

## Effective dipole potentials after angle averaging

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The problems of a freely rotating dipole interacting with a charge, and of a freely rotating dipole interacting with a polarizable surface (dielectric discontinuity), are solved here. Fully analytic expressions for angle-independent, i.e., radially symmetric, effective interaction potentials are derived and analyzed for their asymptotic forms. For the charge-dipole case the exact result takes a simple enough form to permit direct implementation in statistical mechanical calculations, and displays the appropriate limiting forms at large and small separations. The dipole-surface interaction potential is slightly more involved analytically but is nevertheless amenable for application in statistical thermodynamic study of bulk systems. Order parameter analyses demonstrate the orientational behavior of the dipole at small, large, and intermediate distances. [S1063-651X(97)10907-2]

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### INTRODUCTION

The purpose of this paper is to elaborate on the effective potentials polar molecules experience as a result of configurational fluctuations at finite temperatures. The history of this type of problem goes back to the work of Keesom [1], who was interested in effective potentials between freely rotating dipoles (although he erroneously worked with the internal energy rather than the free energy, as first pointed out by Rowlinson [2]). Such problems continue to occupy the efforts of researchers whose interests range from the more practical challenge of predicting or describing protein interactions [3], to more fundamental concerns such as the implementation of effective radially symmetric potentials between multipolar molecules for statistical mechanical modeling of condensed matter systems [4-7].

The best known examples of effective potentials are the closed asymptotic power-law expressions for charge-dipole and dipole-dipole interactions. These are interaction free energies, obtained after Boltzmann averaging over orientations [4,5]:

$$A_{q\mu} = -\frac{1}{6} \frac{q_1^2 \mu_2^2}{(4\pi\epsilon_0\epsilon_r)^2 kTr^4}, \quad A_{\mu\mu} = -\frac{1}{3} \frac{\mu_1^2 \mu_2^2}{(4\pi\epsilon_0\epsilon_r)^2 kTr^6}. \quad (1)$$

These free energy formulas are obtained by evaluating the "configurational integral" for a two body system involving either a charge ( $q_1$ ) and a freely rotating dipole ( $\mu_2$ ) or two freely rotating dipoles ( $\mu_1$  and  $\mu_2$ ), respectively. Integrations are performed over rotational degrees of freedom. In Eq. (1)  $r$  is the distance between the relevant entities,  $T$  is temperature,  $k$  is Boltzmann's constant,  $\epsilon_r$  is the relative permittivity of the medium, and  $\epsilon_0$  is the permittivity of free space. In mathematical form, the configurational average-free energy relationship is written as [4]

$$e^{-A/kT} = \frac{\int e^{-\varphi(r,\Omega)/kT} d\Omega}{\int d\Omega}, \quad (2)$$

where  $\Omega$  represents any and all rotational variables. In Eq. (2)  $\varphi$  is the zero-temperature, angle-dependent interaction energy. For the above two electrostatic cases  $\varphi$  takes the explicit forms [4,5]

$$\varphi_{q\mu} = -\frac{q_1\mu_2}{4\pi\epsilon_0\epsilon_r} \frac{\cos(\theta)}{r^2}, \quad (3a)$$

$$\varphi_{\mu\mu} = -\frac{\mu_1\mu_2}{4\pi\epsilon_0\epsilon_r} \frac{1}{r^3} [2\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1)\sin(\theta_2)\cos(\phi_1 - \phi_2)]. \quad (3b)$$

The angle  $\theta$  in Eq. (3a) is the angle between the dipole vector and the line joining the positions of the charge and the dipole. In expression (3b) the angles  $\theta_1$  and  $\theta_2$  are the angles between the dipole vectors and the line through the dipole positions, the angles  $\phi_1$  and  $\phi_2$  are the azimuthal angles [see Figs. 1(a) and 1(b)]. Inserting Eq. (3) into Eq. (2), and replacing the exponential under the integral sign with its power series expansion, truncated at the third term, leads to the low-energy or high-temperature approximations ( $\varphi < kT$ ) given in Eq. (1).

