When a polar liquid becomes a dielectric?

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J.C. Maxwell

\[ \vec{E} = \vec{E}_0 - 4\pi \vec{P} \]
\[ \vec{D} = \vec{E} + 4\pi \vec{P} \]
\[ \vec{D} = \vec{E}_0 \]

digging cavities...how to define field in a dielectric?

\[ \vec{E}_c = \vec{E}_0 - 4\pi \vec{P} + 4\pi \vec{P} = \vec{E}_0 \]

\[ \vec{E}_c \text{ is the cavity field} \]

\[ \vec{E}_c = \vec{E} \]
Lorentz...what is the local filed acting on electrons in a metal?

\[
\bar{E} = \bar{E}_0 + \bar{E}_{	ext{att}} + \bar{E}_{	ext{sph}}
\]

\[
\bar{E}_{	ext{att}} \quad (\text{cubic}) = 0
\]

\[
\bar{E}_{	ext{sph}} = \frac{4\pi}{3} \bar{P} = \frac{4\pi}{3} \frac{\varepsilon - 1}{\varepsilon} \bar{E}_0
\]

\[
\bar{E} = \bar{E}_\varepsilon = \frac{\varepsilon + 2}{3\varepsilon} \bar{E}_0
\]

physical cavity carved in a dielectric...

\[
\bar{E}_c = \frac{3}{2\varepsilon + 1} \bar{E}_0
\]
dielectric constant...

\[ \mathbf{P} = \frac{\varepsilon - 1}{4\pi} \mathbf{E} = \rho \langle \mathbf{m} \rangle \]

\[ \langle \mathbf{m} \rangle = \frac{1}{\Omega} \int \exp\left( -\beta H_0 + \beta \mathbf{m} \cdot \mathbf{E}_{eoc} \right) \mathbf{m} \, d\mathbf{P} \]

\[ \langle \mathbf{m} \rangle = \frac{\beta m^2}{3} \mathbf{E}_{eoc} \]

\[ \mathbf{E}_{eoc} = \mathbf{E}_L \]

\[ \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\varepsilon - 1}{\varepsilon + 2} = \gamma = \frac{\varepsilon - 1}{\varepsilon + 2} \]

Debye equation, 1914

It works for magnetism where this is known as the mean-field Weiss model, but for electric dipoles...

cavity radius does not enter here
Reaction field... let’s shrink the cavity to the size of the molecule

\[
\vec{P} = \frac{\epsilon - 1}{4\pi} \vec{E} = \frac{\beta m^2 \rho}{3} \left( \frac{3 \epsilon}{2\epsilon + 1} \right) \vec{E},
\]

\[
\frac{(\epsilon - 1)(2\epsilon + 1)}{6\epsilon} = \gamma
\]

Onsager eq. 1936

\[
\vec{E}_{eq} = \vec{E}_c
\]

Reaction field instantaneously adjusting to molecular orientation

\[\epsilon \text{ paraelectric liquid}\]
The fate of the ferroelectric phase is decided by the asymptote of the local field. The equation for the local field is:

\[
\frac{\varepsilon - 1}{4\pi} = 3y^3, \text{ Debye}
\]

\[
= 3y + 3y^2 + \frac{27}{144}y^3 + \ldots
\]

\[-3y^3, \text{ Onsager}\]

Onsager

Debye

ferroelectric transition: \(y = 6.7 - 7.3\)
how a polar liquid can possibly be a dielectric?

Electrostatics suggest that field within a **microscopic** cavity depends on the global shape of the sample.

Correlations (and external perturbations) decay on molecular length-scale.

one needs a description of the dielectric response “from bottom up”, deriving the continuum limit from a microscopic formalism.
excluding polarization from cavity ...

\[ G(\tilde{A}) = \int \exp \left[ -\beta H_B + \tilde{A} \cdot \hat{P} \right] \prod_{r \in \Sigma_0} \delta[\hat{P}(r)] \otimes \hat{P} \]

\[ H_B = \frac{1}{2} \hat{P} \chi^{-1} \hat{P} \]

response function of a homogeneous solvent

\[ \chi(k_1, k_2) = \frac{\sum_j \ln G(\tilde{A})}{\delta \tilde{A}(\tilde{e}_1) \delta \tilde{A}(\tilde{e}_2)} = \chi_5(k_1) d_{k_1 k_2} - \chi^{\text{corr}}(k_1, k_2) \]

correction introduced by the cavity

cavity field:

\[ E_c = E_0 + \tilde{e}_0 \cdot \tilde{T} \times \chi \times \tilde{E}_0 \]

field of the polarized lig.

