

Dielectric Constant of Dilute Polar Gases: A comparison between virial equation of state method and Monte Carlo simulation method

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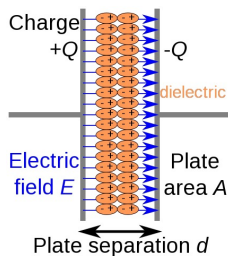
Dielectric constant (relative permittivity)

■ Vacuum

$$C_0 = \frac{Q}{U_0} = \frac{Q}{E_0 \cdot d} \quad (1)$$

■ Dielectric: Polarization

$$C_x = \frac{Q}{U_x} = \frac{Q}{E_x \cdot d} \quad (2)$$



Dielectric Constant

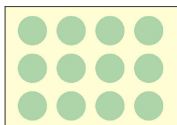
$$\epsilon_r = \frac{C_x}{C_0} \Rightarrow \epsilon_r = \frac{E_0}{E_x} \quad (3)$$

C_x is larger than C_0 , therefore $\epsilon_r > 1$. Or in other words, $E_x < E_0$.

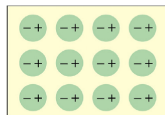
Applications: energy, environment,...

Polarization of molecules

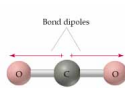
Dipole moment $\vec{\mu}$ is defined as $\vec{\mu} = q\mathbf{d}$.



$$\vec{E}_0 = 0$$



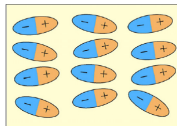
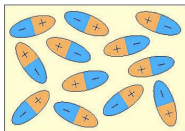
$$\vec{E}_0$$



Overall dipole moment = 0



Overall



$$\vec{E}_0$$

Potential energy of (non-polarizable) dipolar fluids

Simple dipolar fluids:

- Dipolar hard sphere fluids (DHS)
- Stockmayer fluids (dipolar Lennard-Jones fluid, DLJ)

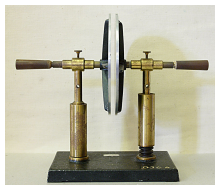
$$u_{12} = u_{12}^0 + u_{12}^{dd} \quad (4)$$

u_{12}^0 : HS or LJ potential

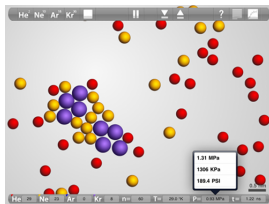
$$u_{12}^{dd} = \frac{1}{4\pi\epsilon_0 r^3} [\mu_1 \cdot \mu_2 - 3(\mu_1 \cdot \hat{r})(\hat{r} \cdot \mu_2)] \quad (5)$$

Experimental methods

Run an experiment: $\epsilon = \frac{C_x}{C_0}$



Run a molecular simulation:



Molecular simulation

Measurements on molecular level \rightarrow macroscopic property (ϵ)

$$\frac{\epsilon - 1}{\epsilon + 2} \left[1 - \frac{\epsilon - 1}{\epsilon + 2} \frac{2(\epsilon' - 1)}{2\epsilon' + 1} \right]^{-1} = \frac{4\pi \langle \mu^2 \rangle}{9kTV} \quad (6)$$

$\langle \mu^2 \rangle$: sum of squared of mean dipole moments in the simulation cell

$\langle \rangle$: ensemble average (NVT)

ϵ' : dielectric constant of the boundary

V : volume of simulation cell

Molecular simulation

- Molecular dynamics
- Monte Carlo

Long range interaction from dipoles

- Ewald Sum
- Reaction Field

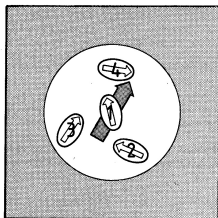
Reaction field method

Alternative to Ewald sum for treatment of long-range electrostatic interactions

In a homogeneous system consisting of N dipolar molecules

A spherical cavity with diameter of r_c centered at molecule i :

- Inside: pair-wise interaction
- Outside: no interaction, dielectric continuum with reaction field potential



(The picture is from Allen, Tildesley, Computer Simulation of Liquids, 1991, page 162)

Reaction field method

Electric field from reaction field

$$E_i^{RF} = \frac{2(\epsilon' - 1)}{2\epsilon' + 1} \frac{1}{r_c^3} \sum_{r_{ij} < r_c} \mu_j \quad (7)$$

For $r_{ij} < r_c$ (within the spherical cavity)

$$u_{ij} = u_{ij}^0 + u_{ij}^{dd} + u_{ij}^{RF} \quad (8)$$

$$u_{ij}^{RF} = -\frac{1}{2} \sum_i^N \mu_i \cdot E_i^{RF} \quad (9)$$

Choice of ϵ'

The result is most accurate when $\epsilon' \geq \epsilon$

■ $\epsilon' = \infty$

■ $\epsilon' = \epsilon$

Theoretical methods

Clausius-Mossotti equation and Debye equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\alpha}{3}\rho + \frac{4\pi\mu^2}{9kT}\rho \quad (10)$$

