions in the present paper.
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