

Computation of Surface Tensions Using Expanded Ensemble Simulations

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A method for the direct simulation of the surface tension is examined. The technique is based on the thermodynamic route to the interfacial tension and makes use of the expanded ensemble simulation method for the calculation of the free energy difference between two inhomogeneous systems with the same number of particles, temperature, and volume, but different interfacial area. The method is completely general and suitable for systems with either continuous or discontinuous interactions. The adequacy of the expanded ensemble method is assessed by computing the interfacial tension of the planar vapor–liquid interface of Lennard-Jones, Lennard-Jones dimers, Gay-Berne, and square-well model fluids; in the latter, the interactions are discontinuous and the present method does not exhibit the asymmetry of other related methods, such as the test area. The expanded ensemble simulation results are compared with simulation data obtained from other techniques (mechanical and test area) with overall good agreement.

I. Introduction

The surface tension has long been recognized as a fundamental thermodynamic property of interfacial systems.^{1,2} Compared with other interfacial properties, such as the interfacial profiles between two coexisting fluids or a fluid in contact with a solid substrate, the interfacial tension is generally more difficult to determine from simulation. This justifies the growing interest in developing simple simulation techniques for the efficient computation of the surface tension (see Gloor et al.³ for a comprehensive review on the subject).

The standard method for the calculation of the surface tension involves a mechanical (virial) approach, which relates the surface tension with the anisotropy of the pressure tensor.^{4,5} However, the evaluation of the components of the pressure tensor in terms of the intermolecular forces can be rather involved or time-consuming for complex systems;⁶ also, additional difficulties may arise for the particular case of systems with impulsive interactions (e.g., the square-well (SW) model). An alternative route to the surface tension involves a thermodynamic approach. For a system containing N particles in a volume V at a temperature T , the surface tension γ can be defined as

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{N,V,T} = \lim_{\Delta A \rightarrow 0} \frac{\Delta F}{\Delta A} \quad (1)$$

This relation suggests that γ can be calculated from the change in Helmholtz free energy ΔF associated with a small change ΔA in the interfacial area. On this basis, Gloor et al.³ have recently developed a novel test-area (TA) technique for the direct simulation of the surface tension. As shown by Gloor et al., the change in free energy associated with a small, virtual deformation of the interface from A_0 to $A_1 = A_0 + \Delta A$ at constant N , V and T can be expressed as

$$\Delta F = -k_B T \ln \langle \exp(-\beta \Delta U) \rangle_0 \quad (2)$$

where $\beta = 1/(k_B T)$, and $\Delta U = U_1 - U_0$ is the perturbation in the configurational energy associated with the area deformation. The angular brackets in the above expression denote an ensemble average over the reference state of interfacial area A_0 . In spite of its generality, this perturbation-based expression⁷ will be of practice only for small area deformations.³ An interesting feature of the TA method is that no explicit calculation of the intermolecular forces is required. It is to be noted that a similar perturbation approach can be invoked for evaluations of first-order derivatives of the free energy (e.g., chemical potential⁸ or pressure^{9–14}) under perturbations of the corresponding conjugate thermodynamic property (number of particles or volume, respectively). Applications of the TA method have been reported for the computation of the surface tension of the vapor–liquid interface of simple model fluids³ and of different models of water.¹⁵ Though originally applied with seeming success to the SW model, there were doubts about the adequacy of the TA method for the computation of the surface tension in systems with impulsive intermolecular forces.¹⁴ In these cases, there is a manifest asymmetry in the free energy difference resulting from perturbations that increase and decrease the interfacial area at constant volume. For the particular case of SW systems, it can be explicitly shown that this asymmetry introduces a bias in the computation of the values of the interfacial tension from the TA method, the main consequence being that this method systematically overestimates the surface tension for SW systems.¹⁶

