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Surface Tension of Dielectric–Air Interfaces

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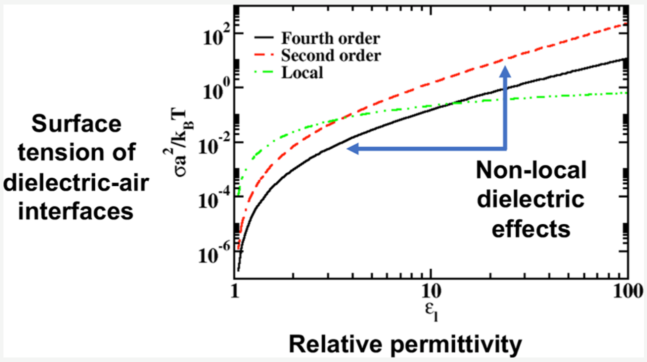
ABSTRACT: Analytical and semianalytical expressions for the surface tension of dielectric–air interfaces are presented after considering local and nonlocal dielectric effects near interfaces. It is shown that the nonlocal effects of dielectrics are significant for highly polar dielectric fluids such as water. Far from the interface, nonlocal dielectric effects are shown to cause not only the oscillatory potential of the mean force but also a reversal of sign at intermediate distances.



■ INTRODUCTION

Understanding the effects of electrostatics near surfaces is of fundamental and technological interest.[1,2] In this regard, the effects of molecular interactions (including electrostatics) on the surface tension of fluids have been studied extensively. These studies include fluid–air and fluid–fluid interfaces involving polar/nonpolar liquids[1,3] and electrolytes[4−18] starting from the works by van der Waals[1] and Onsager–Samaras,[4] respectively. Extensions of these studies to macromolecular systems involving polymers have been poineered by Helfand–Tagami–Sapse[19−22] and later on, extended to polymer–polymer–solvent[23−28] systems. In the most of these studies, *excess* contribution to the surface tension (e.g., resulting from added electrolytes to a fluid) is either computed or studied experimentally, circumventing complications from the estimations of the surface tension of the underlying liquid–liquid or liquid–air interfaces.

Due to primary focus on the excess contribution to the surface tension, our fundamental understanding about the structure of pure fluid interfaces remain incomplete. For example, the experimentally measured value of the surface tension of the water–air interface[29] is 72 mN/m at 25 °C. However, there is no existing theoretical expression, which can be used to justify the experimentally measured value. The situation is the same for other polar liquid–air interfaces. The best estimate for the surface tension of the water–air interface can be obtained using an expression derived by Mahanty and Ninham,[29] which is a rigorous extension and improvement over previous estimates based on assumption of a pairwise summation of dispersion forces.[2] The expression was derived using Lifshitz's theory of van der Waals forces[30] and requires knowledge of a length scale, which was introduced to get convergent results for the surface tension. By choosing the length scale to be the mean interaction spacing in water, the surface tension of the water–air interface was estimated[29] to be 20 mN/m. A similar approach using the Lifshitz's theory of van der Waals forces and relating surface tension to work done in creating surfaces was taken by Holmes.[31] Using an ad hoc method for estimating the surface tension, the final expression for the surface tension was found to be divergent and required knowledge about the closest distance between two plane surfaces which form an interface between two fluids. Papazian had used this approach to relate the surface tension of the organic liquid–air interfaces to dielectric constant of the liquids[32,33] with limited success. Taking another approach based on the assumption of infinitely sharp interfaces between two dielectrics (e.g., water and air), the surface tension was estimated using analytical expressions for the Green's functions of the underlying electrostatic boundary value problems.[34−36] However, even in this case, the expression for the surface tension remains divergent[34,35] requiring empirical inputs for estimations.