Clearly, considering the limitations that accompany Eqs. (1), significant benefit would be achieved by improving upon these high-temperature results. This is the ambition here, where we investigate the two cases of a charge-dipole interaction in otherwise free space, and a dipole approaching the boundary between two dielectric media. These systems have not received a great amount of attention compared to the dipole-dipole case, presumably because of the importance of first attaining an accurate description of a pure bulk dipolar fluid. A heterogeneous system, as is implied by the intermolecular potentials we investigate here, by definition represents a more complex problem. Nevertheless, we present analytic formulas for the interaction free energy, total en-

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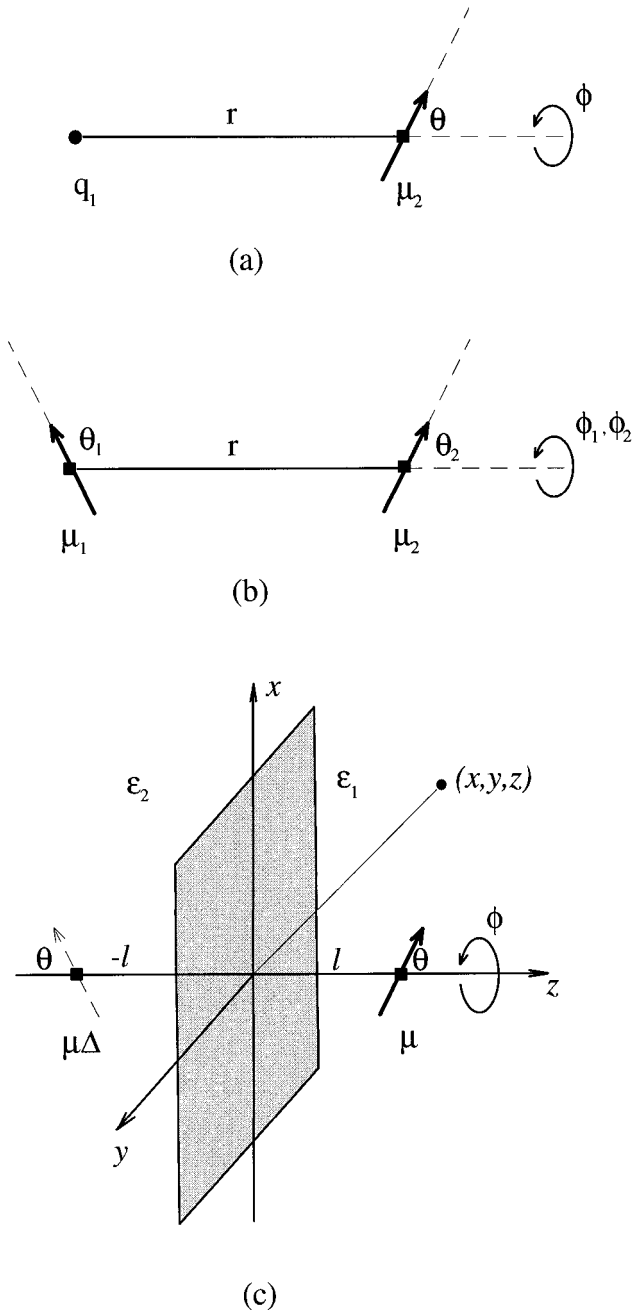


FIG. 1. Schematic figures describing the geometry and notation of the three different interacting systems discussed in the text. (a) The geometry used for a charge,  $q_1$  interacting with a freely rotating dipole,  $\mu_2$ . (b) The system of two freely rotating dipoles,  $\mu_1, \mu_2$ . (c) The case of a dipole  $\mu$  a distance  $l$  from a polarizable surface, the boundary of two semi-infinite dielectric media (permittivity is  $\epsilon_1$  and  $\epsilon_2$ ). In all cases the  $\theta$ 's are the polar angles between the dipole vector(s) and the line joining the multipoles, the  $\phi$ 's are the azimuthal angles.  $r$  and  $l$  are distances.

ergy, and order parameter for the above two cases, valid at arbitrary distances, and demonstrate limiting behavior at small and large separations.

### FREE SPACE INTERACTION OF A CHARGE AND A DIPOLE

Our first purpose here is to provide an explicit and exact form for the angle-averaged, effective potential between a

charge and a freely rotating, thermal fluctuating dipole. Coen *et al.* [3] have shown by numerical evaluation of the integral in Eq. (2) using Eq. (3a) that the true potential exhibits great departures from Eq. (1a) as separation decreases. Although not explicitly mentioned by Coen *et al.* this departure arises from the fact that a freely rotating dipole will tend to align itself in the presence of the field, in its most favorable orientation. The energy of interaction will then more likely represent that between a charge and a fixed dipole [Eq. (3a)] with polar angle  $\theta=0$  or  $\pi$  depending on the sign of the charge. Despite the apparent triviality of the exercise, it appears unappreciated that an analytic form for the effective interaction potential,  $A_{q\mu}$  is actually tractable. That is, one is not restrained to the high-temperature limit to produce an analytic angle-independent potential, nor does one need to resort to numerical integration to get values at arbitrary separations. An analytic form for  $A_{q\mu}$  is certainly much more desirable for practical reasons, such as estimating second virial coefficients at low concentrations or as input into more intensive numerical calculations (simulations and/or integral equation theories) for finite density systems.