Here, we consider a generic and efficient method for the direct simulation of the surface tension. As will be shown, this approach does not suffer from the asymmetry existing for impulsive systems. This method involves the thermodynamic route to the interfacial tension embodied in eq 1, incorporating the expanded ensemble technique¹⁷ to the calculation of the free energy difference $\Delta F = F_M - F_0$ between the actual system of interfacial area A_0 and a system of interfacial area $A_M = A_0 + \Delta A$, both with the same number of particles and volume, and at the same temperature. Simple prescriptions are given to select the parameters that control the application of the expanded

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ensemble to the evaluation of the surface tension. This approach is applied to the computation of the surface tension of planar vapor–liquid interfaces for a variety of model systems, including simple (Lennard-Jones and SW) fluids and more complex molecular fluids, such as the two-center Lennard-Jones model for diatomic molecules and the Gay-Berne model appropriate for liquid crystals. A careful comparison is made with interfacial tension data obtained from the conventional virial route and the TA method. An independent assessment of the validity of expanded ensemble methods to the computation of surface tensions has recently been published by Errington and Kofke.¹⁸

As a final remark, we note that the expanded ensemble method presented here bears some resemblance to the methodology recently proposed by MacDowell and Bryk¹⁹ in which the interfacial area is allowed to fluctuate randomly and the surface tension follows from the analysis of the resulting probability distribution. In a way, our approach can be regarded as a discrete (and arguably, simpler) version of the continuum version of the wandering interface developed by MacDowell and Bryk. Related schemes based on a thermodynamic approach to the surface tension have also been used by Miyazaki et al.,²⁰ and Salomons and Mareschal,²¹ who consider Bennetts's method²² for the calculation of the free energy difference between two inhomogeneous systems with slightly different interfacial areas.

II. Expanded Ensemble Technique

The expanded ensemble method, originally proposed by Lyubartsev et al.,¹⁷ is designed for the efficient calculation of the free energy difference between two systems, here denoted by 0 and M . One assumes that both systems can be connected by a discrete set (or chain) of intermediate subsystems, each characterized by an interaction energy $U_m \equiv U(\mathbf{r}^N; \alpha_m)$, with $m = 0, 1, \dots, M$, where the α_m are arbitrary coupling parameters such that, for $m = 0$, $U_0(\alpha_0)$ corresponds to the potential energy of system 0, while for $m = M$, $U_M(\alpha_M)$ is the potential energy of system M ; \mathbf{r}^N denotes the positions and orientations of the molecules. The coupling parameters are quite general and can be any macroscopic or microscopic property that enters, explicit or implicitly, into the Hamiltonian of the system. A global canonical partition function $Q(N, V, T)$ for the expanded ensemble can be defined as a weighted sum of the (canonical) partition functions of the subensembles $Q_m \equiv Q(N, V, T, \alpha_m)$

$$Q(N, V, T) = \sum_{m=0}^M \exp(\beta W_m) Q_m \quad (3)$$

where

$$Q_m = \frac{1}{N! \Lambda^{3N}} \int d\mathbf{r}^N \exp[-\beta U_m(\mathbf{r}^N; \alpha_m)] \quad (4)$$

Here, Λ is the de Broglie wave length, and W_m in eq 3 is a weight factor for the potential U_m . From eq 3, the probability of finding the system in any of the microstates of subensemble m when sampling the expanded ensemble is given by

$$p_m \equiv p_m(N, V, T) = \frac{Q_m \exp(\beta W_m)}{Q(N, V, T)} \quad (5)$$

By considering that $F_m = -k_B T \ln Q_m$, it follows that the free energy difference of two arbitrary subsystems i and j can be expressed as

$$\Delta F_{ij} \equiv F_j - F_i = -k_B T \ln \frac{p_j}{p_i} + (W_j - W_i) \quad (6)$$

Adding up all free energy differences between consecutive subsystems along the chain, one arrives at the following expression for the free energy difference between systems 0 and M ,

$$\Delta F \equiv F_M - F_0 = -k_B T \ln \frac{p_M}{p_0} + (W_M - W_0) \quad (7)$$