In this work, we present results for infinitely sharp dielectric–air interfaces. In contrast to previous studies, we get convergent results for the surface tension by introducing a molecular size-related length scale (a) in the underlying electrostatic boundary value problem. Introduction of the length scale brings chemical specificity in the final expression for the surface tension of dielectric interfaces and nonlocal

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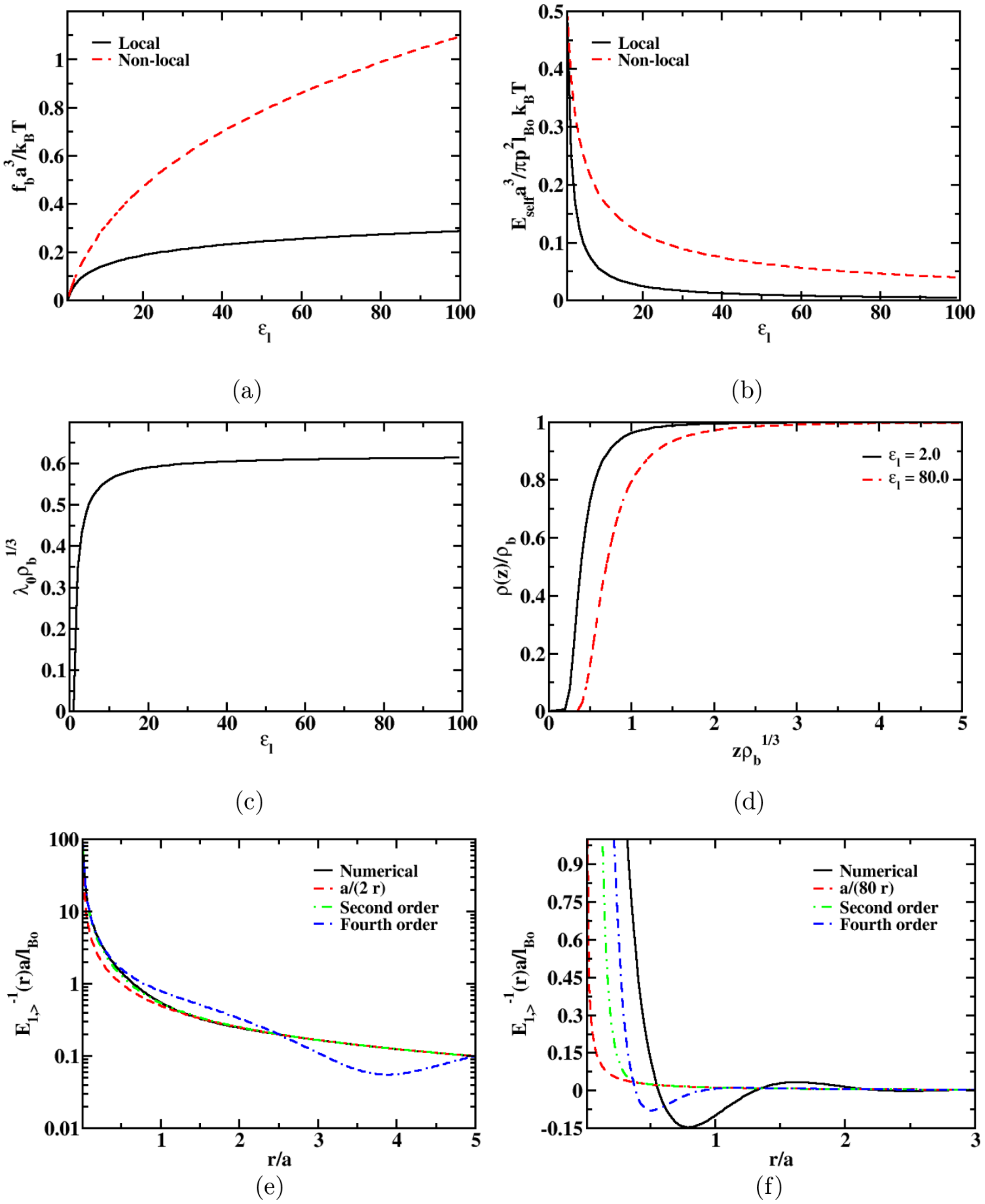

