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Surface tension increment due to solute addition

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Addition of solute into solvent may lead to an increase in surface tension, such as salt in water and water in alcohol, due to solute depletion at the interface. The repulsion of the solute from the interface may originate from electrostatic forces or solute-solvent attraction. On the basis of the square-well model for the interface-solute interaction, we derive the surface tension increment $\Delta\gamma$ by both canonical and grand-canonical routes (Gibbs adsorption isotherm) for a spherical droplet. The surface tension is increased linearly with the bulk concentration of the solute c_b and the interaction range λ. The theoretical results are consistent with those obtained by experiments and Monte Carlo simulations up to a few molarity. For weak repulsion, the increment is internal energy driven. When the repulsion is large enough, the surface tension increment is entropy driven and approaches the asymptotic limit, $\Delta\gamma \simeq c_b k_B T \lambda$, due to the nearly complete depletion of the solute at the interface. Our result may shed some light on the surface tension increment for electrolyte solutions with concentration above $0.2M$.

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I. INTRODUCTION

It is well known that on addition of the surface-active solute, e.g., surfactant, the surface tension of the aqueous solution is lowered [1,2]. The surface-active solute prefers to stay at the interface and hence a concentrated layer of solute is built up in the vicinity of the interface. In other words, the solute concentration is not uniform and can be characterized by the concentration profile $c(z)$, where z is a distance from the interface (the Gibbs dividing surface for solvent). For dilute solutions, the solute-solvent interactions in the bulk are neglected, and the concentration profile of the solute can then be elucidated in terms of the "interface-solute" interaction [3]. For surface-active solutes, the interface-solute interaction is attractive and the surface free energy is reduced due to the adsorption of the solute onto the interface. The entropy loss associated with different solute concentrations at the interface and in the bulk is compensated by the energy gain associated with the interface-solute attraction (negative interaction energy). On the basis of the thermodynamics of interfaces, the Gibbs adsorption isotherm [1,2] is obtained from the Gibbs-Duhem equation at constant temperature T and volume V,

$$\left(\frac{d\gamma}{d\mu}\right)_{T,V} = -\Gamma, \tag{1}$$

where γ is the surface tension and μ the chemical potential. For a planar surface, the surface excess Γ is defined as

$$\Gamma = \int_0^\infty [c(z) - c_b]dz, \tag{2}$$

where c_b denotes the bulk concentration. Since the thermodynamic stability requires $d\mu/dc > 0$, the *positive* surface excess ($\Gamma > 0$) leads to a decrease in surface tension $d\gamma/dc < 0$.

In contrast to dilute surfactant solutions, the surface tension can be increased on addition of solute, $d\gamma/dc > 0$. For example, inorganic salt is added in water and water in alcohol. Based on the criterion of thermodynamic stability, such events take place when the surface excess is negative ($\Gamma < 0$). In other words, the interface-solute interaction is repulsive and the solute concentration in the vicinity of the solvent-air interface is lower than the bulk concentration. The depletion of the solute from the interface may originate from electrostatic or molecular interactions. While the latter is short ranged, the former belongs to long-range interactions. The surface tension of the aqueous solution rises with increasing the electrolyte concentration. In 1924, Wagner provided a quantitative explanation for this curious phenomenon based on the Debye-Hückel theory of strong electrolytes. The ions are repelled from the interface mainly due to the dielectric discontinuity. Following Wagner's approach, Onsager and Samaras (OS) [4] obtained the increase in surface tension of water due to z:z electrolytes in a closed-form expression by treating the ions as point charges. For very dilute solutions, the OS limiting law is given by

$$\Delta\gamma = c_b k_B T l_B \left[-\ln\frac{\kappa l_B}{2} - 2\gamma_E + \frac{3}{2}\right], \tag{3}$$

where $\kappa = [8\pi c_b z^2 e^2/\epsilon k_B T]^{1/2}$ represents the inverse Debye length, $l_B = e^2/\epsilon k_B T$ the Bjerrum length, and $\gamma_E = 0.5772$, Euler's constant. ϵ is the dielectric constant of aqueous solution and e is the fundamental charge.

Besides electrolyte solutions, addition of small amount of polar solute, e.g., water, into an apolar solvent such as alcohol can lead to an increase of the surface tension. It is natu-

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rally anticipated that addition of a solute, whose surface tension is greater than that of the solvent, results in the surface tension increment of the solution. For example, the surface tension (surface free energy per unit area) of normal alcohol is 20–30 mJ/m^2 and that of pure water is 72.8 mJ/m^2 [1]. Neglecting the solute-solvent interactions in the bulk, the solute molecules prefer to stay in the bulk in order to reduce the surface free energy. In other words, the negative adsorption of the solute can be simply explained in terms of the interface-solute repulsion (positive interaction energy). Since the attraction between solute and solvent molecules is stronger than that between solvent molecules, the force acting on the molecule on the surface by the solute is greater than that by the solvent. The entropy loss associated with nonuniform solute concentrations is balanced by the energy gain associated with solute depletion on the interface due to interface-solute repulsions.