What makes the exercise possible is the fact that  $\varphi_{q\mu}$  is a function of the polar angle  $\theta$  but is independent of the azimuthal angle,  $\phi$ . The integral (2) can be written as

$$e^{-A_{q\mu}/kT} = \frac{\int_0^{2\pi} \int_0^\pi e^{-\varphi(\theta)/kT} \sin(\theta) d\theta d\phi}{\int_0^{2\pi} \int_0^\pi \sin(\theta) d\theta d\phi}, \quad (4)$$

where  $\varphi(\theta)/kT = -\alpha\beta \cos(\theta)$ ,  $\beta = 1/kT$ . The integral over  $\phi$  is trivially evaluated. The integral over  $\theta$  is an elementary one. After effecting a variable change,  $s = \cos(\theta)$ , it is in fact simply

$$e^{-A_{q\mu}/kT} = \frac{1}{2} \int_{-1}^1 e^{\alpha\beta s} ds = \frac{\sinh(\alpha\beta)}{\alpha\beta}. \quad (4')$$

As  $\alpha = q_1\mu_2/4\pi\epsilon_0\epsilon_r r^2$ , the complete expression for effective charge-dipole interaction free energy,

$$A_{q\mu} = -kT \ln \left[ \frac{4\pi\epsilon_0\epsilon_r kTr^2}{|q_1|\mu_2} \sinh \left( \frac{|q_1|\mu_2}{4\pi\epsilon_0\epsilon_r kTr^2} \right) \right], \quad (5)$$

shows a much more complicated distance dependence than that implied by the power-law form of Eq. (1a). In Eq. (5) we have written the absolute value for the charge since the result is independent of its sign. A plot of the interaction free energy is shown in Fig. 2.

The angle-averaged *total energy* of interaction, as opposed to *free energy* [2], is just as easily obtained. It is respectively defined by the following and evaluated to be

$$\begin{aligned} \bar{\varphi}_{q\mu}(r) &= - \frac{kT \int_0^{2\pi} \int_0^\pi \alpha\beta \cos(\theta) e^{\alpha\beta \cos(\theta)} \sin(\theta) d\theta d\phi}{\int_0^{2\pi} \int_0^\pi e^{\alpha\beta \cos(\theta)} \sin(\theta) d\theta d\phi} \\ &= -kT \{ \alpha\beta \coth(\alpha\beta) - 1 \}. \end{aligned} \quad (6)$$

[Eq. (6) is valid for the case when the relative permittivity does not depend on temperature. In cases where  $\epsilon_r = \epsilon_r(T)$ , a multiplicative factor of  $1 - \beta \partial \ln \epsilon_r / \partial \beta$  must be introduced to correct Eq. (6).] That is,

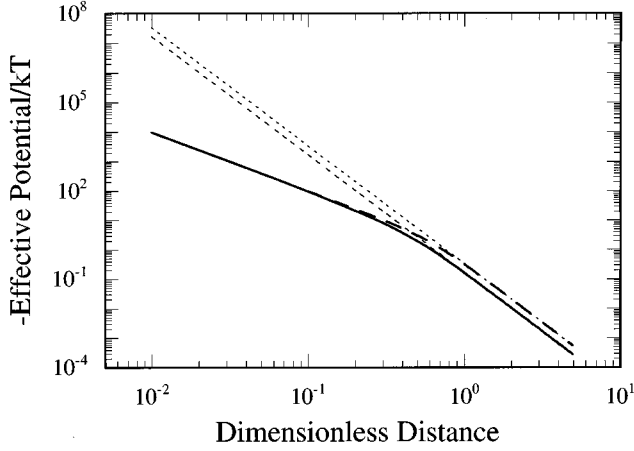


FIG. 2. Plots of effective potentials describing the interaction between a charge and a freely rotating dipole. The thick solid line is the full expression for the interaction free energy, Eq. (5), the thick dashed line represents the total internal energy, Eq. (7). The two thinner dashed lines represent the asymptotic forms of these quantities. The lower of these represent the interaction free energy while the upper curve represents the large- $r$  limit of the total energy. Energies are quoted in units of  $kT$ , while the nondimensional charge-dipole distance is defined as  $r_{\text{nondim}} = r\sqrt{4\pi\epsilon_0\epsilon_r kT}/|q_1\mu_2|$ . In order to present the results on a log-log plot and so highlight the power-law behavior, the attractive potentials have been multiplied by  $-1$ .

