Relation between the local field at large distances from a charge or dipole and the dielectric constant

(molecular dynamics/local polarization/screening)

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ABSTRACT The local field at large distances from a charged or dipolar impurity in a nonpolar polarizable fluid is related to the dielectric constant of the medium. The predicted local field agrees accurately with molecular dynamics results. In contrast, the usual continuum theory prediction is only accurate to first order in the polarizability and leads to serious errors for realistic values of the polarizability. At smaller distances these relations cannot be used to define a physically reasonable local dielectric constant and consequently the local field is more satisfactorily described in terms of a screening function.

One of the surprising results of molecular dynamics studies (1, 2) on the local electric fields (the field at a particle) around charged or dipolar impurities in a nonpolar polarizable solvent was the failure of the continuum theory to relate the local field to the dielectric constant of the solvent even at large distances from the impurity. The continuum theory was shown to be exact in the limit of small dielectric constant or to terms linear in ρα, where ρ is the density and α the polarization of the solvent (1–3). The large discrepancies at higher dielectric constants between the continuum model and the molecular dynamics results must be ascribed to differences in the nonlinear terms caused by the unnecessary introduction of cavities. The introduction of cavities results in boundary charges on their surface which affect interactions at all solvent-particle-impurity separations. The present work avoids the introduction of cavities and successfully predicts the local field at large distances in terms of the dielectric constant. Given this asymptotically valid relation we then address the question of whether it can be sensibly applied at small distances; in other words, whether one can define a physically meaningful local dielectric constant around a charged or dipolar impurity.

Rigorous relations between the local field and the dielectric constant for the nonpolar polarizable fluid can be derived because the polarization of a particle is determined by its local field. If the average local field of a particle at r from the impurity is denoted (δr(δ)), then the average polarization for a particle at r is obtained by multiplying by the polarizability, α. Further multiplication by the probability of finding a particle at r, ρg(r), where g(r) is the pair distribution function, gives the average polarization density at r:

\[ \bar{P}(r) = \frac{\alpha}{\rho} \bar{\phi}(r) \]  \[ 2.1 \]

The dielectric constant is defined by the relation between the polarization density and the Maxwell field, \( \bar{E}(r) \),

\[ \bar{P}(r) = \frac{\epsilon(r) - 1}{4\pi} \bar{E}(r). \]  \[ 2.2 \]

Strictly speaking, the Maxwell field involves a spatial average of the microscopic electric field over a volume large compared to particle sizes but, at large distances from the impurity, a time or ensemble average is sufficient and a further spatial average is unnecessary.

Finally, \( \bar{E}(r) \) can be related, by a straightforward electrostatics calculation, to the polarization density and the field of the impurity. Substituting this expression into Eq. 1.2, solving the resulting relation for \( \bar{P}(r) \), and equating it to the expression given by Eq. 1.1 yields a relation between the local field and the dielectric constant valid at large r. Since the electrostatic calculation is different for the two types of impurities, they are treated separately. The simpler case of the charged impurity is dealt with first.

CHARGED IMPURITY

The averaged polarization density around the charge Q must have the form

\[ \bar{P}(r) = \epsilon \bar{p}(r) \]  \[ 2.3 \]

by radial symmetry. The electric potential

\[ \phi(r) = Q \int \frac{1}{|r - r'|} \bar{P}(r') d^3r' \]  \[ 2.4 \]

is well defined since \( \bar{P}(r) \) vanishes near the origin. Combining the above two equations leads to

\[ \phi(r) = \frac{Q}{r} - 4\pi \int \rho(r') dr' \]  \[ 2.5 \]

and thus to

\[ \bar{E}(r) = -\bar{\phi}(r) = \frac{Q}{r^3} - 4\pi \bar{P}(r). \]  \[ 2.6 \]

Substitution of Eq. 2.4 into Eq. 1.2 and eliminating \( \bar{P}(r) \) by Eq. 1.1 gives the desired relation between the local field and the dielectric constant. In the molecular dynamics calculations (1, 2) the measured local field was described by a screening function \( S(r) \), defined by

\[ \langle \bar{\phi}(r) \rangle = \bar{S}(r) Q \frac{\rho}{r^3}. \]  \[ 2.7 \]

In terms of \( S(r) \) our relation is

\[ \epsilon(r) = \left[ 1 - 4\pi \rho \bar{g}(r) S(r) \right]^{-1} \]  \[ 2.8 \]

or for large distances

\[ \epsilon = \left[ 1 - 4\pi \rho \bar{g}(r) S \right]^{-1}. \]  \[ 2.9 \]

This equation permits the solvent dielectric constant to be calculated from the molecular dynamics values for S. The values of \( \epsilon \) obtained verify the accuracy of the Clausius–Mosotti relation

\[ \frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \rho \alpha + O(\alpha^3) \]  \[ 2.10 \]