A conventional Metropolis algorithm can be constructed in order to sample the global configuration space defined by the expanded ensemble. In addition to the usual Monte Carlo (MC) moves, one also considers trial moves where the coupling parameter is changed. In the canonical ensemble, the probability of acceptance of the transition $i \rightarrow j$ between subsystems i and j is simply given by

$$\mathcal{P}_{i \rightarrow j} = \min\{1, \exp[-\beta(\Delta U_{ij} - \Delta W_{ij})]\} \quad (8)$$

where $\Delta U_{ij} = U_j - U_i$, and $\Delta W_{ij} = W_j - W_i$. The probabilities in eq 5 involve a ratio of partition functions and can be estimated from the frequency of visits to each subensemble in the course of a (MC or molecular dynamics) simulation. As suggested by Errington and Kofke,¹⁸ the ratio p_j/p_i in eq 6 can alternatively be estimated using a transition-matrix scheme. In general, microstates pertaining to consecutive subensembles in the chain will be separated by a large free energy barrier, so subsystems with high free energy will be poorly sampled; as a result, the corresponding probabilities may differ in several orders of magnitude and the scheme turns inefficient. This situation can be easily alleviated by a suitable choice of weighting coefficients; though ΔF_{ij} should not depend on ΔW_{ij} , the probability ratio p_j/p_i is strongly dependent on the weight factors, as can be seen after manipulating eq 6:

$$\frac{p_j}{p_i} = \exp[-\beta(\Delta F_{ij} - \Delta W_{ij})] \quad (9)$$

This expression suggests that the choice $\Delta W_{ij} \approx \Delta F_{ij}$ ensures a nearly uniform sampling with $p_i \approx p_j$. This choice, however, would require prior knowledge of the quantities that one is trying to compute. Nonetheless, it is straightforward to devise a simple scheme that systematically corrects the set of weight factors:²³ starting from a suitable initial guess, and making use of expression 6, the weight factors are successively refined according to

$$(\Delta W_{ij})_{\text{new}} = (\Delta W_{ij})_{\text{old}} - k_B T \ln \frac{p_j}{p_i} \quad (10)$$

during the course of a preliminary short simulation run.

The expanded ensemble simulation technique has proved quite efficient in a variety of problems involving the computation of free energy differences; examples include the calculation of the free energy^{17,24} and chemical potential²⁵ of dense model fluids and crystalline solids,^{23,26} or the solvation free energies of solute molecules into different solvents,²⁷ just to mention a few applications.

III. Application to the Calculation of the Surface Tension

The application of the expanded ensemble technique to the computation of the surface tension is fairly straightforward and involves using the interfacial area as the coupling parameter α

introduced in the previous section. In principle, one considers a set of $M + 1$ subsystems all having the same number of particles, volume, and at the same temperature, but different values of the interfacial area, A_0, A_1, \dots, A_M . One end of this sequence corresponds to the actual system with interfacial area A_0 , while the other end of the chain corresponds to the system with interfacial area $A_M = A_0 + \Delta A$. A conventional Metropolis algorithm is used to sample the global configuration space defined by the expanded ensemble. This is achieved by performing the usual MC (or molecular dynamics) moves, which involve translational and rotational displacements of the particles for the present value of the interfacial area, in combination with trial moves to change the interfacial area. As the latter is performed at constant volume, a change in the interfacial area is accompanied by the corresponding rescaling of the positions of the molecular centers of mass. Transitions between adjacent subsystems are accepted according to the probability given by eq 8. In the most general case, the weight factors are corrected after a short run, as explained earlier. From eq 1, the interfacial tension is calculated from $\gamma = \Delta F / \Delta A$, where ΔF follows from eq 7 after computation of the average probabilities of visiting systems 0 and M during the simulation.