For surface-active solutes, the surface tension drop can be described based on the Frumkin adsorption isotherms [3],

$$\Delta\gamma=\Gamma_\infty k_BT\left[\ln\left(1-\frac{\Gamma}{\Gamma_\infty}\right)-\frac{1}{2}\frac{A}{k_BT}\left(\frac{\Gamma}{\Gamma_\infty}\right)^2\right], \tag{4}$$

where Γ_∞ denotes the maximum surface excess and A the interaction energy between solutes on the surface. Because the surface is crowded with surface-active solutes, the intermolecular interaction, including the excluded volume, must be taken into account and is manifested by Γ_∞ and A. On the other hand, the surface tension increment due to the negative adsorption on the interface indicates that the finite size effect of the solute can be negligible in the dilute solution. Nevertheless, studies on the surface tension increment due to solute addition is scarce besides electrolyte solutions. In this paper, the surface tension increment is derived by both canonical and grand-canonical approaches [5] in terms of the interface-solute interaction, of which the physical meaning will be explained later. We perform surface tension experiments and Monte Carlo (MC) simulations to support the theoretical results.

II. THEORY

A. Canonical partition function

Consider a spherical droplet of radius R and there are N solutes inside. We adopt the pseudo-one-component model and keep track of the solute molecules only, just as the primitive model used for electrolyte solutions [6]. The force acting on the solute in the bulk is different from that in the vicinity of the interface. Therefore, the system is essentially divided into two subsystems with volumes V_s and V_b. If the center of the solute is located in the interfacial shell (s), the internal energy is increased by ε. In the bulk (b), the solute behaves just as a hard sphere. The potential energy of the solute is then described by a square-well model,

$$u(r)=\begin{cases}0, & r<R-\lambda\\ \varepsilon, & R>r\geqslant R-\lambda\\ \infty & r\geqslant R.\end{cases} \tag{5}$$

The foregoing interaction arises from uneven forces acting on the solute by the solvent molecules at the interface and can be regarded as the interaction between the interface and the solute with interaction range λ. This scenario is similar to the surfactant adsorption onto the interface. In fact, the well-known Langmuir adsorption isotherm is derived based on the interface-solute interaction. The solute cannot escape from the droplet or penetrate the boundary.

There are n solutes in the interfacial shell and N-n in the bulk. The canonical partition function is given by

$$\begin{aligned}\mathcal{Z}&=\frac{1}{N!}\sum_{n=0}^{N}C_n^N\left[\Pi_{i=1}^{n}\int_{V_s}e^{-\beta\varepsilon}d\mathbf{r}_i\right]\left[\Pi_{j=N-n}^{N}\int_{V_b}d\mathbf{r}_j\right]\\ &=\frac{1}{N!}\sum_{n=0}^{N}C_n^N(V_se^{-\beta\varepsilon})^n(V_b)^{N-n},\end{aligned} \tag{6}$$

where β is the inverse of the thermal energy k_BT. The factor $N!$ results from overcounting indistinguishable solutes and $C_n^N=N!/n!(N-n)!$. In term of the total volume $V=V_s+V_b$, one has

$$\mathcal{Z}=\frac{V^N}{N!}(1-x+xe^{-\beta\varepsilon})^N, \tag{7}$$

where the volume ratio of the interfacial shell to the spherical droplet is defined as

$$x=V_s/V\simeq 3\frac{\lambda}{R}\quad\text{as}\quad\frac{\lambda}{R}\ll 1. \tag{8}$$

The summation in Eq. (6) is the binomial expansion. The expected number of solutes in the interfacial region is found from the partition function

$$\begin{aligned}\langle n\rangle&=\frac{V^n\Sigma_{n=0}^{N}(n)C_n^N(xe^{-\beta\varepsilon})^n(1-x)^{N-n}/N!}{\mathcal{Z}}\\ &=N\frac{xe^{-\beta\varepsilon}}{1-x+xe^{-\beta\varepsilon}}.\end{aligned} \tag{9}$$

Note that as $\langle n\rangle=Nx$ as $\varepsilon=0$, and the solutes distribute according to the volume ratio V_s/V. The internal energy of the system is simply

$$\langle U\rangle=\frac{V^n\Sigma_{n=0}^{N}(n\varepsilon)C_n^N(xe^{-\beta\varepsilon})^n(1-x)^{N-n}/N!}{\mathcal{Z}}=\langle n\rangle\varepsilon. \tag{10}$$

The Helmholtz free energy can be determined by the relation $\mathcal{F}=-k_BT\ln\mathcal{Z}$,

$$\mathcal{F}=-k_BTN\left[\ln(1-x+xe^{-\beta\varepsilon})-\ln\left(\frac{N}{V}\right)+1\right], \tag{11}$$

where Stirling's approximation, $\ln N!\simeq N\ln N-N$, is used. The entropy change is then given by

$$-T\Delta S=-Nk_BT\left[\ln(1-x+xe^{-\beta\varepsilon})+(\beta\varepsilon)\,\frac{xe^{-\beta\varepsilon}}{1-x+xe^{-\beta\varepsilon}}\right].\tag{12}$$