$$\bar{\varphi}_{q\mu}(r) = -kT \left\{ \frac{|q_1|\mu_2}{4\pi\epsilon_0\epsilon_r kTr^2} \coth\left(\frac{|q_1|\mu_2}{4\pi\epsilon_0\epsilon_r kTr^2}\right) - 1 \right\}. \quad (7)$$

Figure 2 also displays the complete distance dependence of this average energy. These formulas have the appropriate limiting dependences. In the limit of large  $r$  or large  $T$ , using the fact that  $\sinh(x) \approx x + x^3/6$ ,  $\coth(x) \approx 1/x + x/3$ , and  $\ln(1+x) \approx x + x^2/2$  one readily confirms that Eq. (5) reduces to Eq. (1a), while Eq. (7) adopts twice that value, each being that expected for a freely rotating dipole in the high-temperature limit [4]. In the limit of small  $r$ ,  $\sinh(x) \approx \exp(x)/2$  while  $\coth(x) \approx 1 + 2\exp(-2x) + 2\exp(-4x)$ , so that both Eqs. (5) and (7) tend to Eq. (3a) [with  $\cos(\theta) = \pm 1$  as appropriate for the particular sign of  $q$ ] to leading order. Explicitly, these limiting results take the form

$$A_{q\mu}(r) = -\frac{|q_1|\mu_2}{4\pi\epsilon_0\epsilon_r r^2} + \ln\left(\frac{|q_1|\mu_2}{2\pi\epsilon_0\epsilon_r kTr^2}\right), \quad r \rightarrow 0 \quad (8)$$

$$A_{q\mu}(r) = -\frac{|q_1|^2\mu_2^2}{6(4\pi\epsilon_0\epsilon_r)^2 kTr^4} \left\{ 1 - \frac{|q_1|^2\mu_2^2}{30(4\pi\epsilon_0\epsilon_r)^2 kTr^4} + O(r^{-8}) \right\}, \quad r \rightarrow \infty$$

for the interaction free energy, while the average total internal energy tends to the forms

$$\bar{\varphi}_{q\mu}(r) = -\frac{|q_1|\mu_2}{4\pi\epsilon_0\epsilon_r r^2} \left\{ 1 + 2 \exp\left(-\frac{|q_1|\mu_2}{2\pi\epsilon_0\epsilon_r kTr^2}\right) \right\}$$

$$+ 2 \exp\left(-\frac{|q_1|\mu_2}{\pi\epsilon_0\epsilon_r kTr^2}\right) + \dots \Big\}, \quad r \rightarrow 0, \quad (9)$$

$$\bar{\varphi}_{q\mu}(r) = -\frac{|q_1|^2\mu_2^2}{3(4\pi\epsilon_0\epsilon_r)^2 kTr^4} \left\{ 1 - \frac{|q_1|^2\mu_2^2}{15(4\pi\epsilon_0\epsilon_r)^2 kTr^4} + O(r^{-8}) \right\}, \quad r \rightarrow \infty,$$

the last formula being twice the corresponding large- $r$  limit of free energy, with the difference between the two representing the loss of entropy due to increasing alignment. The difference between the free energy and internal energy is always the entropy loss, however, the factor of two is only valid in this large- $r$  limit. The trend is demonstrated in Fig. 2. The small- $r$  limit demonstrates the preferential alignment of the dipole in the strong Coulombic field of the charge. Although Eq. (5) has an additional logarithmic divergence as  $r$  vanishes (a small term compared to the  $1/r^2$  contribution), the preferred orientation of the dipole as implied by the leading term is quite apparent. The benefit of implementing Eq. (5) and/or Eq. (7) rather than Eq. (1a) in more practical situations should not be underestimated. The variation in the distance dependence is a manifestation of the dipole's physical response to the field of the charge; the dipole undergoes a transition from that of a freely rotating (i.e., weakly oriented) to a strongly polarized molecule. This can be best appreciated by evaluating the dipole's order parameter  $S$ , which is a quantitative measure of the alignment tendencies.  $S$ , defined as [8]

$$S = \langle P_2(\cos(\theta)) \rangle = \frac{(1/4\pi) \int_0^{2\pi} \int_0^\pi \frac{1}{2} [3\cos^2(\theta) - 1] e^{-\varphi(\theta)/kT} \sin(\theta) d\theta d\phi}{(1/4\pi) \int_0^{2\pi} \int_0^\pi e^{-\varphi(\theta)/kT} \sin(\theta) d\theta d\phi}, \quad (10)$$

