Generalized van der Waals Theory VIII. An Improved Analysis of the Liquid/Gas Interface

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We extend a preceding application of the GvdW theory to the prediction of interface profiles and surface tension in simple fluids by incorporating a variational determination of the effective hard-sphere diameter. This has previously been found to improve the predicted equation of state. Here we find that it also improves the prediction of interface profiles and surface tension in LJ(12-6) fluids. The agreement with experiment and simulation when these quantities are considered as functions of T/T_c is to within about 5%. As in our earlier calculations the nonlocal entropic effects are found to reduce the surface tension by 5%–10%. In the present conceptually more accurate theory this significantly improves the agreement with experiment and simulation.

KEY WORDS: Simple fluids; interface profile; surface tension; nonlocal entropy; variational hard-sphere diameter.

1. INTRODUCTION

In a preceding article[1] in this series devoted to the development and testing of the generalized van der Waals (GvdW) theory we have examined the accuracy with which a gas/liquid interface in a simple fluid could be resolved. This first article focused on the simplest approximations available including calculations for step-function profiles and the use of a moment expansion method which reduces the theory to a form similar to that of van der Waals[2] and Cahn and Hilliard.[3] We also calculated the interface profile and surface tension using an assumed tanh functional form for the profile and four of the simplest GvdW free energy functionals. Two of

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these functionals corresponded to a coarse-grained (CG) theory wherein the entropy is a local functional while the other two were fine-grained (FG) in the sense that the entropy was nonlocal in recognition of the finite range of the excluded volume effects. The results of these calculations showed that a step-function profile leads to an overestimate of the surface tension by about 50% at the triple point, the moment expansion (or density gradient) method leads to an overestimation of about 20%, and the simple GvdW functionals without the above-mentioned simplifications underestimate the experimental values by about 10%. These comparisons assume that we use T/T_c rather than T as the independent variable. Otherwise the errors in the predicted critical temperatures would cause widely varying and generally larger deviations between theory and experiment. It was found that nonlocal entropic effects tend to decrease the surface tension (and the width of the profile) by about 10%. The profile widths agree reasonably well with the simulation results of Chapela et al.[4]

The work summarized above has demonstrated the applicability of the GvdW theory and its satisfactory accuracy relative to its mathematical and physical simplicity. Its success may be difficult to understand by comparison with the recently dominant theories of dense fluids which emphasize correlation effects.[5-7] The problems and progress made in applying pair correlation function methods to the liquid/gas interface have recently been reviewed by Croxton,[8] Abraham,[9] and Evans.[10] Our own work is more closely related to the constant chemical potential method originally developed by Hill[11] and later extended by Plesner and Platz,[12] Lentz et al.,[13] and Widom.[14] The results of our initial calculations summarized above show that correlation effects beyond simple excluded volume effects are only of minor importance in determining interface profiles and surface tension in a simple liquid. This conclusion is significant not only for its theoretical implications but perhaps more so for its promise of putting a more complete qualitative and quantitative understanding of interfacial phenomena within reach of nonspecialists.

The aim of the present work is to show that the accuracy of the GvdW calculations can be improved by use of more sophisticated free-energy functionals than those used in the preceding calculations summarized above. Thus we are here using the variational hard-sphere form of the theory referred to as GvdW(VHS-I) in two preceding articles[15,16] where it was applied to uniform simple fluids in three dimensions and two dimensions, respectively. Apart from the conceptually satisfying feature that the division of the potential into hard and soft parts is now done in such a way as to minimize the overall free energy (see Kozak and Rice,[17] Mansoori and Canfield,[18] and Rasaiah and Stell[19] for similar ideas applied to reference fluid perturbation theory) there is the practical advantage that the

equation of state of simple fluids, and, in particular, the critical parameters are now more accurately reproduced. This will automatically improve the resolution of interface phenomena which are, of course, directly related to the phase separation and the critical parameters. Plotted against T/T_c the results already obtained were quite good but there were some anomalies, e.g., the fact that the coarse-grained theory was more accurate than the fine-grained theory and the underestimation of the surface tension in a variational calculation where, owing to a limitation on the shape of the interface profile, one would have expected an overestimation. These anomalies do not seriously affect the utility of the simplest methods previously explored. Nevertheless, it is reassuring to know that they can be largely eliminated by a straightforward and simple extension of the theory.