B. Surface tension increment

The free energy change $\Delta\mathcal{F}=\mathcal{F}(\varepsilon)\mathcal{F}(0)$ can also be obtained by the thermodynamic integration [7], similar to the charging process for electrolyte solutions [8],

$$\begin{aligned}\Delta\mathcal{F}&=\int_0^1\left\langle\frac{\partial U}{\partial\chi}\right\rangle_{\chi}d\chi\\&=\int_0^1\langle n(\chi\varepsilon)\rangle\varepsilon\,d\chi\\&=-k_BTN\ln(1-x+xe^{-\beta\varepsilon}),\end{aligned}\tag{13}$$

where $u(r)=\chi\varepsilon$ in Eq. (5). The increment of surface tension can then be obtained by the canonical route,

$$\Delta\gamma=\frac{\mathcal{F}(R;\varepsilon)-\mathcal{F}(R;0)}{4\pi R^2},\tag{14}$$

where $\mathcal{F}(R;0)$ corresponds to the free energy of the spherical volume of radius R with the solute behaving the same as the solvent, $\varepsilon=0$. Equation (14) indicates that the surface tension increment is canonically equivalent to the surface Helmholtz free energy density. Substituting Eq. (13) into Eq. (14) yields

$$\Delta\gamma=N\frac{k_BT}{4\pi R^2}x(1-e^{-\beta\varepsilon})\cong c_bk_BT\lambda(1-e^{-\beta\varepsilon}),\tag{15}$$

where the bulk concentration is defined as $c_b=N/(4\pi R^3/3)$ and $x\ll 1$ generally.

One can also obtain Eq. (15) by the grand-canonical route: the Gibbs adsorption isotherm approach,

$$d\gamma=-\int\Gamma\,d\mu.\tag{16}$$

The chemical potential can be computed by

$$\begin{aligned}\mu=\left(\frac{\partial\mathcal{F}}{\partial N}\right)_{T,V}&=-k_BT\ln(1-x+xe^{-\beta\varepsilon})+k_BT\ln\frac{N}{V}\\&=-k_BT\ln c_b^*=\varepsilon+k_BT\ln c_s^*,\end{aligned}\tag{17}$$

where the bulk and surface concentrations associated with the droplet are defined as $c_b^*=(N-\langle n\rangle)/(V-V_s)$ and $c_s^*=\langle n\rangle/V_s$, respectively. According to the definition of the surface excess, $\Gamma=\int_0^R[c(r)-c_b]4\pi r^2dr$, one has

$$\Gamma=-\frac{N}{4\pi R^2}\,\frac{x(1-e^{-\beta\varepsilon})}{1-x+xe^{-\beta\varepsilon}}=-c_b^*(1-e^{-\beta\varepsilon})\frac{xR}{3}.\tag{18}$$

Inserting Eqs. (17) and (18) into Eq. (16) and performing the integration yields the surface tension increment

$$\Delta\gamma=c_b^*k_BT(1-e^{-\beta\varepsilon})\frac{xR}{3},\tag{19}$$

which reduces to Eq. (15) as $x\ll 1$ because of $c_b^*\cong c_b$ and $x\cong 3\lambda/R$.

III. SURFACE TENSION MEASUREMENT

The surface tension data of the water-alcohol mixture, including methanol and ethanol, have been reported for the whole mole fraction range [9]. Nevertheless, in the dilute limit (mole fraction less than about 0.1), the thorough results for the surface tension increment of alcohol due to water addition is absent. In order to examine our theory, we perform the surface tension measurement for dilute water in methanol and ethanol solutions, up to about 3 M. Pendant bubble tensiometry enhanced by video digitization was used for the measurement of surface tension [10,11]. The pendant bubble was created in the water-alcohol solution, which was enclosed in a thermostatic air chamber. The temperature variation of the solution is less than ±0.05 K. A parallel light of constant intensity passes through the pendant bubble and forms a shape of a bubble on a video camera. The image was digitized into 480 lines×512 pixels with a level of gray of 8 bit resolution. The theoretical shape of a pendant bubble is derived from the classical Laplace equation, which relates the pressure difference across the fluid interface ΔP to the curvatures of the surface by the surface tension, $\Delta P=\gamma[R_1^{-1}+R_2^{-1}]$, where R_1 and R_2 are the principal radii of curvature of surface. The surface tension was determined from the best fit between the theoretical curve and the data points by minimizing the objective function, which is defined as the sum of squares of the normal distance between the experimental edge points and the theoretical profile evaluated from the Laplace equation. The accuracy and reproducibility of the surface tension measurement obtained by this procedure are 0.02 mN/m.