Figure 1. (a) Bulk free energy density of dielectric based on local (eq 2) and nonlocal (eq 8) dielectric effects. (b) Self-energy of a dipole in the bulk (i.e., $z \to \infty$) based on local (eq 4) and nonlocal (eq 7) dielectric effects. (c) Width of the dielectric−air interface using local dielectric effects (eq 6). (d) Density profile of dipoles near dielectric−air interfaces (eq 5). (e) Potential of mean force in bulk of a dielectric of permittivity 2 based on numerical (eq 9), second order (eq 10), and fourth order (eq 11) expansion of the exponential in the nonlocal dielectric function and the Coulomb's law ($\sim 1/\epsilon_l|\mathbf{r}|$). (f) Potential of mean force in bulk of a dielectric of permittivity 80 using the same approximations as in panel (e).

dielectric effects appear naturally in these calculations. Similar approaches to include a molecular size-related length scale in the electrostatics of polar fluids have been taken by Kornyshev,[36,37] Markovich et al.,[18] and Netz and co-workers.[38,39] In particular, the effects of nonlocal and nonlinear dielectric functions near interfaces have been described by Kornyshev and co-workers.[36,37] However, the dielectric functions were not derived in a self-consistent manner and were assumed to be known either from a molecular model or extracted from simulations. In extracting the dielectric functions from atomistic simulations, works by Netz and co-workers[38,39] are noteworthy, which highlight anisotropic/tensorial and nonlinear aspects of the dielectric function for interfacial water. These dielectric functions were used in the Poisson−Boltzmann equation to compute the electrostatic potential and capacitance of surfaces.[38] In addition to these developments related to nonlocal dielectric function of interfacial water, there have been attempts to study the effects of chemical (ionic) specificity near dielectric−air interfaces. These attempts are based on a field theory approach and introduce chemical specificity of ions by introducing ion-specific interactions with the surfaces.[18] Although amenable to generalization,[40,41] such a field theory approach has been used for known local dielectric functions. Our approach to study sharp dielctric−air interfaces is based on a field theory approach (see the Supporting Information, SI, for details), in which a molecular size-related length scale is introduced in the particle description of the Hamiltonian. A sharp dielectric−air interface allows analytical and convergent results for the surface tension. However, as a first step with our approach, the calculations are done with linear and isotropic but nonlocal dielectric function. As demonstrated by the works of Kornyshev,[36,37] Markovich et al.,[18] and Netz and collaborators,[38,39] the tensorial and nonlinear aspects of the dielectric function can be important. In the present paper, our focus is to develop a divergence-free field theory for nonlocal dielectric functions, in the simplest situation of sharp interfaces for the linear and isotropic dielectric function, which enables analytical tractability. Generalizations of the theoretical formalism presented here to study nonlinear and tensorial dielectric functions will be attempted in future works.

■ RESULTS AND DISCUSSION

We first estimate the surface tension of dielectric−air interfaces solely on the basis of electrostatics involving the *local* dielectric function. Free energy (F) of a dielectric (having a local dielectric constant, ϵ_l) with volume V and an infinitely sharp dielectric−air interface with area A can be written as (see the SI for the derivation) follows:

$$\frac{F}{k_BT} = \frac{f_bV}{k_BT} + \frac{\sigma A}{k_BT} \tag{1}$$

$$\frac{f_b}{k_BT} = \frac{1}{16a^3}\ln[\epsilon_l] \tag{2}$$

$$\frac{\sigma}{k_BT} = -\frac{\pi}{16a^2}\ln\left[1 - \left\{\frac{\epsilon_l - 1}{\epsilon_l + 1}\right\}^2\right] \tag{3}$$