The basic theory and its numerical implementation in the present application are summarized in the following section. We then present and discuss the results for interface width and surface tension in Section 3. The last section contains some conclusions that we draw from the present work and a comparison with alternative theories.

2. GvdW(VHS-I) THEORY AND IMPLEMENTATION FOR THE LIQUID/GAS INTERFACE

The basic derivation of the GvdW theory has been described in the first article in this series[20] and its extension to the VHS-I form to be used below is contained in the third[21] and fourth article. We shall not repeat the basic arguments here but merely summarize the features of the theory which are essential for the understanding of the calculations reported below. The GvdW theory is a variational theory based on a free-energy density functional reflecting the contribution to the partition function of a subset of configurations defined by an r-space particle density which is coarse-grained to some degree. Although the most important simplification is due to a neglect of correlations in evaluating binding energies it is worth emphasizing that the theory is not a mean field theory in the traditional sense. The GvdW theory is a theory of fluctuations. The basic idea is to choose a dominant subensemble of configurations and work out the contribution to the free energy made by this subensemble. The correlations neglected are those of the subensemble, which often differ considerably from those of the full equilibrium ensemble. The success of the theory is dependent upon the construction of simple yet accurate free-energy functionals for the class of model or real systems that are to be studied. The numerical implementation in a given application then generally involves finding an approximate solution, i.e., an optimal particle density which minimizes the free energy, of the variational principle. Since the functional

is an estimate of the total (or configurational) free energy the thermodynamic properties are then easily obtained.

The two free-energy functionals that we shall use here are

CG—GvdW(VHS-I):

$$\mathscr{F}_c(\bar{n}(\mathbf{r})) = -kT \int d\mathbf{r}\, \bar{n}(\mathbf{r})\left\{ -\ln \bar{n}(\mathbf{r}) + (2\pi/3)\ln\left[1 - d^3\bar{n}(\mathbf{r})\right]\right\}$$

$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}'\, \bar{n}(\mathbf{r})\bar{n}(\mathbf{r}')\phi_s(\mathbf{r} - \mathbf{r}') \tag{1}$$

FG—GvdW(VHS-I):

$$\mathscr{F}_c(\tilde{n}(\mathbf{r})) = -kT \int d\mathbf{r}\, \tilde{n}(\mathbf{r})\left\{ -\ln \tilde{n}(\mathbf{r}) + (2\pi/3)\ln\left[1 - d^3\bar{n}(\mathbf{r})\right]\right\}$$

$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}'\, \tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')\phi_s(\mathbf{r} - \mathbf{r}') \tag{2}$$

where $\bar{n}(\mathbf{r})$ is in (2) to be obtained from $\tilde{n}(\mathbf{r})$ by the relation

$$\bar{n}(\mathbf{r}) = \left(4\pi d^3/3\right)^{-1} \int_{|\mathbf{r}-\mathbf{r}'|<d} d\mathbf{r}'\, \tilde{n}(\mathbf{r}') \tag{3}$$

Here k is the Boltzmann constant and T the temperature as usual and all integrals are over the entire volume containing the fluid unless otherwise specified. The subscript c in $\mathscr{F}_c$ indicates that we are here only estimating the configurational contribution to the free energy. The velocity part is, of course, trivial in the case of classical systems and the canonical ensemble (at the usual level of approximation). We have assumed here that the system consists of a set of identical point particles interacting via a pair potential $\phi(r)$ which is spherically symmetric. In fact, we shall take $\phi(r)$ to be the usual Lennard-Jones (LJ) potential. In obtaining the functionals above we have divided $\phi(r)$ into a hard and soft part,

$$\phi_h(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right], \qquad r < d$$

$$= 0, \qquad\qquad\qquad\qquad r \geqslant d \tag{4}$$

$$\phi_s(r) = 0, \qquad\qquad\qquad\qquad r < d$$

$$= 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right], \qquad r \geqslant d \tag{5}$$

It has been assumed that $\phi_h(r)$ acts like a hard-sphere potential excluding interparticle distances less than d. Thus the first terms on the right in (1) and (2) are estimates of $-TS$, where S is the entropy, and the factor

$$\chi_f(\bar{n}(\mathbf{r})) = \left[1 - d^3\bar{n}(\mathbf{r})\right]^{2\pi/3} \tag{6}$$

is the free volume fraction at **r**. The second term in $\mathscr{F}_c$ is the estimate for the total potential energy E.

