

# Contrasting Dielectric Properties of Electrolyte Solutions with Polar and Polarizable Solvents

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We examine the static dielectric constant of electrolyte solutions with a polar and/or polarizable small-molecule solvent using a classical field-theoretic approach. We compute corrections to the dielectric constant and screening length due to intra- and inter-molecular correlations via a renormalized one-loop approximation, accounting for the excluded volume of both solvent and electrolyte. In the salt-free case, we verify the one-loop theory by comparison with full numerical solutions of the field theory. The one-loop theory predicts either a non-linear dielectric decrement or increment with increasing salt, depending on whether the fluid correlations are dominated by the dipolar or polarizable nature of the solvent. These contrasting regimes of non-linear dielectric behavior are consistent with experimental trends in high- and low-dielectric constant electrolyte solutions.

The interplay between the dielectric properties of a fluid and the structure of the charged species therein is a topic of great interest due to its relevance in biology, electrochemistry, and polymer and colloid science. On one hand, the dielectric environment in a fluid affects the distribution of charged species and their tendency to aggregate; on the other hand, the incorporation of charged objects into a fluid is known to influence its dielectric properties. A classic example of the latter is the decrease in dielectric constant of aqueous electrolyte solutions with increasing salt concentration [1]. Such phenomena are not unique to water: the dielectric constant of an electrolyte solution typically exhibits a monotonic but non-linear dependence on the ion concentration [2]. In high-dielectric constant polar solvents, a dielectric decrement is typically observed [3] and attributed to the hydration shell that effectively reduces the number of dipoles that are able to orient in response to an external electric field. In low-dielectric constant polar and non-polar solvents, a dielectric *increment* is instead observed [4], which has typically been attributed to a dielectric contribution of ion pairs.

The properties of electrolyte solutions are often studied using the Poisson-Boltzmann (PB) theory, which treats ions as point-like, assumes a continuum dielectric background, considers only Coulomb interactions and, due to its mean-field nature, ignores *correlations*. Modifications to the PB theory, accounting for van der Waals interactions, non-electrostatic interactions such as steric repulsion, and/or an explicit description of the polar solvent, have also been considered. These theories have been successful in explaining phenomena such as the ion distribution near charged surfaces or interfaces [5–7], and the stability of colloidal suspensions [8]. However, in concentrated electrolyte solutions or ionic liquids, correlations should not be ignored. Even in pure polar liquids, correlations produce important corrections to the dielectric constant that were originally addressed in the theories

of Onsager [9] and Kirkwood [10]. Since then, many researchers have applied fluctuating field theories [11–15] and so-called dressed-ion theories [16] to address correlation effects in this class of problems. Notably, the authors of Refs. [13, 14] computed fluctuation corrections to a dipolar PB theory using a field-theoretic loop expansion, and showed that in order to describe the dielectric decrement of aqueous electrolyte solutions, both correlation effects and steric effects should be accounted for. However, the effects of the *polarizability* of the solvent and/or ions have generally been ignored in such fluctuation theories, with the notable exception of Ref. [12] which accounted for the ion polarizability in a field-theoretic model of a dielectric slab between charged plates.

Given the growing current interest in low-dielectric constant ion-containing soft media, such as salt-doped polymers, ionomers, and polymeric ionic liquids, it is crucial to develop more sophisticated theoretical treatments of component polarizability. In this Letter, we demonstrate that for electrolytes in polar *and polarizable* small-molecule solvent, *both* phenomena of dielectric decrement and increment can be observed when electrostatic and structural correlations are accounted for. In our field-theoretic approach, polar solvent molecules with dipole moment  $\mu$  are granted polarizability via embedded classical Drude oscillators [17]. We also include an excluded volume interaction that enables control of the fluid compressibility via a repulsion parameter  $u_0$ . We use a renormalized loop expansion, following the procedure of Ref. [18], to self-consistently compute corrections to the dielectric constant and screening length of the electrolyte solution. Our approach is flexible and can be modified to treat more complicated molecules (e.g., polymers) or boundary conditions (e.g., slab geometries), or to include additional species or molecular architectures.