Equation 1 is obtained using the Langevin-Debye relation for dielectric, ϵ_l, relating it to the dipole moment (p) of molecules constituting the dielectric with the number density of dipoles ρ_b at temperature T. Explicitly, $\epsilon_l = 1 + 4\pi l_{Bo}p^2\rho_b/3$, where $l_{Bo} = e^2/4\pi\epsilon_o k_BT$ is the Bjerrum length in the vacuum characterized by its permittivity ϵ_o, electronic charge, e, and the Boltzmann constant, k_B. In eq 1, the term proportional to the volume V is related to self-energy of dipoles and interactions among the dipoles.[42,43] In particular, *free energy density*, f_b becomes directly proportional to the self-energy of dipoles in the limit when the number density of dipoles (ρ_b) vanishes i.e., $\rho_b \to 0$ e.g., for a dipolar gas. The logarithmic term appearing in the expression for f_b results from multibody interactions among the dipoles and is plotted in Figure 1(a). Here, a is the size of the charge density distribution characterizing a dipole and $a = 0$ represents a point-dipole. Furthermore, the term proportional to the area A in eq 1 can be readily identified as the interfacial contribution to the free energy and is the surface tension (per unit area) of the dielectric−air interface (σ). Equation 3 reveals that the surface tension of dielectric−air interfaces increases with an increase in dielectric constant of the dielectric (cf. Figure 2), which is in qualitative agreement with the estimates based on other theoretical[29,31,44] and experimental works.[32,33] Using typical values for water at room temperature i.e., $\epsilon_l = 80$ at $T = 298$ K, eq 3 gives $\sigma \equiv \sigma_{water} = 2.437 \times 10^{-3}/a^2_{water}$ J/m^2, where we have used 1 $k_BT = 4.11 \times 10^{-21}$ J and $a \equiv a_{water}$ is in units of nm. For the experimental value of $\sigma_{water} = 72 \times 10^{-3}$ J/m^2, this will imply that $a_{water} = 0.18$ nm, which is less than an estimated effective diameter of a water molecule[45] (= 0.27 nm). We have found that inclusion of nonlocal dielectric effects rectifies this issue related to unphysical values of molecular length scale a required to reproduce experimental values for surface tension of polar liquids with $\epsilon_l > 10$.

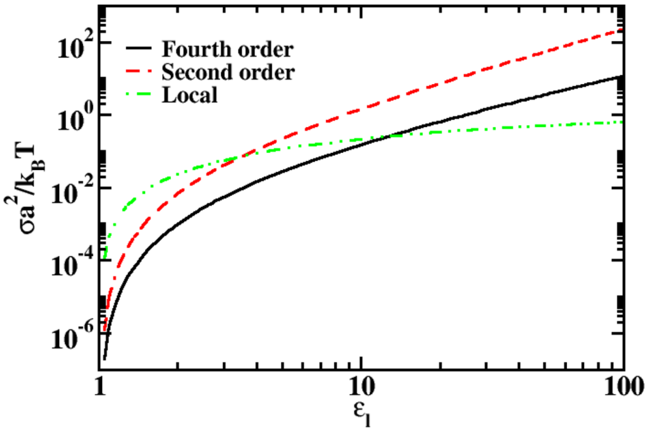

Figure 2. Surface tension of planar dielectric−air interfaces based on local (eq 3) dielectric effects, and different approximations for the nonlocal dielectric effects (eqs 14 and 16 labeled as second order and fourth order, respectively).

Although eq 1 corresponds to an infinitely sharp interface between the dielectric and air, one can estimate the width of the interface by a posteriori analysis using space-dependent self-energy of dipoles. Taking the z-axis along normal to the interface pointing toward the dielectric medium, the self-energy (E_{self}) of a dipole of moment p, can be written as (see the SI) follows:

$$\frac{E_{self}(z)}{k_BT} = \frac{p^2 l_{B0}}{\epsilon_l}\left[\frac{\pi}{2a^3} + \left\{\frac{\epsilon_l - 1}{\epsilon_l + 1}\right\}\frac{1}{z^3}\right] \tag{4}$$

where $z = 0$ plane separates the dielectric from the air. Equation 4 (plotted in Figure 1(b)) reveals that density profile of the dipoles should be as follows:

$$\rho(z) = \rho_b \exp\left[-\left\{\frac{\lambda_0}{z}\right\}^3\right] \tag{5}$$

$$\lambda_0 = \left[\frac{p^2 l_{B0}}{\epsilon_l}\left\{\frac{\epsilon_l - 1}{\epsilon_l + 1}\right\}\right]^{1/3} \tag{6}$$