The difference between the coarse-grained (CG) functional in (1) and the fine-grained (FG) functional in (2) lies in the fact that entropy in (1) is effectively a local quantity [since only the coarse-grained particle density $\bar{n}(\mathbf{r})$ appears] while in (2) the entropy is recognized to be a nonlocal quantity due to the finite but nonzero range of the excluded volume effects. Further discussion of this important point is contained in a preceding article.[21] It should be noted that while the nonlocal excluded volume effect is reasonably estimated by the functional in (2) it is to be regarded as a lowest-level approximation, and room for further development exists.

Finally we note that the important parameter d, the effective hard-sphere diameter in the VHS form of GvdW theory that we are using here, is treated as another independent variable to be determined by minimizing the free energy. This feature plays an important role in the present work and is responsible for the improvements achieved here by comparison with our preceding interface calculations.[1] In the case of a uniform LJ(12-6) fluid the GvdW(VHS-I) theory produces reduced critical parameters $P_c = 0.132$, $\rho_c = 0.309$, $kT_c = 1.18$ in reduced units while the corresponding experimental values for argon are $P_c = 0.116$, $\rho_c = 0.316$, $kT_c = 1.26$. This is good agreement for most practical purposes and it is a considerable improvement over the simpler GvdW functionals lacking the variational hard-sphere feature. In the present application d is also a spatially varying quantity and it is of considerable interest to see how d will vary across the gas/liquid interface.

The implementation of the GvdW(VHS-I) theory described above follows the pattern established earlier in our calculations using further simplifying approximations.[1] The main point to note is that although a computer is needed the programming is straightforward and the calculations comparatively cheap. The general strategy we have used is as follows. We have restricted our search for the optimal profile by assuming that it can be described by a tanh form,

$$n(x) = n_g + (n_l - n_g)/(1 + e^{\alpha x}) \tag{7}$$

where $n(x)$ is $\bar{n}(x)$ in the coarse-grained and $\tilde{n}(x)$ in the fine-grained theory. This should lead to an overestimation of the surface tension (possibly confused by other sources of error) but there is good evidence, e.g., from the simulation work of Chapela et al.,[4] that the error introduced this way is small. Note that the interface in (7) is planar and therefore does not allow for effects of out-of-plane surface modes (riplons). The optimal α value is obtained by minimizing the surface tension using a numerical

parabolic search. Given that one chooses reasonable initial α values, only about 10 or fewer α values need be sampled to produce three significant figures accuracy, e.g., in the surface tension.

The evaluation of the surface tension γ uses a direct subtraction,

$$\gamma \simeq \int_{-h}^{h} dx \left[n(x)f_c(x) \right] - \mathcal{F}^{(0)}(h) \tag{8}$$

where the first term is the free energy of a slice of the fluid containing the interface and $\mathcal{F}^{(0)}(h)$ is the free energy of the corresponding slice of a fluid without surface tension, i.e., the range of entropic and energetic interactions vanish and the profile is a step function. The free energy per particle at x, $f_c(x)$, is obtained by first rewriting the functionals in (1) and (2) in one-dimensional form and then identifying $f_c(x)$ as

$$f_c(x) = kT \left\{ \ln \bar{n}(x) - (2\pi/3)\ln\left[1 - d^3(x)\bar{n}(x) \right] \right\}$$
$$+ \frac{1}{2} \int dx' \, \bar{n}(x')\phi_{s1}(x - x'), \qquad \text{(CG)} \tag{9}$$

$$f_c(x) = kT \left\{ \ln \tilde{n}(x) - (2\pi/3)\ln\left[1 - d^3(x)\bar{n}(x) \right] \right\}$$
$$+ \frac{1}{2} \int dx' \, \tilde{n}(x')\phi_{s1}(x - x'), \qquad \text{(FG)} \tag{10}$$