*Microscopic model and field theory.*—The microscopic model is described in detail in Refs. [17, 18]. We consider a small-molecule solvent that has both an attached

freely-rotating fixed-magnitude dipole (with dipole moment  $\mu = d\delta q'$ , where  $d$  is the length of the rigid link separating the partial charges  $\pm\delta q'$ ) as well as a classical Drude oscillator (with polarizability  $\alpha = (\delta q)^2/K$ , where  $\pm\delta q$  and  $K$  are the oscillator partial charges and spring constant, respectively). This model, which we use for computational convenience, is a semi-quantitative approximation to the more traditional model for polarizable dipoles in which the rigid link is replaced by a spring having a non-zero equilibrium separation. The electrolyte species are modeled as charge-symmetric spherical ions with valency  $z$ . Although polarizable ions may be considered in our framework, here we restrict polarizability to the solvent only, for simplicity. In order to UV regularize the field theory, we smear the density and charge density of all species with Gaussians characterized by a species-specific smearing range  $a_{p/s}$  [11], where the labels  $p$  and  $s$  refer to the polar/polarizable solvent and salt, respectively.

All charges and partial charges in the system interact via the bare Coulomb interaction, while molecules are also subject to a contact excluded volume interaction of strength  $u_0$ . Using the standard Hubbard-Stratonovich transformation [19], the field-theoretic partition function in the canonical ensemble takes the form

$$\mathcal{Z}_c = \mathcal{Z}_0 \int \mathcal{D}w \int \mathcal{D}\varphi e^{-H[w, \varphi]}, \quad (1)$$

where we have introduced auxiliary fields  $w(\mathbf{r})$  and  $\varphi(\mathbf{r})$  to mediate the excluded volume and Coulomb interactions, respectively. The prefactor  $\mathcal{Z}_0$  contains normalizing denominators from the Hubbard-Stratonovich transforms, ideal gas contributions and excluded volume self-interaction corrections and is inconsequential here. The Hamiltonian  $H[w, \varphi]$ , for a system containing  $n_p$  solvent molecules and  $n_+ = n_-$  cations and anions, is given in SI units by

$$\begin{aligned} H[w, \varphi] = & \frac{1}{2\beta u_0} \int d\mathbf{r} w(\mathbf{r})^2 + \frac{\epsilon_0}{2\beta e^2} \int d\mathbf{r} |\nabla \varphi(\mathbf{r})|^2 \\ & - n_p \ln Q_p[\bar{w}_p, \bar{\varphi}_p] - n_+ \ln Q_+[\bar{w}_s, \bar{\varphi}_s] \\ & - n_- \ln Q_-[\bar{w}_s, \bar{\varphi}_s] \end{aligned} \quad (2)$$

where  $\epsilon_0$  is the vacuum permittivity, and the  $Q_{p/+/-}$  are the respective single-molecule partition functions for a solvent molecule, cation, and anion subject to the fluctuating fields  $w(\mathbf{r})$  and  $\varphi(\mathbf{r})$ . The notation  $\bar{f}_{p/s}(\mathbf{r})$  indicates that the field  $f(\mathbf{r})$  has been smeared via a spatial convolution with the normalized Gaussian smearing function  $\Gamma_{p/s}(\mathbf{r}) = (2\pi a_{p/s}^2)^{-3/2} \exp(-r^2/2a_{p/s}^2)$ ; that is,  $\bar{f}_{p/s}(\mathbf{r}) = \int d\mathbf{r}' \Gamma_{p/s}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}')$ . The single-molecule

partition functions have the forms

$$Q_p[\bar{w}_p, \bar{\varphi}_p] = \frac{1}{V} \int d\mathbf{r} \exp \left[ -i\bar{w}_p(\mathbf{r}) - \frac{\alpha}{2\beta e^2} |\nabla \bar{\varphi}_p|^2 \right] \times j_0 \left( \frac{\mu}{e} |\nabla \bar{\varphi}_p| \right), \quad (3)$$

$$Q_{\pm}[\bar{w}_s, \bar{\varphi}_s] = \frac{1}{V} \int d\mathbf{r} \exp [-i\bar{w}_s(\mathbf{r}) \mp iz\bar{\varphi}_s(\mathbf{r})], \quad (4)$$

where  $j_0(x) = \frac{\sin x}{x}$ . In order to arrive at Eqs. (3) and (4), we have invoked a second-order multipole expansion for both the permanent dipole and the Drude oscillator, and integrated over the dipole orientation and spring displacement vectors [17].