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Table 1. Coulomb field screening at large distances

<table>
<thead>
<tr>
<th>$\alpha/r^3$</th>
<th>$S_{MD}^*$</th>
<th>$S_{calc}$</th>
<th>$S_{cont}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.85</td>
<td>0.85</td>
<td>0.84</td>
</tr>
<tr>
<td>0.060</td>
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<td>0.74</td>
<td>0.70</td>
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<td>0.58</td>
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<tr>
<td>0.100</td>
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<td>0.48</td>
</tr>
<tr>
<td>0.125</td>
<td>0.53</td>
<td>0.53</td>
<td>0.39</td>
</tr>
</tbody>
</table>

$\rho\alpha r^3 = 0.844; \ kT/\epsilon_L = 0.85$.  
* $S_{MD}$ has an uncertainty of $\approx 2\%$.

for nonpolar, polarizable fluids. This relation can be used to eliminate $\rho\alpha$ from Eq. 2.7 to give an expression for the long-distance screening function of the local field purely in terms of the dielectric constant:

$$S = \frac{\epsilon + 2}{3\epsilon}.$$  \[2.9\]

This expression is to be contrasted with the continuum model where both the impurity and the solvent particle located at $r$ from the impurity are surrounded by cavities immersed in a dielectric continuum. This model gives

$$S_{cont} = \frac{1}{\epsilon} \frac{3\epsilon}{\epsilon + 1}.$$  \[2.10\]

where the first factor is the screening of the Coulomb field in the continuum and the second factor relates the field in the continuum to that in the cavity. The two expressions for $S$ are not even qualitatively similar at large $\epsilon$.

In Table 1 the molecular dynamics results for the asymptotic screening function around a charge in a solvent of polarizable Lennard-Jones particles, $S_{MD}$, are compared with Eqs. 2.9 and 2.10. The dielectric constant for these last two columns was calculated from Eq. 2.5. Clearly, the new expression describes the computer results to within experimental uncertainties whereas the continuum expression is only accurate for low $\rho\alpha$ values.

Having related the local field at large distances from the charge to the dielectric constant, it is interesting to test the utility of this expression at shorter distances. Application of Eq. 2.6 leads to the dielectric function $\epsilon(r)$ listed in Table 2, where the radial distribution function and the screening function (see also figure 1 of ref. 2) are given as well for two different impurity charges. The lower charge is sufficiently small that the fluid structure is essentially unaltered from the pure fluid case. Even for this case, where one might have thought that the concept could be extended to smaller distances, $\epsilon(r)$ has very erratic behavior, becoming negative in the region of the first peak in $g(r)$ and is more than twice its asymptotic value even at the second peak. By contrast, the screening function is considerably smoother, staying within a few percent of its final value after the second peak in $g(r)$. The screening function, $S(r)$, is clearly the more reasonable way of describing local fields near the charge.

**DIPOLAR IMPURITY**

For the dipolar impurity in a nonpolar polarizable solvent the polarization density consists of two parts: a dipolar component and a reaction field component that points along the impurity dipole moment $\hat{\mu}_0$.\[ Following the treatment of the dielectric constant for dipolar systems by Onsager (4), the approximation of treating all particles, other than the one or two under consideration, as a continuum has been widely used in the theory of dielectrics.

\[3.1\]

where $\hat{\mu}_0$ is a unit vector along $\hat{\mu}_0$ and $\bar{T}$ is the unit tensor. Calculating the electric potential as in Eq. 2.2 and taking the gradient yields

$$E_D(r) = \frac{\mu_0}{r^3} + \frac{1}{r^3} \int_0^r P_R(r')d^3r'$$  
$$- \frac{4\pi}{3} \left[ 2P_D(r) + P_R(r) \right]$$  \[3.2\]

$$E_R(r) = 2 \int_r^\infty \frac{P_D(r')d^3r'}{r'^3} - \frac{4\pi}{3} \left[ 2P_D(r) + P_R(r) \right]$$  \[3.3\]

where the Maxwell field, like the polarization density, splits into a dipolar and a reaction field component. Eq. 3.2 may be conveniently reexpressed in terms of an effective impurity dipole moment

$$\mu_{eff}(r) = \mu_0 + \int_0^r P_R(r'd^3r')$$  \[3.4\]

which has a clear physical interpretation. The dipolar component of the local field can be expressed in terms of the unscreened field times a screening function $S_D(r)$, so from Eq. 1.1,

$$P_D(r) = \alpha S_D(r) \frac{\mu_0}{r^3} \rho(r).$$  \[3.5\]