where

$$\bar{n}(x) = (3/4d^3) \int_{x-d}^{x+d} dx' \, \tilde{n}(x')\left[d^2 - (x' - x)^2 \right] \tag{11}$$

and the effective one-dimensional potential $\phi_{s1}(x)$ is given by

$$\phi_{s1}(x) = 4\pi\epsilon\sigma^2 \left[\frac{1}{5}\left(\frac{\sigma}{x} \right)^{10} - \frac{1}{2}\left(\frac{\sigma}{x} \right)^4 \right], \qquad |x| > d$$
$$= 4\pi\epsilon\sigma^2 \left[\frac{1}{5}\left(\frac{\sigma}{d} \right)^{10} - \frac{1}{2}\left(\frac{\sigma}{d} \right)^4 \right], \qquad |x| \leqslant d \tag{12}$$

In the coarse-grained theory $\bar{n}(x)$ is taken to have the form (7) while in the fine-grained theory $\tilde{n}(x)$ has this form and $\bar{n}(x)$ is obtained from (11). The zero-range free energy can be obtained from

$$\mathcal{F}^{(0)}(h) = 2h\left[yn_l f_c(n_l) + (1 - y)n_g f_c(n_g) \right] \tag{13}$$

$$y = \left[(\Delta N/2h) - n_g \right]/(n_l - n_g) \tag{14}$$

$$\Delta N = \int_{-h}^{h} dx \, n(x) \tag{15}$$

where $f_c(n)$ is the free energy per particle in a uniform fluid at density n and n_l, n_g are the bulk liquid and gas densities, respectively.

We have proceeded by evaluating $f_c(x)$ at typically about 30 lattice points in a lattice which concentrates most of its points close to the midpoint of the interface where the change is most rapid. At the same time h is adjusted to reflect the width of the interface ($h \simeq \text{const}/\alpha$). A specific suggestion for such a lattice was made in our preceding article.[1] However, we have, in fact, used two different numerical integration schemes both giving very nearly the same results, so there are clearly many ways in which the implementation can be carried out. In one of our schemes $n(x)$ is approximated by a piecewise polynomial (cubic) fit whereafter the integrals in (9)–(11) can be carried out analytically. For every x value in the lattice a $d(x)$ value is obtained by a parabolic search for the minimum of $f_c(x)$ and, finally, the integration over $f_c(x)$ in (8) was carried out by a higher-order numerical integration method.

The implementation is comparatively straightforward and free of ill-conditioned numerical problems. Two points may be worthy of mention. The integrations to obtain $f_c(x)$ must be carried outside the active interval $[-h, h]$. For $x < -h$ we have set $n(x) = n_l$ and for $x > h$ we have set $n(x) = n_g$. Also note that when T approaches T_c from below γ becomes a very small difference between two much larger numbers in (8). This does, of course, cause a growth in the error but we have found it possible to approach to within 5% of T_c while still retaining several significant figure accuracy for γ. At the lowest temperature shown the narrow interface and correspondingly narrow active region ($[-15/\alpha, 15/\alpha]$ in reduced units) cause an underestimate of γ by about 1% and an overestimate of α by about 10% due to truncation of energy integrals. However, these errors diminish rapidly as T increases.