*One-loop approximation.*—Following the procedure of Ref. [18], we consider field fluctuations about the homogeneous saddle-point of  $H[w, \varphi]$ , and perform an expansion of the  $Q_{p/+/-}$  to fourth order in powers of the field fluctuations. The resulting Hamiltonian takes the general form [20]

$$\mathcal{H}[w, \varphi] = \frac{1}{2} \sum_{\mathbf{k}} \frac{\hat{w}_{\mathbf{k}} \hat{w}_{-\mathbf{k}}}{\langle \hat{w}_{\mathbf{k}} \hat{w}_{-\mathbf{k}} \rangle_0} + \frac{1}{2} \sum_{\mathbf{k}} \frac{\hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}}}{\langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle_0} + U[w, \varphi] \quad (5)$$

where we have switched to a Fourier representation. The first two terms in Eq. (5) give the Gaussian contribution to  $\mathcal{H}[w, \varphi]$ .  $U[w, \varphi]$  contains the third- and fourth-order vertex functions which couple the fluctuation modes of the  $w(\mathbf{r})$  and  $\varphi(\mathbf{r})$  fields (a complete list of the vertex functions is given in the Supplemental Material). The objects  $\langle \hat{w}_{\mathbf{k}} \hat{w}_{-\mathbf{k}} \rangle_0$  and  $\langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle_0$  are propagators (Green's functions) for the excluded volume and Coulomb interactions, respectively, in the *Gaussian* theory:

$$\langle \hat{w}_{\mathbf{k}} \hat{w}_{-\mathbf{k}} \rangle_0 = \frac{\beta u_0 V}{1 + \beta u_0 c_p \hat{\Gamma}_p^2(k) + 2\beta u_0 c_s \hat{\Gamma}_s^2(k)} = \frac{\beta u_0 V}{\xi(k)}, \quad (6)$$

$$\langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle_0 = \frac{\beta e^2 V}{(k^2 + \hat{\kappa}^2(k)) \hat{\epsilon}(k) \epsilon_0}. \quad (7)$$

Eqs. (6) and (7) describe the screening of the excluded volume and Coulomb interactions in the lowest-order (Gaussian) approximation. Here  $c_p$  and  $c_s$  are the number densities of solvent and salt, respectively, and the  $\hat{\Gamma}_{p/s}(k) = \exp[-a_{p/s}^2 k^2/2]$  are the Fourier-transformed smearing functions. In Eqn. (7) there are dielectric screening effects due to the solvent, contained in the dielectric function  $\hat{\epsilon}(k) = 1 + c_p \epsilon_0^{-1} (\alpha + \beta \mu^2/3) \hat{\Gamma}_p^2(k)$ , and charge screening effects due to the salt, contained in the Debye screening function  $\hat{\kappa}^2(k) = \frac{2\beta c_s z^2 e^2}{\epsilon_0 \hat{\epsilon}(k)} \hat{\Gamma}_s^2(k)$ .

Note that in the Gaussian theory, the bulk dielectric constant is  $\epsilon = \hat{\epsilon}(0) = 1 + c_p \epsilon_0^{-1} (\alpha + \beta \mu^2/3)$  and the bulk inverse Debye screening length is  $\kappa = \sqrt{\frac{2\beta c_s z^2 e^2}{\epsilon_0 \epsilon}}$ . We shall refer to  $\epsilon$  as the *mean-field* dielectric constant, as it does not account for correlation effects. The leading

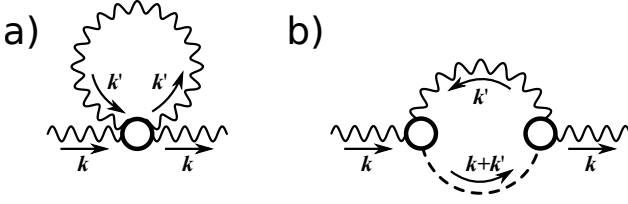


FIG. 1. Irreducible one-loop diagrams for the corrections to the electrostatic propagator  $\langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle$ . Wavy lines correspond to  $\langle \hat{\varphi} \hat{\varphi} \rangle_0$ , dashed lines to  $\langle \hat{w} \hat{w} \rangle_0$ , and circles denote the appropriate vertex function. Arrows indicate momentum flows. Note that in the renormalized one-loop theory, the internal  $\langle \hat{\varphi} \hat{\varphi} \rangle_0$  propagators are replaced by  $\langle \hat{\varphi} \hat{\varphi} \rangle_1$  (we leave  $\langle \hat{w} \hat{w} \rangle_0$  uncorrected).