Figure 1 shows the variation of the surface tension increment with the water concentration at 20 °C. A linear increase in γ with c_b is clearly observed. This result is in agreement with our theory, and one has $d\gamma/dc_b=0.31$ and 0.19 mJ/m^{2}M for methanol and ethanol, respectively. In accordance with Eq. (15), we obtain $\lambda(1-e^{-\beta\varepsilon})=1.25$ Å (CH_3OH) and 0.77 Å (C_2H_5OH). Since the interaction range is about the size of the solute molecule d, we can assume $\lambda=d$. If we adopt the Lennard-Jones size parameter for d, the interface-solute repulsive energy is given by $\varepsilon=0.42\ k_BT$ for methanol and $\varepsilon=0.19\ k_BT$ for ethanol. It should be noted that the surface tension is increased, $\Delta\gamma>0$, only if $\varepsilon>0$. The physical origin of ε is the difference between the solvent-solvent interaction (ε_{11}) and the solute-solvent interaction (ε_{12}), i.e., $\varepsilon=\varepsilon_{11}-\varepsilon_{12}$. For convenience, it is generally assumed $\varepsilon_{11}=0$. Our results indicate that the water-alcohol attraction is stronger than the alcohol-alcohol attraction. Moreover, the net solute-solvent attraction for methanol is larger than that for ethanol.

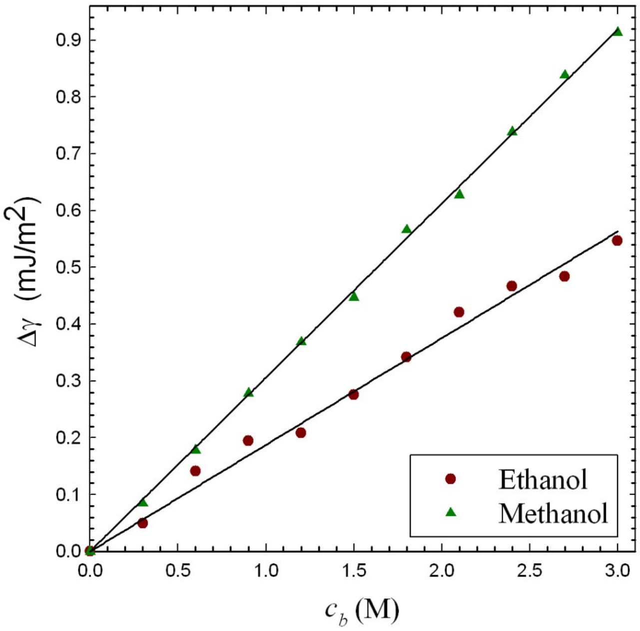

FIG. 1. A plot of the measured surface tension increment against the solute concentration for water addition into methanol and ethanol at 20°C.

IV. MONTE CARLO SIMULATIONS

To verify the theory, which neglects the finite size of the solute, for the surface tension increment, we have performed a standard Monte Carlo simulation with the usual Metropolis algorithm [12] based on the pseudo-one-component model. The system consists of a collection of hard spheres with diameter *d* confined within a cavity of radius *R*. In the vicinity of the interface, the hard sphere is repelled from the boundary according to the interface solute interaction, Eq. (5). The simulations were performed under conditions of constant total number of particles, temperature, and volume $(N,\ V,\ T)$. The system was equilibrated for about 10^4 Monte Carlo steps (MCS) per particle and the production period for each simulation was 10^6 MCS per particle.

The concentration profile $c(r)$ of the solute is calculated for different N and ε/k_BT with $R=10d$. Figure 2 illustrates that the assumption of two regions is reasonable at low volume fractions and $c_s^*=c_b^*e^{-\beta\varepsilon}$ is justified. However, for high enough N and ε/k_BT, a maximum occurs near the boundary of the two regions, i.e., at $r\rightarrow(R-\lambda)^-$. The particle is strongly repelled from the interfacial region and also expelled from the bulk region due to excluded volume effects. As a consequence, one anticipates that the deviation from our theory may become substantial in semidilute solutions as $\varepsilon/k_BT\gg1$. The success of the theory is also shown in Fig. 3 for the expected number of solutes in the interfacial region $\langle n\rangle$ which decays with increasing ε. The MC results for the variation of $\langle n\rangle/N$ with $\beta\varepsilon$ agree quite well with the theoretical expression, Eq. (9), for different values of V_s/V. This consequence justifies the assumptions made in the theory in the dilute limit.

The finite size effect associated with the solute is examined by the chemical potential as shown in Fig. 4. The

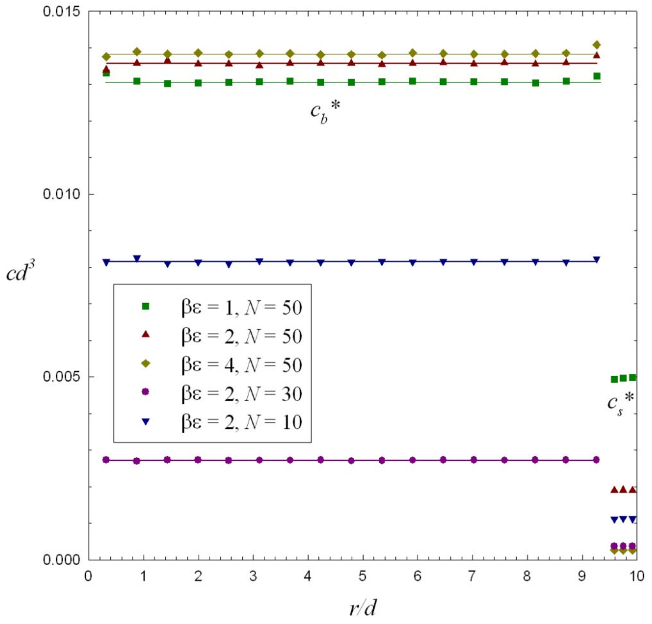

FIG. 2. The variation of the bulk concentration with the radial position for different values of N and ε/k_BT at $R=10d$.