The adequacy and efficiency of the expanded ensemble scheme for the calculation of the surface tension rely on the appropriate choice of a number of controlling parameters, such as the value of ΔA , the number of intermediate subsystems between 0 and M , and the values of the weight factors. Following recommendations in related applications,²⁸ we choose the value of ΔA so as to obtain a rate of about 30% of successful transitions between adjacent subsystems. In principle, one should try to minimize the number of intermediate subsystems for a given value of ΔA ; otherwise, the system is likely to expend most of the time exploring intermediate states, which may give rise to a poor sampling of the relevant subsystems 0 and M . If uniform sampling is achieved along the chain, that is, $p_0 \approx p_M \approx 1/(M + 1)$, an estimate of the absolute error in the free energy difference $\sigma_{\Delta F}$ from propagation of errors in eq 7 yields

$$\sigma_{\Delta F} \approx kT\sqrt{2(M+1)}\sigma_{p_0} \quad (11)$$

where we are assuming that the probabilities p_0 and p_M are computed with similar statistical uncertainties; that is, $\sigma_{p_0} \approx \sigma_{p_M}$. Minimization of the above expression with respect to M would yield an indication of the optimum choice of the number of subsystems M ; however, one should note that σ_{p_0} in eq 11 is not constant but varies when M is changed. According to Errington and Kofke,¹⁸ it seems that $\sigma_{\Delta F}$ is fairly insensitive to the particular choice of M . However, for other applications of expanded ensemble methods,²⁵ $\sigma_{\Delta F}$ appears to slightly depend on the choice of M .

Once the value of ΔA is fixed, the appropriate number of intermediate subsystems will ultimately depend on the height of the free energy barrier ΔF between systems 0 and M : more intermediate subsystems will generally be required to interpolate between systems 0 and M for increasingly larger values of ΔF . As ΔF increases linearly with ΔA (see eq 1), too large a choice for ΔA will typically involve more intermediate states in order to achieve uniform sampling of systems 0 and M . However, we find that there is no need to consider extra intermediate states when the prescription considered here to fix ΔA is used: we then consider $M = 1$, which amounts to sampling only subsystems with interfacial area A_0 and $A_1 = A_0 + \Delta A$. As for the choice of weight factors, only $\Delta W \equiv W_1 - W_0$ is required. Our working equation can therefore be written as

$$\Delta F = -k_B T \ln \frac{p_1}{p_0} + \Delta W \quad (12)$$

As explained earlier, an appropriate choice of weight factors would be $\Delta W = \Delta F$, which for the present case reduces to $\Delta W = \gamma \Delta A$. In principle, using here a rough estimate of γ provides a suitable initial guess for ΔW , which may be adjusted afterward according to the correction scheme presented in the preceding section. We also note that the efficiency of the expanded ensemble in some applications is claimed to critically depend on the appropriate choice of weight factors in order to ensure uniform sampling of the subensembles.^{17,23–28} This is certainly the case for applications involving large free energy differences, but is not for the present application: the thermodynamic approach to the surface tension embodied in eq 1 is restricted to small values of ΔA , and the change in free energy ΔF is therefore expected to be correspondingly small. With the criterium adopted here to choose suitable values of ΔA ($\approx 30\%$ of successful transitions between systems 0 and 1), we find that reliable values of the surface tension can be obtained with no need of further refinement of the initial guess for ΔW .

IV. Results and Discussion

We now turn to analyze the adequacy of the expanded ensemble approach described in the preceding section to the direct computation of the surface tension. For simplicity, we restrict ourselves to interfacial systems that contain a planar vapor–liquid interface. We consider systems of spherical molecules with either Lennard-Jones (LJ) or square-well (SW) interactions. For LJ systems, we make use of a cut and shifted version of the potential energy. Both LJ and SW interactions are characterized by the usual molecular diameter σ and well-depth ϵ parameters; an extra parameter λ defines the range of the attractive interactions for the SW fluids. We consider a cutoff distance of $r_c = 2.5\sigma$ for LJ systems containing $N = 1372$ molecules, and SW systems with $\lambda = 1.25\sigma$ and 1.5σ , containing $N = 864$ molecules. The simulation results obtained here for the surface tension of LJ and SW systems can be compared with existing data obtained from other techniques.^{3,12,13,19,29–33}