corrections due to correlations are obtained by computing the one-loop correction to the Gaussian electrostatic propagator  $\langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle_0$  using the standard techniques of diagrammatic perturbation theory [21, 22]. The one-loop corrected propagator  $\langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle_1$  satisfies a Dyson equation:

$$\langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle_1^{-1} = \langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle_0^{-1} - \Sigma_1(k), \quad (8)$$

where  $\Sigma_1$  is the electrostatic self-energy, which can be broken up into contributions from intra- and inter-

molecular correlations, given by the self-energy parts of diagrams 1a and 1b, respectively. The intra-molecular term (1a) is due to the electrostatic attraction between the partial charges of a solvent molecule and is non-zero *only if the solvent is polarizable* (i.e., diagram 1a vanishes if  $\alpha = 0$ ). The inter-molecular term, given by diagram 1b, can be further decomposed into solvent-solvent, ion-solvent and ion-ion contributions. These correlations are generated by a combination of electrostatic and steric interactions, and vanish in the absence of excluded volume (if  $u_0 = 0$ ). In practice, we renormalize the one-loop theory in Hartree fashion by replacing the factors of  $\langle \hat{\varphi} \hat{\varphi} \rangle_0$ , in the self-energies of Fig. 1, with  $\langle \hat{\varphi} \hat{\varphi} \rangle_1$ .

The corrections to  $\langle \hat{\varphi}_{\mathbf{k}} \hat{\varphi}_{-\mathbf{k}} \rangle_0$  can be absorbed into  $\hat{\epsilon}(k)$  and  $\hat{\kappa}(k)$  to give the renormalized  $\hat{\epsilon}_r(k)$  and  $\hat{\kappa}_r(k)$ . Ultimately, we are interested in the  $k \rightarrow 0$  limits of these renormalized screening functions, which we denote  $\epsilon_r$  and  $\kappa_r$ . The corrections to  $\hat{\epsilon}(k)$  and  $\hat{\kappa}(k)$  can be identified on the basis that they must retain the appropriate asymptotic low- $k$  behavior so as to be consistent with the Gaussian theory. It is therefore appropriate to perform an expansion of  $\Sigma_1(k)$  up to  $\mathcal{O}(k^2 \hat{\Gamma}_i(k) \hat{\Gamma}_j(k))$ , where  $i$  and  $j$  can be  $p$  or  $s$ . This results in a set of coupled one-loop equations for  $\hat{\epsilon}_r(k)$  and  $\hat{\kappa}_r^2(k)$ , given by

$$\begin{aligned} \hat{\epsilon}_r(k) = & \hat{\epsilon}(k) - \frac{c_p \alpha}{6\pi^2 \epsilon_0^2} \left( \alpha + \frac{2\beta\mu^2}{3} \right) \hat{\Gamma}_p^2(k) \int_0^\infty dk' \frac{k'^4 \hat{\Gamma}_p^2(k')}{(k'^2 + \hat{\kappa}_r^2(k')) \hat{\epsilon}_r(k')} \\ & + \frac{\beta u_0 c_p^2}{6\pi^2 \epsilon_0^2} \left( \alpha + \frac{\beta\mu^2}{3} \right)^2 \hat{\Gamma}_p^2(k) \int_0^\infty dk' \frac{k'^4 \hat{\Gamma}_p^4(k')}{(k'^2 + \hat{\kappa}_r^2(k')) \hat{\epsilon}_r(k') \xi(k')} \\ & + \frac{2\beta u_0 c_p c_s}{3\pi^2 \epsilon_0^2} \left( \alpha + \frac{\beta\mu^2}{3} \right) \beta z^2 e^2 \hat{\Gamma}_p(k) \hat{\Gamma}_s(k) \int_0^\infty dk' \frac{k'^4 \hat{\Gamma}_p^2(k') \hat{\Gamma}_s^2(k')}{(k'^2 + \hat{\kappa}_r^2(k')) \hat{\epsilon}_r(k') \xi^2(k')} \\ & \times \left( a_s^2 + a_p^2 + \beta u_0 (c_p \hat{\Gamma}_p^2(k') - 2c_s \hat{\Gamma}_s^2(k')) (a_s^2 - a_p^2) \right) \end{aligned} \quad (9)$$