When introduced into Eq. 3.3, the above expression can be used to show that the reaction field decreases faster than the dipolar field (this is also clear from the computer results) so that, at large $r$, Eq. 3.2 becomes

$$E_D(r) = \frac{\mu_{eff}(r)}{r^3} - \frac{8\pi}{3} P_D(r).$$  \[3.6\]

This equation, together with the defining relation for the dielectric (Eq. 1.2), leads to the following asymptotic expression for the dipolar screening function

$$S_D = \frac{\mu_{eff}}{\mu_0} \left( \frac{3}{4\pi\epsilon \alpha} \right) \left( \frac{r - 1}{2\epsilon + 1} \right) \approx \frac{\mu_{eff}}{\mu_0} \left( \frac{\epsilon + 2}{2\epsilon + 1} \right).$$  \[3.7\]

where the last expression follows from the use of the Clausius–Mosotti relation. This result will be compared with the continuum theory prediction of

$$S_{cont} = \frac{9\epsilon}{(2\epsilon + 1)^2}.$$  \[3.8\]

The asymptotically exact expression for $S_D$ requires calculation of $\mu_{eff}$. Ideally, $\mu_{eff}$ should be obtained according to Eq. 3.4 by integrating $P_R(r)$ from molecular dynamics calculations. However, in the simulations the polarization was set to zero outside a sphere of finite radius. This truncation causes $P_R(r)$ to have a long, weak, negative tail at large $r$, leading to an inaccurate estimate of $\mu_{eff}$. Rather than correct the calculated $P_R(r)$ by repeating the molecular dynamics calculation with Ewald boundary conditions, $\mu_{eff}$ will be obtained from a recently developed model (5) of polarizable fluids. The model, although approximate, has been shown to describe the molecular dynamics results to within their numerical uncertainties. Moreover, use of this model has the advantage of leading to a simple compact expression for $S_D$.

The model makes use of a classical Drude oscillator representation for molecular polarizability. It could then be shown that, to a good approximation, equilibrium properties of a polarizable liquid may be calculated as if the polarizable solvent were replaced by a fluid of permanent dipoles. The equivalent
permanent dipole moment, $\mu_{\text{eq}}$, of the constituents of this fluid is found from the relation (5)

$$\mu_{\text{eq}} = \frac{3\alpha kT}{1 + 2\alpha \frac{U}{\mu_{\text{eq}}^2}}.$$ \[3.9\]

where $U/N$ is the dipolar part of the internal energy per particle of the equivalent fluid of permanent dipoles. The value $\rho a^3 = 0.844; kT/eL_j = 0.85; \alpha/\sigma = 0.10$.

* If the Lennard–Jones parameters for argon are used, the electron charge $Q/\sqrt{\epsilon_L J} = -20$.

of $U/N$ can be easily calculated from the Pade approximants (6) to the free energy of dipolar systems. The effective dipole moment, $\mu_{\text{eff}}$, of Eq. 3.4 is simply related to the Kirkwood $g$ factor (7) which describes the local orientational ordering in the equivalent fluid by

$$\mu_{\text{eff}} = g \mu_0.$$ \[3.10\]

The Kirkwood fluctuation formula (8)

$$y_g = \frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon}.$$ \[3.11\]

relates the dielectric constant to the local orientational ordering—that is, the value of $g$. Since the $g$ value is simply $\mu_{\text{eff}}/\mu_0$, the final expression for the local field screening function becomes

$$S_D = \frac{3}{4\pi \alpha \rho} \frac{(\epsilon - 1)^2}{9\epsilon} \cdot \frac{(\epsilon + 2)(\epsilon - 1)}{9\epsilon}.$$ \[3.13\]

In Table 3 the molecular dynamics results for the asymptotic screening function around a permanent dipole in a polarizable Lennard–Jones solvent, $S_{MD}$, are compared at various $\rho a$ values with the above theory and with the continuum result. The $\mu_{\text{eq}}$ and $\mu_{\text{eff}}/\mu_0$ values are also listed. To within the numerical uncertainties, $S_{MD}$ agrees with the directly determined molecular dynamics values; the continuum model again overestimates the screening of the local field at the higher $\rho a$ values. Ignoring the difference between $\mu_{\text{eff}}$ and $\mu_0$ (last column in Table 3), although an improvement over the continuum model, also overestimates the screening, because the effective increase of the dipole moment over its vacuum value (due to the polarization of the surrounding fluid) has been neglected.

The failure of the continuum theory to account for the results in these simple model systems, where the polarization is proportional to the instantaneous local field, calls into question its accuracy in describing more complicated realistic systems. Furthermore, from the theoretical point of view, the introduction of dielectric discontinuities should be avoided at all costs, even for considerations at macroscopic distances.

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