is found to be

$$S = 1 - 3 \left( \frac{4\pi\epsilon_0\epsilon_r kTr^2}{q_1\mu_2} \right)^2 \left\{ \frac{q_1\mu_2}{4\pi\epsilon_0\epsilon_r kTr^2} \times \coth\left(\frac{q_1\mu_2}{4\pi\epsilon_0\epsilon_r kTr^2}\right) - 1 \right\} \quad (11)$$

with the limiting trends

$$S = \frac{1}{15} \left( \frac{q_1\mu_2}{4\pi\epsilon_0\epsilon_r kT} \right) \times \frac{1}{r^2} - \frac{2}{315} \left( \frac{q_1\mu_2}{4\pi\epsilon_0\epsilon_r kT} \right)^3 \frac{1}{r^6} + O(1/r^{10}), \quad r \rightarrow \infty, \quad (12)$$

$$S = 1 - \frac{12\pi\epsilon_0\epsilon_r kT}{q_1\mu_2} r^2 \left\{ 1 + 2 \exp\left(-\frac{q_1\mu_2}{2\pi\epsilon_0\epsilon_r kT} \frac{1}{r^2}\right) + 2 \exp\left(-\frac{q_1\mu_2}{\pi\epsilon_0\epsilon_r kT} \frac{1}{r^2}\right) + \dots \right\}, \quad r \rightarrow 0.$$

That is, at increasing distances  $S \rightarrow 0$  indicating decreasing correlation while for decreasing distances  $S \rightarrow 1$ , the limit

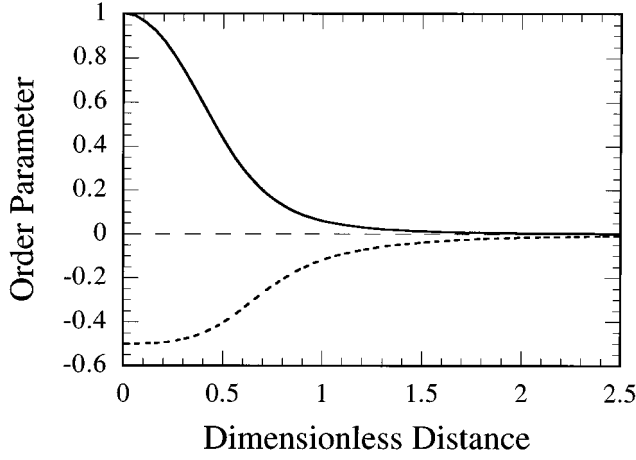


FIG. 3. Plots of the order parameters for the two systems studied in the text: (a) the charge-dipole system, Eq. (11) (solid line); (b) the dipole-polarizable wall system, Eq. (19) (dashed line). Note that the distances have been scaled differently for these two systems. For (a)  $r_{\text{nondim}} = r\sqrt{4\pi\epsilon_0\epsilon_r kT/|q_1|\mu_2}$ , while for (b)  $l_{\text{nondim}} = l(32\pi\epsilon_0\epsilon_r kT/\mu^2\Delta)^{1/3}$ .

expected for a perfectly oriented molecule. The full distance dependence of  $S$  is shown in Fig. 3. Another matter of no small importance, in connection with a point charge interacting with a freely rotating point dipole, is the contribution of the surrounding medium. In particular, one can quite simply include the screening ability of an aqueous solution containing excess electrolyte (at a Debye length  $\kappa^{-1}$ ). In this case, the zero-temperature, salt-screened Coulomb potential between a charge ( $q_1$ ) and an ideal dipole ( $\mu_2$ ) imbedded in a sphere of radius  $a$  is found to be [9]

$$\varphi_{q\mu}(\theta, r) = -\frac{q_1\mu_2}{2\pi\epsilon_0\epsilon_r} \frac{e^{-\kappa(r-a)}(1+\kappa r)}{1+\kappa a} \times \frac{3e^{\kappa a}}{[2+2\kappa a+(\kappa a)^2+(1+\kappa a)\epsilon_r/\epsilon_d]} \frac{\cos(\theta)}{r^2}, \quad (13)$$

$$\varphi_{q\mu}(\theta, r) = -\alpha_s \cos(\theta)$$

( $\epsilon_d$  is the dielectric constant of the dipole sphere).

Because of the identical angle dependence, the angle-averaged free energy then has exactly the same functional form as Eq. (5), i.e., replacing  $\alpha$  in (4') with  $\alpha_s$  above in the argument of the sinh function and its prefactor. A similar substitution in the angle-averaged total energy expression, Eq. (6), leads to an analogous generalization of Eq. (7) (apart from corrections due to the temperature dependence of the dielectric permittivities).