We also test the performance of the expanded ensemble method for the computation of the surface tension of the vapor–liquid interface for more complex systems of nonspherical molecules. We first consider a two-center Lennard-Jones (2CLJ) model for molecular dimers formed by two identical LJ sites (monomers) of diameter σ and dispersive energy ϵ , with segment–segment bond distance fixed to $L = \sigma$. The site–site LJ interactions are truncated (but not shifted) at a cutoff distance of $r_c = 6\sigma$, and systems containing $N = 2000$ dimers are considered. Our results are compared with data for the surface tension reported by Duque et al.³⁴ (one should bear in mind that their molecular dynamics results correspond to a cut-and-shifted version of the site–site interactions, so small differences might be anticipated even when such a large value of the cutoff distance is used). Results are also reported for complex interfacial systems in which the molecules interact through the Gay–Berne (GB) potential model,³⁵ which can be regarded as an anisotropic version of the LJ potential. The GB model is widely used in simulation of thermotropic liquid crystals (see ref 36 for a recent review). The explicit form of the potential and the meaning of the parameters that define the model can be found elsewhere.³⁵ Here, we consider the original parametrization of the interactions³⁵ with model parameters $\kappa = 3$ (length-to-breadth ratio) and $\kappa' = 1$ (energy anisotropy). According to previous studies,^{37,38} this model exhibits a vapor–

TABLE 1: Simulation Results for the Surface Tension of the Planar Vapor–Liquid Interface for Different Models (LJ, Lennard-Jones; 2CLJ, Two-Center Lennard-Jones; GB, Gay-Berne; and SW, Square Well for Two Values of the Potential Range, 1.25σ and 1.5σ) as Obtained from Expanded Ensemble Simulations (γ_E^*), Virial Route (γ_{vir}^*), and Test-Area Method (γ_{TA}^*) at Different Values of the Reduced Temperature $T^* = k_B T/\epsilon^a$

system	T^*	L/σ	$(\Delta A/A_0) \times 10^3$	$\Delta W/\epsilon$	p_0	γ_E^*	γ_{vir}^*	γ_{TA}^*	γ^*
LJ	0.70	11.8959	4.59	0.7579	0.4995(17)	0.582(3)	0.583(5)	0.581(3)	0.581(8) ^b
	0.80	11.8959	5.63	0.6464	0.4982(21)	0.400(3)	0.404(5)	0.404(6)	0.403(7) ^b
	0.90	11.8959	6.36	0.4176	0.5004(12)	0.233(2)	0.232(4)	0.232(5)	0.239(6) ^b
2CLJ	1.00	17.50	2.78	1.6100	0.5005(10)	0.948(17)		0.947(17)	0.87(2) ^c
	1.20	17.50	3.43	1.3818	0.503(6)	0.665(10)		0.659(20)	0.60(1) ^c
	1.40	17.50	4.08	0.9525	0.495(6)	0.369(10)		0.382(15)	0.36(2) ^c
GB	0.59	17.6851	2.40	0.5235	0.503(8)	0.354(8)	0.348(16)	0.349(16)	0.349(13) ^d
	0.67	17.6851	2.88	0.3492	0.494(6)	0.184(7)	0.195(7)	0.195(7)	0.202(7) ^d
SW (1.25)	0.62	10.04808	0.238	0.01315	0.4999(3)	0.268(11)	0.274(14)	0.35(5)	0.278(12) ^e
	0.64	10.07075	0.266	0.01291	0.4999(4)	0.235(15)	0.239(13)	0.30(4)	0.230(10) ^e
	0.66	10.25986	0.275	0.01137	0.5003(4)	0.210(13)	0.196(9)	0.24(3)	0.184(8) ^e
SW (1.5)	0.70	10.25986	0.285	0.04506	0.4997(4)	0.739(14)	0.751(9)	0.77(6)	
	0.90	10.25986	0.399	0.0355	0.5002(3)	0.432(11)	0.423(15)	0.46(3)	0.423(10) ^f
	1.05	10.25986	0.513	0.0228	0.4999(4)	0.209(8)	0.211(10)	0.22(4)	0.202 (11) ^f