3. RESULTS AND DISCUSSION

The interface profile [$\bar{n}(x)$ in the case of the coarse-grained theory and $\tilde{n}(x)$ in the fine-grained theory], the free energy per particle $f_c(x)$ and the effective hard-sphere diameter $d(x)$ at $T^* = 0.7$ in reduced units ($T^* = kT/\epsilon$) are shown in Figs. 1 and 2 for the coarse- and fine-grained forms of the GvdW(VHS-I) theory, respectively. Note that this temperature is roughly equivalent to the triple point temperature for argon. We can see that the width of the interface is of the order of 2σ or twice the hard-sphere diameter. The surface tension is associated with a peak in $f_c(x)$ at the interface due mainly to the loss in binding energy of the outermost liquid layer at the interface. The effective hard-sphere diameter changes smoothly from the lower liquid to the higher vapor value. However, in the case of the coarse-grained theory $d(x)$ shows a maximum slightly to the gas side of the interface. This is presumably due to the fact that the attractive energy is
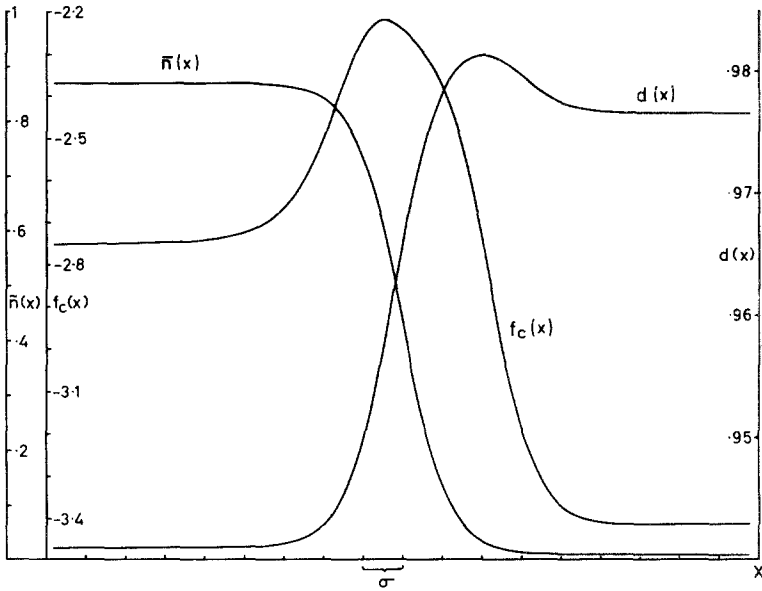
Fig. 1. The interface profile $\bar{n}(x)$, the local free energy per particle (configurational only) $f_c(x)$, and the local effective hard-sphere diameter $d(x)$ as obtained from the coarse-grained GvdW(VHS-I) theory.
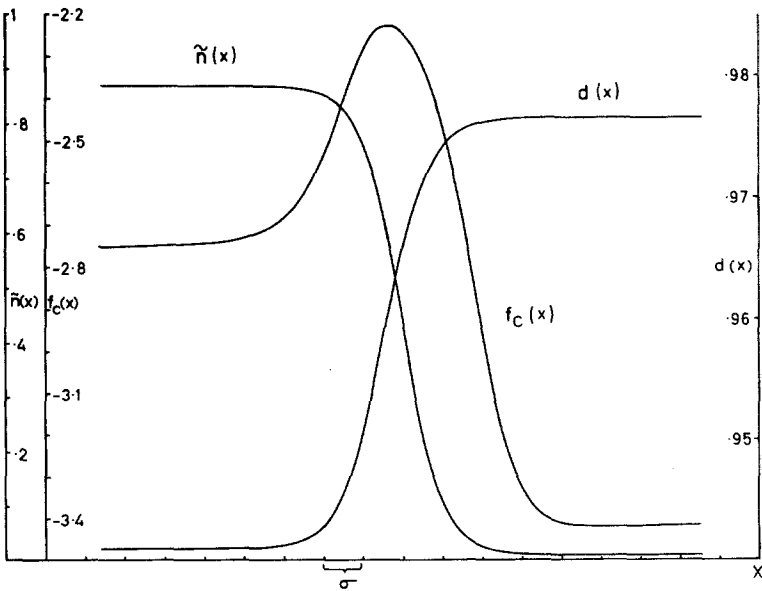

Fig. 2. As in Fig. 1 but the interface profile is that of $\tilde{n}(x)$ and the results were obtained from the fine-grained GvdW(VHS-I) theory.

nonlocal and higher than bulk attractive energies at this local density due to the proximity of denser liquid but the entropy is still evaluated as a local function. Thus the balance between energetic factors driving $d(x)$ towards σ and entropic factors driving $d(x)$ towards lower values is now shifted in favor of the energetic effects causing $d(x)$ to lie above the local "bulk" value. In the fine-grained theory this maximum in $d(x)$ has disappeared and $d(x)$ is monotone and roughly of the same shape (although with direction reversed) as the interface profile.