#### THE INTERACTION BETWEEN A DIPOLE AND A POLARIZABLE SURFACE

Another important case for study is that of a freely rotating dipole approaching a dielectric discontinuity. This can be considered relevant to the problem of adsorption of, say, a polar macroparticle or biological macromolecule (protein) to a surface that is the interface of two dielectric media (e.g., air and water). Consider the geometry of Fig. 1(c). Using the method of images to describe induced surface polarization

effects, the electrostatic potential  $V$  at an arbitrary point in the region with dielectric constant  $\epsilon_1$  due to a point dipole  $\mu$  at a distance  $l$ , from a dielectric of relative permittivity  $\epsilon_2$  is

$$V_\mu(x, y, z) = \frac{\mu}{4\pi\epsilon_0\epsilon_1} \left( \frac{x \sin(\theta) + (z-l)\cos(\theta)}{x^2 + y^2 + (z-l)^2} + \frac{\Delta(x \sin(\theta) - (z+l)\cos(\theta))}{x^2 + y^2 + (z+l)^2} \right), \quad (14)$$

where  $\Delta = (\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)$  is the dielectric disparity of the two media, and  $(x, y, z)$  is a point in the region with dielectric constant  $\epsilon_1$ . However, of greater significance here is the electric field derived from this potential, but acting specifically at a point  $z \neq l$  on the  $z$  axis. This is given by

$$\begin{aligned} E(0, 0, z) &= -\frac{\mu}{4\pi\epsilon_0\epsilon_1} \frac{1}{(z-l)^3} (\sin(\theta), 0, -2\cos(\theta)) \\ &\quad -\frac{\mu}{4\pi\epsilon_0\epsilon_1} \frac{\Delta}{(z+l)^3} (\sin(\theta), 0, 2\cos(\theta)) \\ &= \mathbf{E}_{\text{dir}}(0, 0, z) + \mathbf{E}_{\text{pol}}(0, 0, z). \end{aligned} \quad (15)$$

The first term in either Eq. (14) or Eq. (15) is the direct contribution from a free space dipole, while the second in each case is the contribution from surface polarization charges.

What we are interested in evaluating is the work done in bringing the dipole, in a given orientation with respect to the surface, from an infinite distance to a finite distance  $l$  from the dielectric boundary. This work is done in opposition to surface polarization charges. The relevant expression is

$$\varphi_\mu(l, \theta) = -\boldsymbol{\mu} \cdot \mathbf{E}_{\text{pol}} = \frac{\mu^2}{4\pi\epsilon_0\epsilon_1} \frac{\Delta}{(2l)^3} (\sin^2(\theta) + 2\cos^2(\theta)). \quad (16)$$

Note that Eq. (16) can also be trivially obtained from Eq. (3b) assuming  $r = 2l$ ,  $\mu_1 = \mu$ ,  $\mu_2 = \mu\Delta$ ,  $\theta_1 = \theta$ ,  $\theta_2 = \pi - \theta$ , and  $\phi_1 = \phi_2$ . These latter assignments are based on the image model in which the orientation of the image dipole is intrinsically associated with the orientation of the original dipole. The above energy change, or work performed, is positive or negative according only to the sign of the dielectric disparity,  $\Delta$ . Irrespective of orientation, it is energetically favorable to bring the dipole towards a medium of higher dielectric permittivity ( $\epsilon_2 > \epsilon_1$ ), and unfavorable to bring the dipole towards a lower dielectric medium ( $\epsilon_2 < \epsilon_1$ ). Since the most common situation of interest involves polar molecules in an aqueous (high dielectric) environment adjacent to a lower dielectric medium (e.g., hydrocarbon or air) we shall, in what follows, assume that  $\Delta > 0$ .

Writing Eq. (16) as  $\varphi_\mu(l, \theta)/kT = \alpha\beta[1 + \cos^2(\theta)]$ , and substituting this into the argument of the exponential in Eq. (4), results in the following expression for the free energy of interaction:

$$A_\mu(l, T) = \alpha - \frac{1}{\beta} \ln \left[ \frac{1}{2} \left( \frac{\pi}{\alpha\beta} \right)^{1/2} \text{erf}(\sqrt{\alpha\beta}) \right]. \quad (17)$$

In a manner analogous to the derivation of Eq. (6) we can evaluate the angle-averaged total internal energy

$$\bar{\varphi}_\mu(l, T) = \alpha + \frac{1}{2\beta} - \left(\frac{\alpha}{\pi\beta}\right)^{1/2} \frac{e^{-\alpha\beta}}{\operatorname{erf}(\sqrt{\alpha\beta})}. \quad (18)$$