^a All values of the surface tension are expressed as $\gamma^* = \gamma\sigma^2/\epsilon$, where σ and ϵ are the length and energy scales of each model, respectively. ΔA and ΔW are controlling parameters for the expanded ensemble simulations. $A_0 = 2L^2$ is the interfacial area of the reference system 0. p_0 is the average probability of finding the system in the reference state. The last column includes values of the surface tension (mechanical approach) reported by different authors. ^b Results from ref 29. ^c Results from ref 34. ^d Results from ref 13. ^e Results from ref 33. ^f Results from ref 31.

isotropic–nematic triple point at a temperature of $k_B T/\epsilon \approx 0.63$. Results are reported here for temperatures at which the fluid in coexistence with a vapor phase is orientationally disordered (isotropic, $k_B T/\epsilon = 0.67$) and orientationally ordered (nematic, $k_B T/\epsilon = 0.59$). The GB interactions are cut and shifted at a distance $r_c = 4\sigma$, and systems containing $N = 1372$ GB molecules are considered.

All MC simulations are performed with a standard Metropolis scheme appropriate to sample the expanded ensemble (see eq 8). The initial setup of the simulations is fairly standard and widely used for the direct simulation of fluid interfaces. A liquid slab containing N molecules is placed in the central part of a rectangular box with dimensions $L_x = L_y \equiv L$ and $L_z = 3L$. Both sides of the liquid film along the z direction are initially left empty, and usual periodic boundary conditions are applied in all three directions. If the temperature of the system is below the critical temperature, the system stabilizes two (planar) vapor–liquid interfaces parallel to the x – y plane with an overall interfacial area of $A = 2L^2$. Once the interface is well equilibrated, run averages are taken over N_{run} MC cycles, where one MC cycle consists of N attempts to displace the molecules, N attempts to rotate the molecules (for nonspherical particles) and one trial transition $0 \rightarrow 1$ (or $1 \rightarrow 0$) between subsystems with interfacial area A_0 and $A_1 = A_0 + \Delta A$. In order to avoid serial correlations, averages and estimates of the errors are calculated by dividing the simulation run into N_b blocks. An estimate of the statistical uncertainty of the sample average of any property, a , is given by the standard deviation in the block averages calculated from $\text{var}(a)/\sqrt{N_b}$, where $\text{var}(a)$ is the variance of the block averages.³⁹ The total length of the simulations is $N_{\text{run}} = 2.5 \times 10^6$ (LJ), 0.5×10^6 (2CLJ), 10^6 (GB), and 60×10^6 (SW) MC cycles. The number of blocks is $N_b = 10$, except for SW systems, for which we consider $N_b = 30$.

The values of the controlling parameters ΔA and ΔW used in the expanded ensemble simulations are included in Table 1 for each of the temperatures and models considered here. As argued earlier, ΔA is chosen in each case so as to ensure an acceptance ratio of about 30% for the transitions between systems with interfacial area A_0 and A_1 . With this choice, $\Delta A/A_0$ is seen to be 1 order of magnitude smaller for SW fluids than for the rest of models with continuum interactions. We

also note that the values of this ratio are of the same order of magnitude as the relative size of the area perturbations in the TA method.³ The values of ΔW given in the table follow from $\Delta W = \gamma\Delta A$, with γ being the corresponding surface tension obtained from other techniques; this should ensure a nearly uniform sampling (i.e., $p_0 \approx p_1 \approx 0.5$) with no need of further adjustment of the weight factors. As shown in Table 1, these values of ΔW are significantly smaller for SW systems, which suggests that the choice $\Delta W = 0$ must be good enough for a reliable sampling of subsystems 0 and 1 for the case of SW interactions. This is tested by carrying out a number of unweighted ($\Delta W = 0$) expanded ensemble simulations for some of the SW systems considered here. In practice, the main output property of the simulation scheme proposed here is the probability p_0 of visiting the system with interfacial area A_0 during the simulation (obviously, $p_1 = 1 - p_0$). The resulting values of p_0 are included in Table 1. From these values, the surface tension follows from $\gamma = \Delta F/\Delta A$, with ΔF computed from eq 12. Estimated errors in the computed averages of the probabilities and surface tensions are reported as twice the standard error (i.e., 96% confidence level).