Virial equation of state

$$\frac{\epsilon - 1}{\epsilon + 2} = A\rho + B\rho^2 + C\rho^3 + D\rho^4 + \dots \quad (11)$$

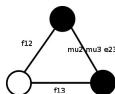
$$P/kT = \rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + \dots \quad (12)$$

Virial equation of state

Non-polarizable fluids:

$$B = \frac{4\pi}{9kT} \left\langle \int \mu_1 \cdot \mu_2 \exp(-u_{12}/kT) dr_{12} \right\rangle_{\omega_1, \omega_2} \quad (13)$$

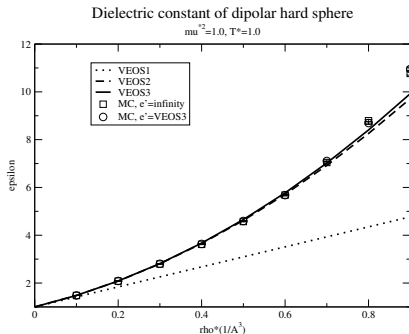
$$C = \frac{4\pi}{9kT} \left\langle \int \mu_2 \cdot \mu_3 (e^{-\frac{u_{12}}{kT}} - 1) e^{-\frac{u_{23}}{kT}} (e^{-u_{13}/kT} - 1) dr_{12} dr_{13} \right\rangle_{\omega_1, \omega_2, \omega_3} \quad (14)$$



$$\epsilon = 1 + (3A)\rho + (3B + 3A^2)\rho^2 + (3C + 6AB + 3A^3)\rho^3 + (M)\rho^4 \quad (15)$$

Dielectric constant of dipolar hard sphere fluids

$$\rho^* = \rho\sigma^3, T^* = kT/\epsilon\sigma^3, \mu^{*2} = \frac{\mu^2}{\sigma^3 kT}$$



In "Low-Density Fluid Phase of Dipolar Hard Spheres" (PRL, 1996), Sear stated that "recent computer simulations studies failed to find a liquid phase for dipolar hard spheres. We argue that the liquid was not observed because the dipolar spheres form long chains which interact weakly..."

Figure: Dielectric constant of a dipolar hard sphere fluid at $T^*=1.0, \mu^{*2} = 1.0$

Dielectric constant of Stockmayer fluids

Kriebel and Winkelmann: at $T^*=2.0$, Stockmayer fluids are at supercritical state for $\mu^*{}^2$ no greater than 3.0. From "Vapour-liquid equilibria for Stockmayer fluids with rigid and RESEARCH NOTE polarizable dipoles", Molecular Physics, 2010

$$\rho^* = \rho\sigma^3, T^* = \frac{kT}{\epsilon}, \mu^*{}^2 = \frac{\mu^2}{\epsilon\sigma^3 kT} \quad (17)$$

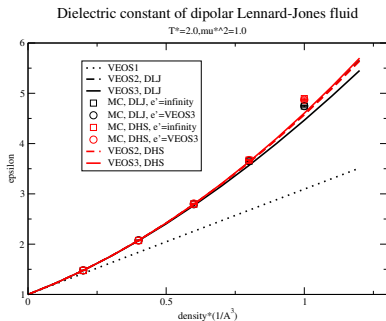


Figure: Dielectric constant computed from virial expansion for a dipolar hard sphere fluid and a Stockmayer fluid. $T^*=2.0$, $\mu^*{}^2=1.0$

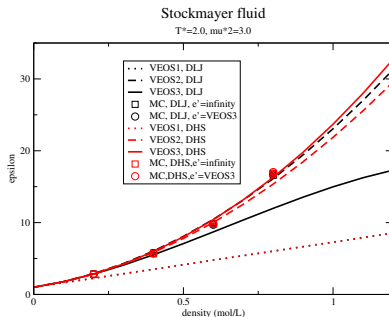


Figure: Dielectric constant computed from virial expansion for a dipolar hard sphere fluid and a Stockmayer fluid. $T^*=2.0$, $\mu^*{}^2=3.0$

Summary and future work

- Virial equation of state method can be applied to predict the dielectric constant of dilute gases with simple molecular models, such as dipolar hard spheres fluids and Stockmayer fluids
- VEOS1 corresponds to Clausius-Mossotti equation (Debye equation) and can predict the dielectric constants at only very low densities, although its contribution continues to be significant at higher densities.
- VEOS2 includes the contributions from pair interactions, and it greatly improves the accuracy of the prediction of dielectric constants from medium to high densities.
- VEOS3 includes the contributions from three-molecule interactions. VEOS are not always sufficient to agree with MC simulation data.

Future work:

- Reformulate virial expansion to obtain better convergence
- Extend the application of VEOS to more realistic molecular models including polarizable models, e.g. GCPM water

References

Book: Gray, Gubbins and Joslin. The Theory of Molecular Fluids.
Vol. 2: Applications.

Article: Joslin. The third dielectric and pressure virial coefficients
of dipolar hard sphere fluids. Molecular Physics, 1980.