Similarly, from definition (10), the order parameter, measuring the probability of alignment, is found to be

$$S = \frac{3}{4\alpha\beta} - \frac{3}{2} \frac{1}{\sqrt{\pi\alpha\beta}} \frac{e^{-\alpha\beta}}{\operatorname{erf}(\sqrt{\alpha\beta})} - \frac{1}{2}. \quad (19)$$

In Eqs. (17)–(19),  $\alpha$  is now

$$\alpha = \frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1} \frac{1}{8l^3}, \quad (20)$$

while  $\operatorname{erf}(x)$  is the error function:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) dt. \quad (21)$$

Reference [10] provides several different ways of evaluating the error function based on rational approximations. These avoid the necessity of evaluating the integral definition explicitly (Secs. 7.1.25–28.) Despite the relatively simple closed forms these relations take, the physical behavior of the molecule that these formulas attempt to describe remains obscure. For the purpose of extracting information on the physics, the asymptotic laws valid in the limit of small or large distances again prove useful. Since the angle-

independent term in Eqs. (17) and (18) ( $\alpha$ ) dominates at all separations, we quote the departures from this contribution in the limiting laws below (as well as plotting these energy differences in figures). For large  $l$  it can be shown that the above three quantities tend to the limiting forms

$$\Delta A_\mu(l) = \frac{1}{3} \frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1} \frac{1}{8l^3} \left[ 1 - \frac{2}{15} \frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3} + O\left(\frac{1}{l^6}\right) \right],$$

$$\Delta \bar{\varphi}_\mu(l) = \frac{1}{3} \frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1} \frac{1}{8l^3} \left[ 1 - \frac{4}{15} \frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3} + O\left(\frac{1}{l^6}\right) \right],$$

and

$$S = -\frac{2}{15} \frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3} \left[ 1 + \frac{11}{7} \frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3} + O\left(\frac{1}{l^6}\right) \right]. \quad (22)$$

Since the  $1/l^3$  dependence is also expected from the attractive dispersion force between a neutral atom and a wall [4], it is not immediately obvious that a polar molecule (such as a protein) will adsorb or desorb because of the repulsive contribution predicted here. For small  $l$  and  $\Delta > 0$  we have that

$$\begin{aligned} \Delta A_\mu(l) &= -\frac{kT}{2} \ln\left(\frac{\pi^2\varepsilon_0\varepsilon_1 kT}{\mu^2\Delta} 8l^3\right) + kT\left(\frac{4\varepsilon_0\varepsilon_1 kT}{\mu^2\Delta} 8l^3\right)^{1/2} \exp\left(-\frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3}\right) [1 + O(l^3)] \\ &\quad + O\left[\exp\left(-\frac{\mu^2\Delta}{2\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3}\right)\right], \end{aligned} \quad (23)$$

$$\Delta \bar{\varphi}_\mu(l) = \frac{kT}{2} - \left(\frac{\mu^2\Delta kT}{4\pi^2\varepsilon_0\varepsilon_1} \frac{1}{8l^3}\right)^{1/2} \exp\left(-\frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3}\right) + O\left[\exp\left(-\frac{\mu^2\Delta}{2\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3}\right)\right],$$

and

$$S = \frac{3}{4} \frac{4\pi\varepsilon_0\varepsilon_1 kT}{\mu^2\Delta} 8l^3 - \frac{3}{2} \left(\frac{4\varepsilon_0\varepsilon_1 kT}{\mu^2\Delta} 8l^3\right)^{1/2} \exp\left(-\frac{\mu^2\Delta}{4\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3}\right) + O\left[\exp\left(-\frac{\mu^2\Delta}{2\pi\varepsilon_0\varepsilon_1 kT} \frac{1}{8l^3}\right)\right] - \frac{1}{2}.$$

Equations (22) are actually valid for either positive or negative  $\Delta$ , while Eqs. (23) are strictly valid only for *positive*  $\Delta$ . Different physical behavior is expected at small distances when  $\Delta < 0$ .