where ρ_b should be considered as the number density of dipoles far from the dielectric−air interface. For water at room temperature, choosing $pe = 4.81$ D so that $\epsilon_l = 1 + 4\pi l_{B0}p^2\rho_b/3 \equiv 80$ at $T = 298$ K, $\rho_b = 33.46$ nm^{-3} $\equiv 1$ g/cm^3, width of the water−air interface can be estimated to be of the order $\lambda_0^{water} = 0.19$ nm, which is of almost the same magnitude as the molecular length scale a_{water} estimated using the surface tension. In other words, electrostatic considerations based on the local dielectric reveal that the interfacial width characterized by λ_0 (Figure 1(c)) is on the order of the molecular size, and the density profiles of the dipoles are monotonically changing (cf. eq 5 and plotted in Figure 1(d)) with distance from the dielectric−air interface. Equation 5 is in agreement with the work of Buff and Goel[46] relevant for estimating surface tensions of zwitterions.

So far, we have neglected nonlocal effects of the dielectric and these have been shown to be very important near surfaces such as water−air interfaces[47] and in the bulk of dipolar fluids.[37,48] For example, nonlocal dielectric effects are considered to be responsible for the oscillatory force−distance relations observed experimentally.[47] In the following, we show that consideration of nonlocal dielectric effects resulting from the finite size of the dipoles can lead to significant deviations from the predictions for the dielectric−air interfaces based on local dielectrics. Even in the bulk, i.e., far from the interface, the self-energy of the dipoles gets affected by the nonlocal dielectric effects. Specifically, writing the Fourier transform of the spatially variant dielectric function $\epsilon(\mathbf{r})$ as $\epsilon_q = 1 + (\epsilon_l - 1) e^{-q^2a^2/\pi}$, we get (see the SI for details) the following:

$$\frac{E_{\mathrm{self}}(z \to \infty)}{k_{\mathrm{B}}T} = \frac{\pi p^2 l_{\mathrm{B0}}}{2a^3}\left[-\frac{\mathrm{Li}_{3/2}\{-(\epsilon_l - 1)\}}{\epsilon_l - 1}\right] \tag{7}$$

where $\mathrm{Li}_n(x) = \sum_{k=1}^{\infty} x^k/k^n$ is the polylogarithmic function. Comparing eq 7 with eq 4 (also see Figure 1(b)), it is established that the self-energy of dipoles estimated in the bulk on the basis of local dielectrics can differ significantly from the estimates based on nonlocal effects, especially for $\epsilon_l > 1$. Furthermore, bulk contribution to the free energy can be calculated using the following:

$$\frac{f_{\mathrm{b}}}{k_{\mathrm{B}}T} = -\frac{1}{16a^3}\mathrm{Li}_{5/2}\{-(\epsilon_l - 1)\} \tag{8}$$

Similar to the self-energy, comparing eqs 8 and 2 (Figure 1(a)), nonlocal dielectric effects are found to be significant for $\epsilon_l \gg 1$. In order to understand the effects of the nonlocal dielectric in the bulk, we have computed the potential of mean force ($E_{1,>}^{-1}(|\mathbf{r}|)$) by numerically evaluating (Figure 1(e)-(f))

$$E_{1,>}^{-1}(|\mathbf{r}|) = 4\pi l_{\mathrm{Bo}} \int \frac{d^3\mathbf{q}}{(2\pi)^3} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{q^2\epsilon_q} \tag{9}$$

Integral over q in eq 9 can be evaluated analytically using either $\epsilon_q = 1 + (\epsilon_l - 1)e^{-q^2a^2/\pi} \simeq 1 + (\epsilon_l - 1)/(1 + q^2a^2/\pi)$ or $\epsilon_q \simeq 1 + (\epsilon_l - 1)/(1 + q^2a^2/\pi + q^4a^4/2\pi^2)$. These approximations are valid for $a \to 0$ and capture effects of second as well as fourth order gradients in the underlying electrostatic boundary value problem. Using the second order expansion of the exponential in ϵ_q, approximation to eq 9 becomes

$$\tilde{E}_{1,>}^{-1}(|\mathbf{r}|) = \frac{l_{\mathrm{Bo}}}{\epsilon_l|\mathbf{r}|}\left[1 + (\epsilon_l - 1)\exp\left[-\sqrt{\pi\epsilon_l}\frac{|\mathbf{r}|}{a}\right]\right] \tag{10}$$