The values of the interfacial tension obtained from expanded ensemble simulations are compared with those obtained from the usual virial expression and the TA method. For the virial route, we employ the standard expression for planar interfaces,

$$\gamma_{\text{vir}} = \frac{1}{2} L_z (P_N - P_T) \quad (13)$$

which relates the interfacial tension with the anisotropy of the pressure tensor. Here, P_N and P_T are the (macroscopic) normal and tangential components of the pressure tensor,^{13,14} respectively. The Cartesian components of the pressure tensor are defined with respect to a frame in which the z axis is taken perpendicular to the interface, so that $P_N \equiv P_{zz}$ and $P_T = P_{xx} = P_{yy}$. The factor of 2 in eq 13 accounts for the existence of two interfaces in the system. P_N and P_T are calculated from appropriate averages of the microscopic pair virials,⁴⁰ which for the case of SW systems involves the computation of the number of molecular pairs at distances where the interaction potential is discontinuous.^{14,31,33,41,42} Data obtained from the virial route are included in Table 1.

Values of the surface tension are also calculated from the TA method.³ A test-area deformation of magnitude ΔA is performed at constant N , V , and T every MC cycle. By using eqs 1 and 2, the surface tension follows from

$$\gamma_{\text{TA}} = -k_{\text{B}}T \lim_{\Delta A \rightarrow 0} \frac{1}{\Delta A} \ln \langle \exp(-\beta \Delta U) \rangle_0 \quad (14)$$

where ΔU is the energy of the perturbation. All values of γ_{TA} included in Table 1 correspond to a combination of increasing-area ($\Delta A > 0$) and decreasing-area ($\Delta A < 0$) perturbations; this corresponds to a central-difference approximation for the first-order derivative of the Helmholtz free energy with respect to the area of the interface (see eq 64 in ref 3). Values of the surface tension obtained from the virial route by Vrabec et al.²⁹ (LJ system), Duque et al.³⁴ (2CLJ system), de Miguel and Jackson¹³ (GB system), and Orea et al.^{31,33} (SW systems) are also included in the table for comparison.

As can be seen from the table, the expanded ensemble technique yields values of the surface tension in quantitative agreement with the values obtained from the virial route with a similar degree of accuracy, irrespective of the continuous or discontinuous nature of the molecular interactions. The expanded ensemble approach seems to also perform satisfactorily for complex molecular systems with no sign of deterioration in accuracy. Full consistency is also found when the values determined from expanded ensemble simulations are compared with results obtained from the TA method in those cases where the latter is applicable; as already pointed out, the TA method becomes inaccurate when applied to systems with impulsive interactions due to the asymmetric nature of the area perturbations in systems with discontinuous interactions.¹⁶ As shown in Table 1, the TA method overestimates the surface tension of SW systems, more particularly for short ranges of the interactions and at low temperatures. Our current values of the surface tension are also seen to be fully consistent with available data for all systems. As anticipated earlier, the small differences between our results and those reported by Duque et al.³⁴ for 2CLJ systems are to be ascribed to the slightly different representation of the site-site interactions and not to the different approaches to the computation of the interfacial tension.