As stated above, in Eqs. (22) and (23) we have quoted the difference between the interaction free energy or total internal energy and the minimum energy configuration of the dipole, in which state the dipole is aligned parallel to the dielectric interface [ $\cos(\theta)=0$ ]. That is,  $\Delta A_\mu = A_\mu(l) - \varphi_\mu(l, \pi/2)$  and  $\Delta \bar{\varphi}_\mu(l) = \bar{\varphi}_\mu(l) - \varphi_\mu(l, \pi/2)$ . Both quanti-

ties are also shown in Fig. 4. The interaction between a *freely rotating* dipole and a surface of polarization is dominated by the *static* dipole-image dipole,  $1/r^3$  dependence [from Eq. (3b)], and does *not* vary with separation as does the leading term in the case of a freely rotating dipole and a charge or as is expected for two freely rotating dipoles [6]. This is, of course, due to the fact that in this case these two dipoles (the real one and its image) are *always* correlated, except at infinite distance. As the order parameter in Eq. (22) suggests, these dipoles become uncorrelated at a rate proportional to

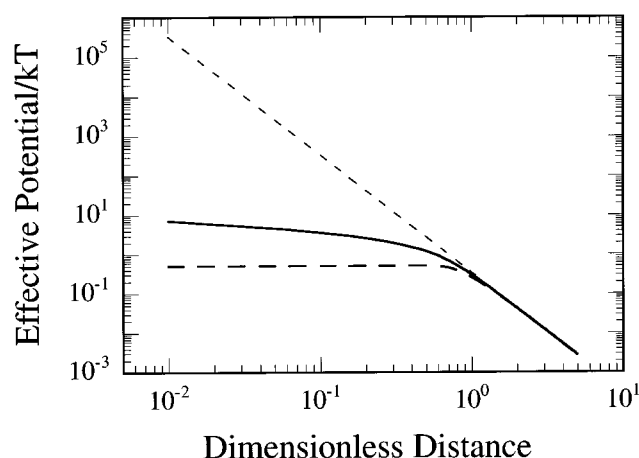


FIG. 4. Plots of effective potentials describing the interaction between a freely rotating dipole with a surface of polarization. These are plotted as differences in energies relative to the minimum energy configuration as described in the text. The thick solid line is the full expression for the interaction free energy, Eq. (17), the thick dashed line represents the total internal energy, Eq. (18). The thinner dashed line represents the common leading term in the asymptotic form of these quantities as quoted in Eq. (22). The energies are given in units of  $kT$ , while the nondimensional dipole-wall distance is defined as  $l_{\text{nondim}} = l(32\pi\epsilon_0\epsilon_r kT/\mu^2\Delta)^{1/3}$ .

the direct interaction. The order parameter's full distance dependence is shown in Fig. 3.

In the limit of zero distance the minimum energy orientation is the naturally preferred one. The real dipole tends to line up parallel to the interface ( $\theta = \pi/2$ ) with otherwise arbitrary azimuthal orientation, hence the fact that the order parameter  $S \rightarrow -1/2$  (Fig. 3); the dipole's free energy appropriately retains a finite entropy contribution giving rise to the difference between total internal energy and free energy functions shown in Fig. 4. This is in contrast to the previous example of the dipole-charge interaction wherein  $S \rightarrow 1$  as  $r \rightarrow 0$  (perfect alignment) and the total energy equals the free energy.

There are two further features associated with the above results. The first concerns the large distance approximations for the free energy and internal energy. For both, the averaging contributes a (repulsive) term that has the  $1/r^3$  form, but with a prefactor of  $1/3$  [this comes from the angle average of  $\cos^2(\theta)$ ]. Thereafter, the next contribution is the more familiar (attractive)  $1/r^6$  form for freely rotating dipoles as found by Keesom, with the recognizable factor of 2 differ-

ence between energy and free energy, for reasons discussed previously. The second feature is the contribution of  $kT/2$  to the internal energy, which is retained in the small- $l$  limit. This is characteristic of the *equipartition of energy* applied to classical systems with Hamiltonians possessing terms involving quadratics of a degree of freedom, this being  $\cos(\theta)$ .

## SUMMARY AND CONCLUSIONS

We have derived exact expressions for radially symmetric interaction free energies and internal energies for two systems involving freely rotating dipoles. The cases are those of a point charge interacting with a point dipole, and a point dipole interacting with a polarizable surface. The interaction free energies given here, as effective two-body potentials (i.e., pair potentials), represent important tools to be implemented in statistical mechanical studies of heterogeneous bulk and/or inhomogeneous liquid systems. Although their application to finite density systems must be accompanied by the approximate assumption of additivity (because they neglect any many-body contributions), the significance of Eqs. (5) and (17) remains in the fact that they correctly describe the physical response of the dipoles involved, to an external influence, a feature absent from the asymptotic potential forms currently used.

While the free energy formulas are useful in representing interactions between entities in finite density simulations, it should be remembered that the expressions for the angle-averaged total energies, Eqs. (7) and (18), are important for the correct evaluation of quantities such as total entropy or energy of a system. This requirement is due to the fact that the true energy or entropy of a system of freely rotating polar molecules is partitioned into a configurational part and a rotational part. The latter contribution can only be accessed with Eqs. (7) and (18).

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