On the whole the fine-grained theory produces smoother profiles for $f_c(x)$ and $d(x)$. This is reasonable since this is the more accurate theory conceptually. In particular, it is more consistent in that nonlocality is allowed for in evaluating both entropy and energy. The fine-grained theory predicts a somewhat narrower interface. It should, however, be remembered that the two theories are used to predict different quantities. If we were to plot $\bar{n}(x)$ as predicted by the fine-grained theory this function would show a broader profile more directly comparable with the $\bar{n}(x)$ prediction obtained from the coarse-grained theory. The fine-grained prediction for $f_c(x)$ is slightly lower than the corresponding coarse-grained prediction. Thus the fine-grained surface tension is lower. This is a reflection of the fact that the nonlocality of the excluded volume effects tends to increase the entropy and thus lower the surface tension.

The results for the interface profile and the surface tension γ are collected in Table I. Note that we shall use the measure of width w

Table I. Interface Profiles and Surface Tension as Predicted by the Coarse-Grained (CG) and Fine-Grained (FG) Forms of the GvdW(VHS-I) Theory[a]

	Profile α		Width w		Surface tension γ	
T^*	CG	FG	CG	FG	CG	FG
0.50	2.522	3.385	1.586	1.182	1.559	1.409
0.60	2.076	2.516	1.927	1.590	1.262	1.152
0.70	1.707	1.978	2.343	2.022	0.978	0.900
0.80	1.386	1.561	2.886	2.563	0.710	0.657
0.90	1.093	1.208	3.660	3.311	0.464	0.432
1.00	0.809	0.880	4.94	4.55	0.247	0.232
1.10	0.498	0.534	8.03	7.49	0.0768	0.0723
1.12	0.424	0.454	9.43	8.81	0.0507	0.0477
1.14	0.341	0.364	11.73	10.99	0.0282	0.0266
1.15	0.294	0.312	13.60	12.82	0.0187	0.0176
1.16	0.239	0.254	16.74	15.75	0.0105	0.0099
1.17	0.171	0.181	23.4	22.1	0.0040	0.0038
1.18	0.054	0.057	74	70	0.000134	0.000127

[a] Reduced units are used such that $\sigma = 1$, $\epsilon = 1$, $T^* = kT/\epsilon$. Note that $T_c^* = 1.181$ in both theories.

Table II. **Bulk Properties of a LJ(12-6) Fluid According to the GvdW(VHS-I) Theory** ($\epsilon = \sigma = 1$, $T^* = kT/\epsilon$)

T^*	P	n_l	n_g	d_l	d_g
0.50	2.239E-4	0.9858	4.497E-4	0.9386	0.9824
0.60	1.441E-3	0.9298	2.445E-3	0.9397	0.9794
0.70	5.332E-3	0.8691	7.997E-3	0.9410	0.9766
0.80	1.413E-2	0.8024	1.955E-2	0.9425	0.9737
0.90	3.018E-2	0.7270	4.022E-2	0.9442	0.9707
1.00	5.568E-2	0.6382	7.524E-2	0.9464	0.9674
1.10	9.255E-2	0.5227	0.1381	0.9495	0.9634
1.15	1.158E-1	0.4378	0.1971	0.9519	0.9605

proposed by Chapela et al.,[4] who used the same functional form,

$$w = 4/\alpha \tag{16}$$

The corresponding bulk values for the density n and the effective hard-sphere diameter d are contained in Table II. The reduced surface tension is compared to experimental results for Ar[22] and simulation results by Chapela et al.[4] We have plotted γ^* against T/T_c in order to eliminate the deviations which would be directly related to the variation in critical temperatures. Note that in reduced units T_c^* is 1.26 for Ar while the GvdW(VHS-I) theory yields 1.18 and the simulations about 1.32 (see, e.g., Refs. 5 and 6). Figure 3 shows that the coarse-grained theory produces γ values which are about 15% higher than the experimental values for argon for temperatures close to the triple point but cross over at about $T/T_c \sim 0.9$ to lie below experiment close to T_c. This decrease in surface tension is due to the nonlocal entropic effects and it brings the predicted surface tension into significantly better agreement with experiment. Around the triple point we overestimate the experimental value by about 7% but this percentage drops as we approach T_c and the curves cross at about $T/T_c \sim 0.8$. The simulation results (both Monte Carlo and molecular dynamics calculations were carried out by Chapela et al.[4]) show some scatter but the apparently most accurate results are in close agreement with experiment. It would seem therefore that our fine-grained calculations produce surface tensions in good agreement with both experiment and simulation.