instead of the $l_{\mathrm{Bo}}/(\epsilon_l|\mathbf{r}|)$, i.e., the Coulomb potential. Equation 10 reveals that the spatial dependence of $\tilde{E}_{1,>}^{-1}(|\mathbf{r}|)$ changes from $l_{\mathrm{Bo}}/|\mathbf{r}|$ to $l_{\mathrm{Bo}}/\epsilon_l|\mathbf{r}|$ in the limits of $|\mathbf{r}| \ll a$ and $|\mathbf{r}| \gg a$, respectively. In other words, the dielectric effects appear at distances $|\mathbf{r}| \gg a$ in the form of $1/\epsilon_l$, affecting the Coulomb potential.

The fourth order expansion leads to another approximation for $E_{1,>}^{-1}(|\mathbf{r}|)$, written as follows:

$$\hat{E}_{1,>}^{-1}(|\mathbf{r}|) = \frac{l_{\mathrm{Bo}}}{\epsilon_l|\mathbf{r}|}\left[1 + (\epsilon_l - 1)\exp\left[-t_1\frac{\sqrt{\pi}|\mathbf{r}|}{a}\right]\left\{\cos\left[t_2\frac{\sqrt{\pi}|\mathbf{r}|}{a}\right] + \frac{\sin\left[t_2\frac{\sqrt{\pi}\,|\mathbf{r}|}{a}\right]}{\sqrt{2\epsilon_l - 1}}\right\}\right] \tag{11}$$

where we have defined, $t_1 = [(\sqrt{2\epsilon_l} + 1)/2]^{1/2}$ and $t_2 = [(\sqrt{2\epsilon_l} - 1)/2]^{1/2}$. Equation11 reveals that the nonlocal effects can lead not only to an oscillatory behavior of the intermolecular potential but also can reverse the sign of the potential. Equations 10 and 11 are plotted in Figure 1(e, f). Comparisons with numerical evaluations of eq 9 reveal that the second order expansion is more appropriate for $\epsilon_l \leq 2$ while it fails for higher values ϵ_l in terms of capturing sign reversal of the potential of mean force. The fourth order expansion qualitatively captures the reversal of sign for higher values of ϵ_l as shown in Figure 1(f) and is a better approximation for polar fluids such as water. The reversal of sign for the potential of mean force at intermediate distances is in qualitative agreement with other related works dealing with nonlocal dielectric effects.[36,38]

Solving the underlying electrostatic boundary value problem by including second order derivatives resulting from the nonlocal dielectric, the space-dependent self-energy and the surface tension can be computed readily. In particular, the space-dependent self-energy of the dipoles can be written as $\Delta\tilde{E}_{\mathrm{self}}(z) = \tilde{E}_{\mathrm{self}}(z) - \tilde{E}_{\mathrm{self}}(\infty)$, where

$$\frac{\Delta\tilde{E}_{\mathrm{self}}(z)}{k_{\mathrm{B}}T} = \frac{[\pi(\epsilon_l - 1)]^{3/2}p^2 l_{\mathrm{Bo}}}{a^3}\int_{\sqrt{\frac{\epsilon_l}{(\epsilon_l - 1)}}}^{\infty} \mathrm{d}t \exp\left[-\frac{2z\sqrt{\pi(\epsilon_l - 1)}}{a}t\right]\{t - \sqrt{t^2 - 1}\}^2 \tag{12}$$

For $\epsilon_l/(\epsilon_l - 1)) \to 1$, this becomes (see Figure S1 in the SI for accuracy of this approximation) the following:

$$\frac{\Delta\tilde{E}_{\mathrm{self}}(z)}{k_{\mathrm{B}}T} \simeq \frac{[\pi(\epsilon_l - 1)]^{3/2}p^2 l_{\mathrm{Bo}}}{a^3}\left[\frac{[2 + \overline{z}]^2}{\overline{z}^3}\exp[-\overline{z}] - \frac{2}{\overline{z}}K_2(\overline{z})\right] \tag{13}$$