chemical potential is given by

$$\mu=k_BT\ln c(r)d^3+\mu^{ex}(r)=k_BT\ln c_b^*d^3+\mu^{ex}(c_b^*),\tag{20}$$

where μ^{ex} denotes the excess chemical potential. For convenience, the reference chemical potential is set to zero, $\mu_0=0$. The excess chemical potential arises from the hard-

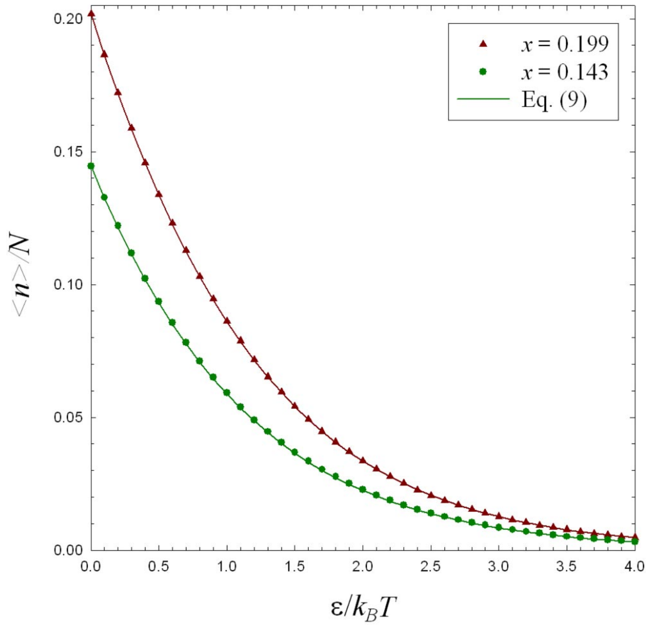

FIG. 3. The variation of the expected number of solutes in the interfacial region with ε/k_BT for different $x=V_s/V$. The case of $N=50$ and $R=10d$ corresponds to $x=0.143$, and $N=17$ and $R=7d$ to $x=0.199$.

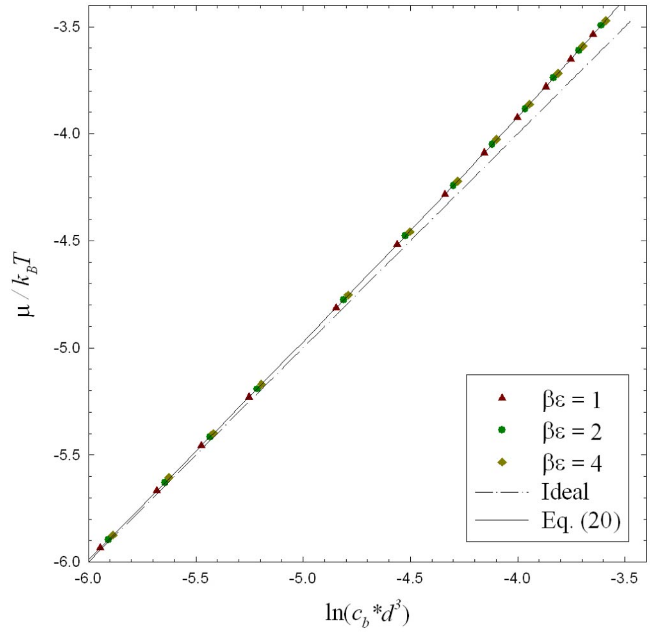

FIG. 4. A plot of the total chemical potential μ against the bulk concentration c_b^* for different values of $\beta\varepsilon$ with $R=10d$. The data points are obtained from MC. The dashed line denotes the ideal chemical potential and the solid line incorporates the hard-sphere interaction.

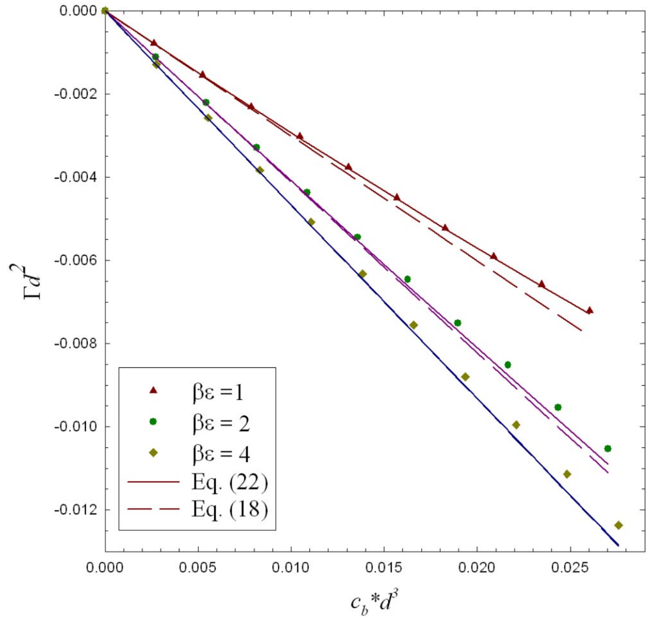

FIG. 5. The variation of the surface excess with the bulk concentration for different values of $\beta\varepsilon$ with $R=10d$.