As a final remark, we mention that the values of the interfacial tension of SW systems obtained from unweighted ($\Delta W = 0$) expanded ensemble simulations (not included in Table 1) are found to be in full agreement with those reported in the table. For SW systems, we have also considered the unweighted scheme in combination with values of ΔA three times as large as those used in the series of expanded ensemble simulations with $\Delta W \neq 0$ (see Table 1). With this choice, the computed values of the interfacial tension are again seen to be in full agreement with data obtained from the weighted expanded ensemble simulations or the virial route, even when the rate of successful transitions between systems 0 and 1 is now seen to decrease to about 4%. This appears to confirm our expectation that the simple choice $\Delta W = 0$ ensures a reliable sampling of the expanded ensemble for SW systems and to provide accurate values of the surface tension even with relatively large values of ΔA .

V. Conclusion

A simulation technique for the direct computation of the surface tension has been examined. The method is based on a thermodynamic approach to the surface tension and makes use of expanded ensemble simulation for the computation of the free energy difference between two systems, denoted by 0 and

1, with the same number of particles, volume, and temperature, but which differ ΔA in their interfacial area. There must be some compromise when considering the optimum choice of ΔA . On the one hand, it should be small enough so that the finite-difference approximation used in eq 1 becomes justified, but on the other hand, a too small value of ΔA yields a large fraction of accepted transition moves, so the configuration space is poorly explored (i.e., consecutive microstates are highly correlated).⁴⁰ Here, the value of ΔA is chosen in each case so as to ensure a transition rate between systems 0 and 1 of about 30%. Other criteria may well yield a better sampling of the configuration space of the expanded ensemble for this particular application. This is similar to the problem of finding optimum values of the maximum molecular displacement, or the maximum volume fluctuation for the standard translational or volume moves in a Monte Carlo scheme.⁴⁰ For SW systems, our results seem to indicate that a transition rate as low as 4%, obtained after using larger values of ΔA , appears to be good enough to provide reliable values of the interfacial tension. The relation between the precision of surface tension estimates and the magnitude of the interfacial area change ΔA has been examined by Errington and Kofke¹⁸ in an independent publication where the expanded ensemble approach is used with consideration of a set of $M = 10$ subensembles. Both approaches can be regarded as discretized implementations of the wandering interface approach of MacDowell and Bryk,¹⁹ where continuum changes in the interfacial area are allowed. In principle, a (discrete or continuum) multiple-state sampling of systems of different areas can be used to estimate the error involved in the computation of the surface tension with different choices of ΔA .

The other key controlling parameter is the weight factor ΔW . An appropriate choice of ΔW allows the system to sample important regions of the configuration space which are otherwise inhibited by the presence of a large free-energy barrier. However, the free energy differences involved in the present application are not very large, and the choice of weight factors does not seem to be as critical as in other related applications. A rough estimate of ΔW seems to be good enough in order to get reliable values of the surface tension. This estimate can be successively corrected during a short preliminary run, but this was not necessary in the cases considered here. We even find that the simplest choice $\Delta W = 0$ provides good results for the interfacial tension of SW systems.

The adequacy of our approach is assessed by comparing simulation results obtained from expanded ensemble simulations with existing data and new data obtained from the usual mechanical and test-area methods. At variance with methods based on a mechanical approach, the expanded ensemble approach has the advantage that no explicit evaluation of the forces is required; this calculation can be complicated for complex systems and is not required for sampling the configuration space with a Monte Carlo scheme. This advantage is also shared by the test-area or the wandering interface methods. Also, the scheme considered here is completely general, and the underlying algorithm is quite simple and directly usable for systems with continuous or discontinuous interactions. For systems with impulsive interactions, the calculation of the surface tension from a virial approach requires special care. As argued here, the expanded ensemble approach yields accurate values of the surface tension for these systems, for which the test-area method produces unreliable estimates. This feature is also shared by the wandering interface method.

It has been our intention to highlight the promising route offered by the combination of a thermodynamic-based approach

with robust and well-developed schemes for the computation of free energy differences in the calculation of properties such as the surface tension. Extensions of this approach to the study of the interfacial tension in more complex situations of practical interest (e.g., fluids in contact with solid substrates) should pose no particular difficulty. In addition, the method can be easily generalized to ensembles other than the canonical ensemble considered here. It is hoped that this work stimulates further research in the field.

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