where $\overline{z} = \frac{2z\sqrt{\pi(\epsilon_l - 1)}}{a}$. Equations 12 and 13 need to be compared with eq 4 and are plotted in Figure S2 in the SI. These plots show that the interfacial width of the dielectric−air interfaces get affected by the nonlocal dielectric effects. Furthermore, the free energy for the nonlocal dielectric of volume V with an interfacial area A for the dielectric−air interface can be written in the same form as eq 1 but with the surface tension written as follows:

$$\frac{\sigma}{k_{\mathrm{B}}T} = -\frac{1}{16a^2}\left[2 - 2\sqrt{\epsilon_l} + \epsilon_l(1 - 2\sqrt{\epsilon_l}) + \epsilon_l^2(1 - \ln 4) + \epsilon_l \ln 16 + 2(\epsilon_l - 1)^2 \ln\frac{\sqrt{\epsilon_l} + 1}{\sqrt{\epsilon_l}} + \ln \epsilon_l/4\right] \tag{14}$$

For the water−air interface so that $\epsilon_l = 80$ at $T = 298$ K, this implies $\sigma_{\mathrm{water}} = 588.65 \times 10^{-3}/a^2_{\mathrm{water}}$ J/m^2, which suggests $a_{\mathrm{water}} = 2.86$ nm for water−air surface tension to be 72×10^{-3} J/m^2. Equation 14 is plotted in Figure 2 and shows that the approximation used here leads to an overestimation of the surface tension of fluids with $\epsilon_l > 10$. The underlying origin of this lies in the effects of the nonlocal dielectric on the space-dependent self-energy of dipoles shown in Figure S2 in the SI.

In an attempt to get a better estimate for the surface tension of dielectric−air interfaces with $\epsilon_l > 10$, we have computed the space-dependent self-energy ($\Delta\hat{E}_{\mathrm{self}}(z) = \hat{E}_{\mathrm{self}}(z) - \hat{E}_{\mathrm{self}}(\infty)$) and the surface tension using fourth order derivatives in the electrostatic boundary value problem. Explicitly,

$$\frac{\Delta\hat{E}_{\mathrm{self}}(z)}{k_B T} = -4\pi l_{\mathrm{Bo}} p^2 \int \frac{d^2\mathbf{q}_{\|}}{(2\pi)^2} \delta\hat{D}_1(q_{\|}, z, z) \tag{15}$$

where $\delta\hat{D}_1$ is presented in the SI, and eq 15 was evaluated numerically. Results of such numerical evaluations are presented in Figure S2 in the SI. Also, the surface tension for a dielectric−air interface can be readily identified as follows:

$$\frac{\sigma}{k_B T} = -\frac{4\pi l_{\mathrm{Bo}} p^2 \rho_b}{6} \int_0^\infty dz'' \int_0^1 d\lambda (\epsilon_l - 1)\lambda \int \frac{d^2\mathbf{q}_{\|}}{(2\pi)^2} \delta \hat{D}_\lambda(q_{\|}, z'', z'') \tag{16}$$

Integrals over z'' were calculated analytically and the integrals over λ and $q_{\|}$ were evaluated numerically. Equation 16 is plotted in Figure 2. The surface tension value computed using eq 16 lies intermediate between the estimates based on local dielectric effects and the second order approximation for $\epsilon_l > 10$, providing physically reasonable values for polar liquids such as water.

■ CONCLUSIONS

In summary, we have shown that nonlocal dielectric effects near the dielectric−air interfaces can affect their surface tension in a significant manner even for the limit of isotropic and linear dielectrics. Using a particle-based Hamiltonian, we have derived divergence-free expressions for the surface tension and density profile of the dielectric from the interface. The nonlocal dielectric effects not only lead to an oscillatory intermolecular potential far from the interfaces but also invert the sign of the potential at intermediate distances. We anticipate the nonlocal dielectric effects to be significant in many other polar fluids including polyelectrolytes, polyzwitterions, and polypeptoids. Furthermore, inclusions of the nonlinear and anisotropic nature of the dielectric function in the theoretical formalism presented here should be considered for more accurate estimates of surface tension, which is relegated to future work.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.0c01430.

Details of the calculations for the surface tension and additional plots (PDF)

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Notes

The authors declare no competing financial interest.

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