and

$$\begin{aligned} \hat{\kappa}_r^2(k) = & \frac{2\beta c_s z^2 e^2}{\epsilon_0 \hat{\epsilon}_r(k)} \hat{\Gamma}_s^2(k) + \frac{2\beta^3 c_s^2 u_0 z^4 e^4}{\pi^2 \epsilon_0^2 \hat{\epsilon}_r(k)} \hat{\Gamma}_s^2(k) \\ & \times \int_0^\infty dk' \frac{k'^2 \hat{\Gamma}_s^4(k')}{(k'^2 + \hat{\kappa}_r^2(k')) \hat{\epsilon}_r(k') \xi(k')}, \end{aligned} \quad (10)$$

where the function  $\xi(k)$  is defined in Eq. (6). The first correction in Eq. (9) is the intra-molecular solvent term, which *reduces*  $\epsilon_r$ , and the second is the inter-molecular solvent-solvent term, which *increases*  $\epsilon_r$ . The third term is an ion-solvent correlation term, which can increase or decrease  $\epsilon_r$ ; this term arises from the finite size of the molecules and vanishes if the fluid is treated as a collec-

tion of point particles and point charges. Eq. (10) gives the correction to  $\hat{\kappa}^2(k)$  due to ion-ion correlations [23]. Note that without the self-consistency condition, which couples Eqs. (9) and (10), the one-loop correction to  $\hat{\kappa}(k)$  would not influence the one-loop correction to  $\hat{\epsilon}(k)$ . This condition is thus crucial in order to capture the effects of charge screening on the dielectric properties at the one-loop level.

*Pure solvent.*—The pure solvent case, described by Eq. (9) with  $c_s = 0$ , already exhibits some interesting and non-trivial behavior. For a purely dipolar fluid ( $\alpha = 0$ ,  $\mu \neq 0$ ), the correlations increase  $\epsilon_r$  relative to  $\epsilon$  and vanish when  $u_0 = 0$ . Their effects plateau in the incompressible limit ( $u_0 \rightarrow \infty$ ). This excluded volume effect for the purely dipolar fluid is consistent with recent work