\[ \tilde{E}_0 = \tilde{E}_0 D_{k,0} \]

homogeneous external field

\[ \tilde{T} = -4\pi D_k \frac{\delta_1(k R_1)}{k R_1} \]

dipole-dipole tensor
after some algebra:

\[ \frac{E_c}{E_0} = \frac{\varepsilon + 2}{3\varepsilon} - \frac{4R_1^2}{3\eta} \frac{\varepsilon - 1}{\varepsilon} \int_0^\infty j_1^2(\kappa R_1) \Delta f(\kappa) \, d\kappa \]

Lorentz field

\[ \Delta f(\kappa) = \frac{S_{\mathrm{T}}(\kappa)}{S_{\mathrm{T}}(\kappa) - A(\kappa)} - \frac{S_{\mathrm{L}}(\kappa)}{S_{\mathrm{L}}(\kappa) + 2A(\kappa)} \]

\( S_{\mathrm{T,L}}(\kappa) \) are the polarization structure factors

\((L)\) longitudinal

\((T)\) transverse

\( \Delta f(\kappa) \rightarrow \Delta f(0) \)

\[ \frac{E_c}{E_0} \rightarrow \frac{3}{2\varepsilon + 1} \]

\[ A(\kappa) = \frac{(\varepsilon - 1)^2}{3\varepsilon y} \frac{j_1(2\kappa R_1)}{2\kappa R_1} \]

\[ R_1 = R_0 + \frac{\varepsilon}{2} \]
There is no single continuum limit!

Singularity appears at

\[ S^L(k) + 2A(k) = 0 \]

Continuum solution branches at the point of singularity
what is the right thermodynamic/continuum limit?

\[ \int f(k) \, dk \rightarrow \sum_{n,m,l} f(k) \]

if first \( R_0 \gg \Lambda \)

then \( L \rightarrow \infty \)

there is no polarization wave and conventional dielectric is not a solution of the dielectric response problem for liquids!
Simulations of spherical cavities in dipolar hard-sphere fluids

\[
E_c / E_0 = 1 + (\beta/3) \langle \delta E_s \cdot \delta M \rangle - E_{corr}
\]

\[
E_{corr} = \frac{2(\epsilon - 1)}{3 \epsilon} \left( 1 + \frac{\epsilon - 1}{2 \epsilon + 1} \left( \frac{R_1}{r_c} \right)^3 \right)
\]

\(M\) is the dipole moment in the cell

\(E_s\) is the field of the dipoles in the cell at the center of the cavity

\(r_c\) is the cutoff distance for the dipolar interactions

Traditional continuum vs new continuum

\(R_0\)
of course it’s not exactly continuum... why?

\[ p(r) = \left\langle \sum_j P_2(r_j \cdot e_j) \delta(r_j - r) \right\rangle \]

\[ P_2(x) = \frac{3x^2 - 1}{2} \]

Orientation of dipoles in a 2D dipolar liquid, Lomba et al, PRE 61, 2000, 3838.

Rotation of dipoles sticking out of the liquid in plane of the surface may be the physical reason for the breakdown of material Maxwell’s equations in application to liquids.
this is actually useful... storing energy in capacitors

Experiments with one-dimensional nanoparticle arrays deposited in membrane narrow channels report dielectric constants of the order of $10^6$

Saha and Chakravorty, J. Appl. Phys.’06

Ferroelectric domains are needed for high dielectric constant

Can one-dimensional geometry help in driving the ferroelectric transition to lower polarities (smaller $y$ values)?
One-dimensional dipolar chains... second-order orientational order/disorder transition

\[ g_K = \sum_{j=1}^{N} \cos(\theta(j)) \]

One-dimensional order facilitates transition to ferroelectric order which happens at

\[ y = 1.8 \]

instead of

\[ y = 6.7 - 7.3 \]

in 3D liquids
we have learned:

Conventional dielectric appears as a singularity in the microscopic response function producing a non-decaying longitudinal polarization wave

...whether this solution actually appears depends on the order of limits taken for the continuum vs thermodynamic limits. This can be established only by laboratory experiments.

Instead of the classical equation

\[
\frac{E_c}{E_0} = \frac{3}{2 \epsilon + 1}
\]

equation

\[
\frac{E_c}{E_0} = \frac{7(\epsilon + 1)^2 + 8 \epsilon}{12 \epsilon (2 \epsilon + 1)}
\]

is supported by the simulation data

Parallel orientation of the dipoles at the interface eliminates surface charge and may change the physical picture of polarizing liquids by external fields making material Maxwell’s equations inapplicable to liquid dielectrics.