sphere interaction and is obtained by Widom's method [13], which is the reversible work required to add a particle to the solution,

$$\mu^{ex} = -k_B T \ln\langle -\Delta U / k_B T\rangle,$$

where ΔU is the change in the total energy due to the particle insertion. As illustrated in Fig. 4 for different values of $\varepsilon/k_B T$, the MC results can be well represented by Eq. (20) with the Carnahan and Starling equation [14],

$$\frac{\mu^{ex}}{k_B T} = \frac{8\phi - 9\phi^2 + 3\phi^3}{(1-\phi)^3}, \tag{21}$$

where the volume fraction is $\phi = (\pi/6) c_b^* d^3$. The hard-sphere interaction becomes significant as $\phi \gtrsim 0.01$, and hence neglecting the excluded volume effect in the theory is justified in the dilute limit.

The negative surface excess calculated by MC is compared to that derived in the theory, Eq. (18), as shown in Fig. 5. The agreement is quite good for $c_b^* d^3 \lesssim 0.015$ for all values of $\beta\varepsilon$. However, at higher concentration, the theory overestimates the amount of solute depletion in the interfacial region because of the absence of the finite size effect. When the excluded volume is taken into account through the chemical potential, we have $c_s^* = c_b^* \exp[-\beta(\varepsilon - \mu^{ex})]$ and the surface excess becomes

$$\Gamma = -c_b^* \{1 - \exp[-\beta(\varepsilon - \mu^{ex})]\} \frac{xR}{3}. \tag{22}$$

At high enough concentrations, the repulsion felt by the solute in the interfacial region is opposed by the hard-sphere interaction in the bulk. Therefore, the solute depletion is no longer dominated by the interface-solute repulsion. Figure 5 shows that for $\beta\varepsilon=1$ Eq. (22) gives a better prediction than Eq. (18). However, both equations overestimate the solute depletion for $\beta\varepsilon=4$, and indicates that the simple two-region scenario is not satisfactory at higher concentrations. The rapid change in the vicinity of the boundary between the two regions must be considered.

The surface tension increment can be calculated from MC based on the Gibbs adsorption isotherm, Eq. (16). Numerical integration of Γ with respect to μ yields $\Delta\gamma$ as shown in Fig. 6 for different values of $\beta\varepsilon$. The agreement between the MC and theoretical results, Eq. (19), is quite good, particularly for small $\beta\varepsilon$. The MC result clearly shows that as the interface-solute repulsion becomes large enough, the surface tension increment approaches the asymptotic limit, $\Delta\gamma \to c_b k_B T \lambda$, which is independent of the interaction energy ε. This consequence also indicates that the maximum contribution to the surface tension increment due to the short-ranged solute-solvent interaction is $d\gamma/dc_b \to k_B T \lambda$, which provides a measure of the role played by the ion-solvent interaction for the surface tension increment associated with electrolyte solutions.

V. DISCUSSION

We have developed a theory for the surface tension increment due to solute addition on the basis of the simple two-region picture. Since the solute-solvent attraction is stronger than the solvent-solvent attraction, the solute is repelled from the interface. In terms of the interface-solute interaction, a linear increase in the surface tension with the bulk concentration is predicted. The theoretical results are consistent

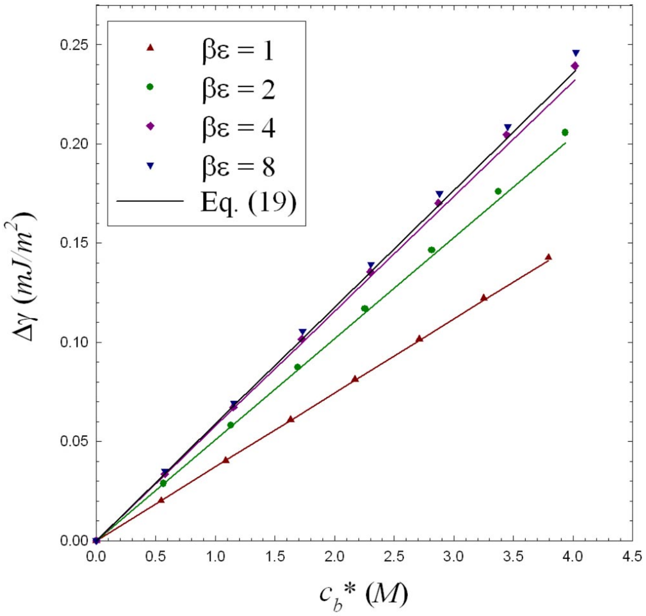

FIG. 6. A plot of the surface tension increment against the solute concentration for different values of $\beta\varepsilon$ with $R = 10d$.

with those obtained by surface tension experiments and Monte Carlo simulations. The asymptotic results can also be obtained from the scaling analysis, which offers essential physical insight. Our theory based on the solute-solvent interaction may give important implication for surface tension increment associated with inorganic electrolyte solutions.