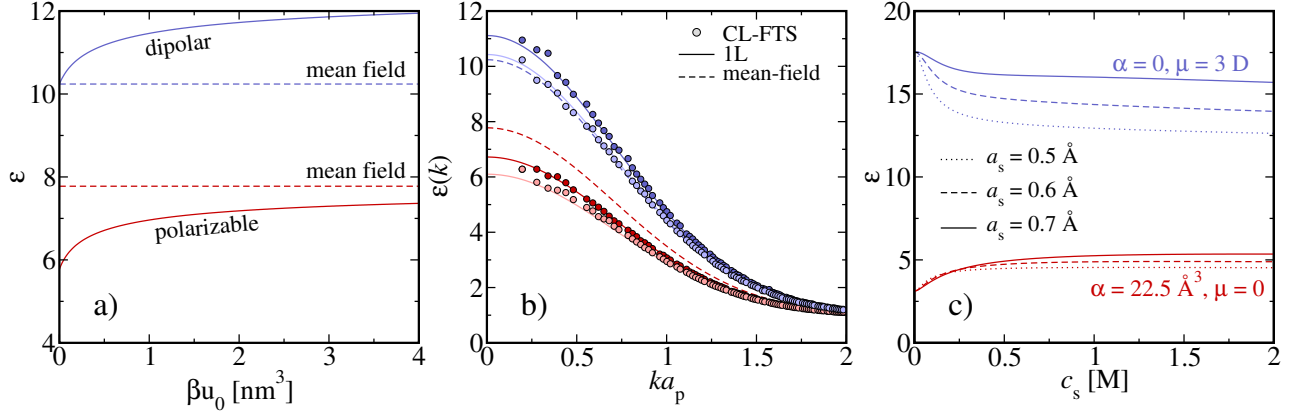


FIG. 2. a) Dependence of the dielectric constant on the repulsion parameter  $u_0$  for examples of purely dipolar (blue,  $\mu = 3$  D) and polarizable (red,  $\alpha_v = 54$  Å<sup>3</sup>) fluids. The mean-field dielectric constants are also shown (dashed line) for both cases. b) Comparison of the dielectric function  $\hat{\epsilon}_r(k)$  in the renormalized one-loop theory (solid lines) and complex Langevin field-theoretic simulations (CL-FTS, points) of the same model for the purely dipolar and polarizable fluids, with excluded volume parameters  $\beta u_0 = 0.04255$  nm<sup>3</sup> (light colors) and  $\beta u_0 = 0.4255$  nm<sup>3</sup> (dark colors). The dashed lines are the corresponding Gaussian approximations. In a) and b) we use  $a_p = 2$  Å. c) Dielectric constant as a function of salt concentration, for various  $a_s$ , for electrolyte solutions of purely dipolar (blue,  $\mu = 3$  D) and purely polarizable (red,  $\alpha_v = 22.5$  Å<sup>3</sup>) solvents with  $a_p = 1.1$  Å and  $\beta u_0 = 2.5$  nm<sup>3</sup>. All of a)-c) use  $T = 300$  K and  $c_p = 10^{28}$  m<sup>-3</sup>.

by other researchers [14]; we emphasize that *there is no one-loop correction to the dielectric constant for a purely dipolar fluid in the absence of excluded volume*.

In contrast, for a non-polar fluid ( $\mu = 0$ ,  $\alpha \neq 0$ ), the correlations overall *reduce*  $\epsilon_r$  relative to the mean-field result, but in the incompressible limit the corrections due to intra- and inter-molecular correlations *cancel identically* and  $\epsilon_r \rightarrow \epsilon$  from below. The dependences of  $\epsilon_r$  on  $u_0$  for purely polarizable and dipolar fluids are shown in Fig. 2a. In Fig. 2b we compare the dielectric function in the one-loop theory to that obtained from field-theoretic simulations of the fully fluctuating field theory (using complex Langevin sampling [19]) of the same model, indicating that the one-loop theory is remarkably accurate for the parameters shown. The simulations clearly verify the reduction of  $\epsilon_r$  in the polarizable case, by the intra-molecular correlation term.

*Electrolyte solution.*—Next, we consider the predictions of the one-loop theory when a monovalent ( $z = 1$ ) salt is added to the system. The addition of salt has two effects on the dielectric constant: the first has its origins in the charge screening of the Coulomb interaction by the ion cloud, and the second is due to the ion-solvent correlations. The former screens the electrostatic solvent-solvent correlations to which  $\epsilon_r$  is strongly sensitive. This is the effect that determines the contrasting dielectric properties of the electrolyte solution with polar and polarizable solvents. The polar, but non-polarizable, fluid tends to exhibit a dielectric *decrement* as the salt screens the solvent-solvent correlations, whereas the non-polar, but polarizable, fluid tends to exhibit a dielectric *increment* for the same reason. Both of these cases are

shown in Fig. 2c, which plots the renormalized dielectric constant as a function of salt concentration for a purely dipolar or polarizable solvent, and for various salt smearing ranges  $a_s$ . Here we use a large but finite repulsion parameter  $\beta u_0 = 2.5$  nm<sup>3</sup>, which corresponds to a weakly compressible fluid. We note that the rate of increment or decrement increases with decreasing  $a_s$ . The ion-solvent correlations appear to be secondary in importance, but their effects can be seen clearly for the polarizable solvent case, where they produce an  $a_s$  dependence of the plateau in  $\epsilon_r$  at large  $c_s$ .

For a solvent that is both polar *and* polarizable, the dielectric behavior (increment or decrement) of the electrolyte solution is controlled primarily by a competition between the dipolar and polarizable nature of the solvent. As a simple illustration of this competition, Fig. 3a plots the renormalized dielectric constant  $\epsilon_r$  of electrolyte solutions as a function of the salt concentration  $c_s$ , for solvents of varying dipole moment  $\mu$  (spanning the range  $\mu = 1 - 5.5$  D) but fixed polarizability  $\alpha_v = 22.5$  Å<sup>3</sup> (solid lines, all other parameters also held fixed). Note that  $\alpha_v = \frac{\alpha}{4\pi\epsilon_0}$  is a polarizability volume. The dielectric behavior changes from dielectric increment for small  $\mu$  to dielectric decrement for large  $\mu$ , and is qualitatively consistent with the range of dielectric behaviors seen experimentally for electrolyte solutions with aprotic solvents (Fig. 3b). Also plotted in Fig. 3a is  $\epsilon_r$  for the same parameter set but with the solvent polarizability set to zero (dashed lines): note that the dielectric decrement is still captured, but the dielectric increment is not.