In the case of the width of the profile we are able to compare only with simulation. Figure 4 shows that there is now considerable scatter in the simulation results.[4] Moreover, the best simulation calculations cover only a rather limited range of temperatures well away from the critical point. Nevertheless, it is clear from the figure that the fine-grained theory is in better agreement with simulation than is the coarse-grained theory. In fact, the fine-grained theory is a reasonably smooth line fit to all the simulation
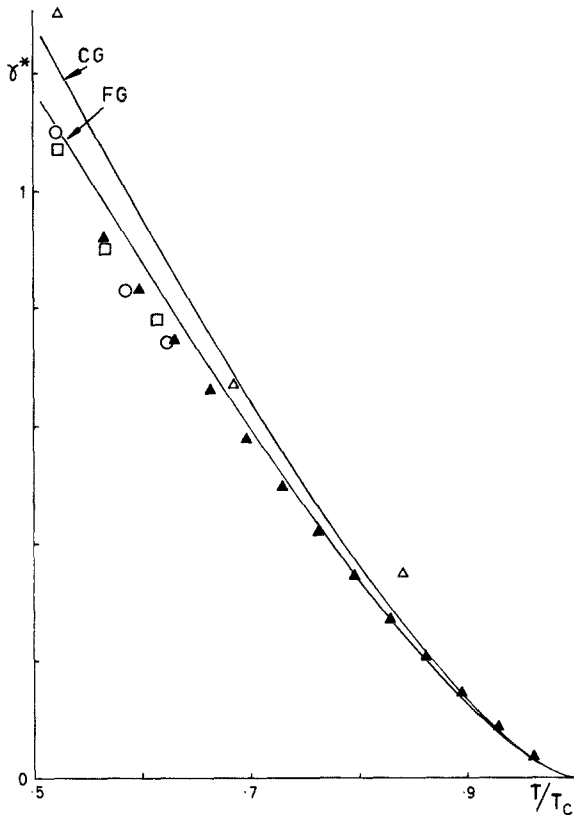
Fig. 3. The reduced surface tension as compared to experimental values for Ar[22] and simulation results of Chapela et al.[4] Notation: Lines are drawn to reproduce results obtained here using the coarse-grained (CG) and fine-grained (FG) GvdW(VHS-I) theory. The experimental results are shown as filled triangles. The simulation results are shown as open triangles (MC255), open squares (MD255), and open circles (MD1020).

data at low temperatures. Although this comparison is far from definitive we conclude that our fine-grained GvdW(VHS-I) theory yields interface widths of quite reasonable accuracy.

We were, of course, able to obtain surface tensions and interface profile widths to reasonable accuracy already using the simple coarse-grained GvdW theory[1] wherein the effective hard-sphere diameter is not optimized but set equal to σ and the excluded volume is density independent and equal to σ^3. The present theory is, however, a distinct improvement in several important respects. The first point is that the critical parameters are predicted to much better accuracy in the present theory. This alone would mean that the present results when plotted against T
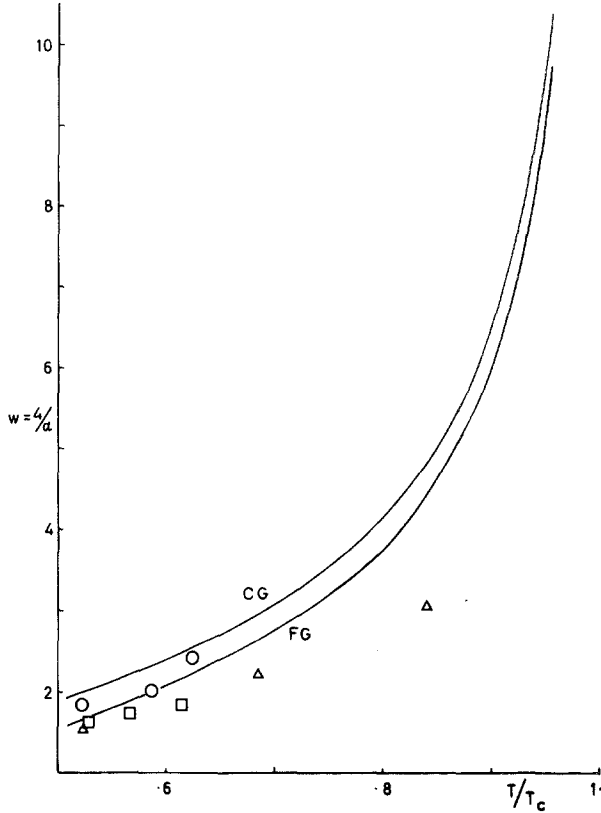
Fig. 4.   The reduced width of the profile plotted against simulation results of Chapela et al.[4]
Notation as in Fig. 3.