A. Scaling analysis

The surface tension increment represents the system free energy change ($\Delta\mathcal{F}$) due to solute addition. As a result, the increase in surface tension may be dominated by the internal energy change (ΔU) or the entropy change ($-T\Delta S$). When the repulsion is weak, i.e., $\beta\varepsilon \ll 1$, one expects that the system free energy increase is primarily due to the existence of the solute in the interfacial region. Since the leading behavior of the number of solute in the interfacial region is about proportional to the interfacial volume, $\langle n \rangle \propto V_s$, we have

$$\Delta\mathcal{F} \approx \Delta U = N \frac{V_s}{V} \varepsilon .$$

As a consequence, the surface tension increment is given by

$$\Delta\gamma \approx \frac{\Delta U}{4\pi R^2} = c_b \lambda \varepsilon . \tag{23}$$

The above result can be recovered from Eq. (15) by expanding $e^{-\beta\varepsilon}$. In the limit of weak repulsion, the surface concentration is essentially the same as the bulk concentration and the surface excess approaches zero. The surface tension is mainly driven by the internal energy increase due to the interface-solute interaction.

On the contrary, strong interface-solute repulsion leads to nearly complete depletion of the solute in the interfacial region. As a result, the internal energy change is negligible because of $\langle n \rangle \approx 0$. The change in the free energy is caused by the increase of the solute in the bulk region. Since the ideal entropy is proportional to $-N \ln V$, one has

$$\Delta\mathcal{F} \approx -T\Delta S = -Nk_BT[\ln(V - V_s) - \ln V].$$

Therefore, the increase in surface tension can be estimated as

$$\Delta\gamma \approx \frac{-T\Delta S}{4\pi R^2} = c_b \lambda k_B T . \tag{24}$$

Again, the foregoing expression can be recovered from Eq. (15) by ignoring $e^{-\beta\varepsilon}$. In the limit of strong repulsion, the solute is completely depleted in the interfacial region and all solute molecules are confined in the bulk. The higher bulk concentration, $N/(V - V_s)$, signifies a decrease in entropy. The surface tension increment is primary caused by the entropy loss. Once the interfacial region is empty of solute, the entropy loss is constant for specified N and V, and the magnitude of ε is irrelevant. Hence $\Delta\gamma$ is independent of the interfacial-solute interaction. As shown in Fig. 7, our scaling analysis is verified by MC. The free energy change $\Delta\mathcal{F}(\varepsilon)$ is obtained by the process of the reversible work, Eq. (13). For intermediate interactions, the number of solutes in the interfacial region reaches the maximum and both internal energy and entropy changes are important.

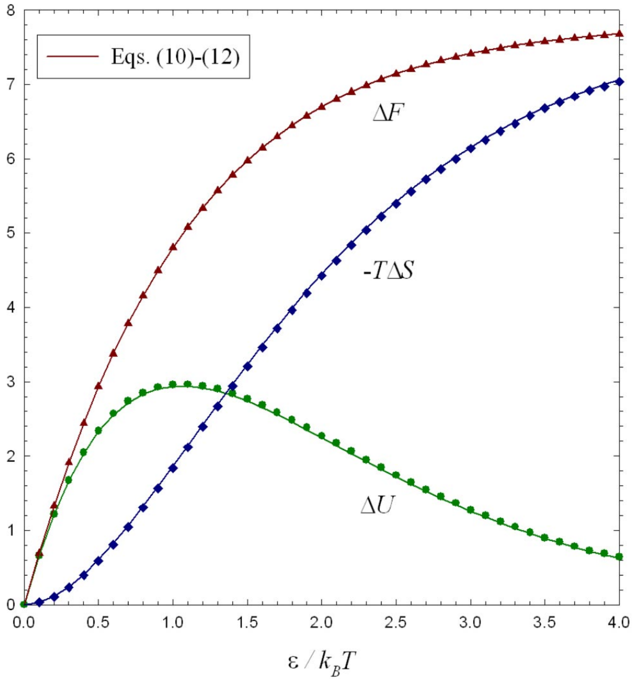

FIG. 7. The variation of the free energy, internal energy, and entropy with the interaction energy ε/k_BT for $N = 50$ and $R = 10d$. The data points are obtained from MC and the lines denote the theoretical results.

When the solute is complete absent in the interfacial region, the mechanical reasoning of the surface tension increment can be explained as followed. The mechanical origin of the surface tension for a pure solvent is the unbalance forces acting on the molecule per unit length on the surface due to the broken symmetry. Note that the average forces exerting on molecules in the bulk is zero. The net force acting on the interface is toward the bulk as illustrated in the Young-Laplace equation [1,2]. The complete deficiency of solutes on the surface leads to a monolayer of solvent molecules, the same as the surface of pure solvent. However, the solute just below the surface may enhance the unbalance forces toward the bulk if the solute-solvent attraction is stronger than the solvent-solvent attraction. As a result, the surface tension is elevated due to solute addition. The possible mechanism for the water-alcohol attraction is the hydrogen bond. The hydrogen bonding between water and alcohol molecules is stronger than that between alcohol molecules.