*Discussion and conclusion.*—In order to place our theory in the context of the literature, we address here sev-

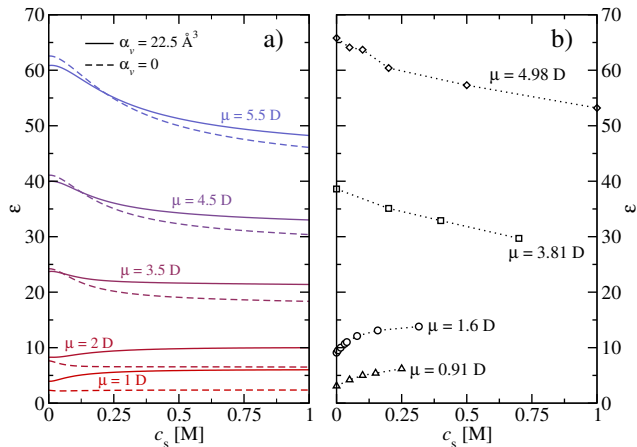


FIG. 3. a) Dielectric constant as a function of salt concentration according to the one-loop theory, for polarizable and polar (solid lines) and purely dipolar (dashed lines) solvents with varying dipole moment. Parameters are  $T = 300 \text{ K}$ ,  $c_p = 10^{28} \text{ m}^{-3}$ ,  $\beta u_0 = 2.5 \text{ nm}^3$ ,  $\alpha_v = 22.5 \text{ \AA}^3$ ,  $a_p = 1.1 \text{ \AA}$ ,  $a_s = 0.55 \text{ \AA}$ . b) Examples of experimental data for polar solvents exhibiting dielectric decrement and increment: NaI in propylene carbonate [3] (diamonds), NaI in dimethylacetamide [3] (squares),  $\text{Bu}_4\text{NClO}_4$  in dichloromethane [24] (circles),  $\text{LiAsF}_6$  in dimethyl carbonate [4] (triangles).

eral points. In Fig. 3b we focus on *aprotic* polar solvents, avoiding protic solvents since our current theory does not account for the effects of hydrogen bonding, which undoubtedly produce strong solvent-solvent correlations that should not be ignored. Indeed, despite water's modest dipole moment ( $\mu_{\text{H}_2\text{O}} = 1.8 \text{ D}$ ), for instance, it exhibits a large dielectric constant  $\epsilon_{\text{H}_2\text{O}} \approx 80$ , presumably in part due to the correlations provided by hydrogen bonding.

The dielectric increment in electrolyte solutions of low-dielectric-constant solvents has often been attributed to the response of ion pairs that readily form in the low-permittivity environment [24, 25]. While ion pairs cannot be ruled out in our model, the qualitative agreement between our theory and the trends seen in experiments suggests that the polarizability of the solvent may play a central role in the dielectric increment. Clearly, the polarizability is a key parameter in our theory. The value  $\alpha_v = 22.5 \text{ \AA}^3$ , which we use in Fig. 3, is on the high end of those typically reported in the literature (which are rarely larger than  $\alpha_v \approx 20 \text{ \AA}^3$  [26]). This apparent discrepancy can be resolved by recalling that the intra-molecular correlation term (diagram 1a) is caused by the electrostatic attraction between a molecule's partial charges. This interaction provides a restoring force against the displacement of the partial charges, additional to that of the tethering spring, that *reduces the effective polarizability* but is subject to electrostatic screening (by added salt, for instance). In fact, for the non-polar case it can be

shown that diagram 1a is just the first term in a perturbation series for the renormalized polarizability  $\alpha_r$ . The full series can be summed to give

$$\alpha_r = \alpha \left[ 1 + \frac{\alpha}{6\pi^2\epsilon_0} \int dk \frac{k^4 \hat{\Gamma}_p^2(k)}{(k^2 + \hat{\kappa}_r^2(k))\hat{\epsilon}_r(k)} \right]^{-1}. \quad (11)$$

In the Supplemental Materials [27] we show that  $\alpha_r$  should have the general form of Eq. (11), using simpler arguments that do not rely on perturbation theory. It is the renormalized polarizability  $\alpha_r$ , rather than the bare polarizability  $\alpha$ , which should correspond to those reported in the literature.

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