B. Implication for electrolyte solutions

It has been experimentally observed that the excess surface tension $\Delta\gamma$ is approximately linear with the concentration of electrolyte for concentrated solutions ($\sim$3 M) [1,15]. All the theoretical approaches considered electrostatic interactions among ions due to dielectric discontinuity based on the restrictive primitive model, in which the solvent is represented by a continuum medium of uniform dielectric constant [6]. Nevertheless, the deviation from the experimental results is quite significant. It is speculative that the molecular nature of the solvent becomes important in addition to the electrostatic interaction. The OS limiting law, Eq. (4), yield negative $\Delta\gamma$ for high enough concentrations. Despite the fact that the OS theory [4] gives a fairly good quantitative description for salt concentration up to 0.1 M, it consistently underestimates the increase in the interfacial tension above 0.1 M. Recently, Levin and Flores-Mena [16] solved the linearized Poisson-Boltzmann equation and took into account the finite ion size just below the Gibbs dividing surface. They obtained results in agreement with experimental up to relatively high salt concentrations of 1 M. Ho *et al.* [17] performed MC simulation with solving Poisson equation directly [18,19]. They also found that hydration around ions plays a very important role in interfacial tension increment.

Evidently, for high salt concentrations, consideration of the electrostatic interaction only is not enough to explain the surface tension increment [8,16,17]. The reason is that the electrostatic screening becomes very substantial so that the electrostatic repulsion due to dielectric contrast is not large enough to expel most of ions from the interfacial region. Another possible repulsion may come from the solute-solvent attraction. For electrolyte solutions, this local interaction corresponds to the ion-water attraction (charge-diople interaction). It is well known that the binding between water molecules and an inorganic ion such as sodium is very strong and a hydration layer of water molecules are formed around an ion, for example, the hydration number for Na^+ is about 5 and the hydrated diameter is about 4 Å [20], which is a few times larger than the bare ion. In the previous studies, this solute-solvent interaction is either absent or introduced by the excluded volume effect associated with an ion on the surface. Here we can estimate the contribution due to ion-water attraction based on our theoretical result.

The surface tension increment per 1 M solute addition $d\gamma/dc_b$ can be considered from two sources. The electrostatic repulsion due to dielectric mismatch gives $d\gamma_d/dc_b$. The repulsion caused by the solute-solvent attraction may be estimated from Eq. (15). We express the ion-water attraction in terms of the interface-solute interaction ε. Since the ion-water attraction is much greater than the water-water interaction, it is reasonable to assume $\varepsilon/k_BT \gg 1$ and one has $c_s \to 0$ (approaching complete depletion). For a $z_+:z_-$ electrolyte solution, there are 2 species with the total concentration $(z_+ + z_-)c_b$. As a result, we estimate the surface tension increment due to ion-water attraction by

$$\frac{d\gamma_s}{dc_b} = (z_+ + z_-)\lambda k_B T. \tag{25}$$

Let us take the characteristic interaction range λ as the radius of the hydrated ion, say 0.213 nm. Here the sizes of both cation and anion are assumed the same. One obtains $d\gamma_s/dc_b \simeq 5.27\times10^{-7}$ J m/mol for a neutral solute. The experimental result usually displays $d\gamma/dc_b \simeq 1-2$ mJ/(m^2 M) $=1-2\times10^{-6}$ J m/mol for 1:1 inorganic salts. For example, $d\gamma/dc_b$ for NaCl is 1.55 mJ/(m^2 M). If Eq. (25) is applied to the 1:1 electrolyte solution, then one has $d\gamma_s/dc_b \simeq 1.05$ mJ/(m^2 M), which is quite close the experimental result. Note that the ion concentration is 2 M for $c_b = 1$ M. This consequence reveals that for high enough salt concentrations, the major part of the surface tension increment can be attributed to nearly complete depletion of the solute at the interface. That is, the hydration of water molecules around an ion prevents the ion approaches the interface and leads to a monolayer of water on the surface.

One can compare the two contributions in the dilute limit. The OS limiting law, Eq. (3), gives the surface tension increment $\Delta\gamma_d$ due to dielectric contrast. On the other hand, Eq. (25) represents the surface tension increment $\Delta\gamma_s$ due to ion-water attraction. Since $\lambda < l_B \ll \kappa^{-1}$, one has $\Delta\gamma_d \gg \Delta\gamma_s$, that is, the effect of the dielectric discontinuity dominates in the very dilute electrolyte solution. However, the screening length κ^{-1} decays with increasing the salt concentration. As a result, the role played by dielectric mismatch becomes less important at higher concentration. In fact, for concentrated concentrations, the size (corresponding to the characteristic length λ) and the nature of the short-range interactions of the various salts (the interaction energy ε) become essential, and each salt shows individual behavior. In other words, the surface tension of electrolyte solutions show specific ion effects and generally follows the Hofmeister series [1]. Rigorously speaking, the two different contributions for surface tension increment due to salt addition are not additive. The combined result is currently under investigation by performing MC with solving the Poisson equation for electrostatic repulsion and incorporating the square-well interface-solute interaction simultaneously.

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