rather than T/T_c would look much better than those previously obtained
by the simple GvdW theory. Secondly the deviations observed here are
smaller and healthier in the sense that they can, at least partially, be related
to the fact that we have used a constrained functional form for our
interface. It is quite likely that more flexibility in the choice of interface
profile would lower the surface tension to produce even better agreement
with experiment in the case of the GvdW(VHS-I) theory. In the case of the
previous calculations the results would move marginally the wrong way. It
is also very important conceptually that we have now verified that the
supposedly most accurate form of the GvdW theory, i.e., the fine-grained
GvdW(VHS-I) theory in the present calculations, actually does produce the
most reliable picture of the interface and its surface tension. The present

results confirm in a very graphic manner the need for the fine-grained theory with its recognition of the nonlocality not only of the energetic but also the entropic effects.

There are, of course, a number of other theoretical approaches to the problem of interface profiles and surface tension. An extensive review and discussion of alternative methods can be found in the recent text by Croxton.[8] The precise relationship between the simple free energy density functional approach of the GvdW theory and the reference system perturbation theories or the attempts to extend the uniform fluid integral equations for the radial distribution function to theories of nonuniform fluids is of very great interest. However, it is not our purpose to carry out a detailed comparison here. We merely wish to mention the methods of Toxvaerd,[23] Evans,[10] Abraham,[9] and in particular, Ebner et al.[24] as alternatives apparently able to produce accuracies similar to what we have achieved here. We believe our present theory offers considerable advantages in terms of physical and mathematical simplicity. Although the neglect of detailed correlation effects obviously causes some loss of accuracy this allows the GvdW theory to largely avoid the intricacies of pair correlation effects in nonuniform fluids which, as discussed by Croxton,[8] present considerable difficulties in the case of interface profile theory. As a result the GvdW theory is considerably easier to interpret and extend to allow for the particular features of, e.g., nonuniform fluids. It is also easier to numerically implement. Even in the most sophisticated calculations reported here a profile and the corresponding surface tension can be generated at minimal cost ($\sim$50 sec on a Cyber 72) using only straightforward subroutines. It might be mentioned in this connection that it was not really necessary to individually optimize the effective hard-sphere diameters at each grid point. We also tried a form

$$d(x) = d_g + (d_l - d_g)/(e^{\alpha x} + 1) \tag{17}$$

with α the same as in the density profile (d_l and d_g are the liquid and gas bulk values for d) and found that it gave the same surface tension to within a percent or so.

4. CONCLUSION

We feel that the results of the present calculations can be regarded as very satisfactory from both a basic theoretical and a practical point of view. This work supports the conceptual development of the GvdW theory in that the accuracies of the several forms of the theory agree with expectation and for the best theory, allowing for a density- and temperature-dependent

effective hard-sphere diameter and nonlocal entropic effects, the errors are quite small ($\sim 5\%$). It is noteworthy that nonlocal entropic effects decrease the surface tension by between 5% and 10%. This effect is either not accounted for or not readily understood in earlier theories so far as we are aware.

From a practical point of view this work is important because it clearly places accurate prediction of interface phenomena in simple fluids within reach of a wider range of chemists and physicists, most of whom are not specialists in statistical mechanics of nonuniform fluids nor in the implementation of lengthy computer calculations. The GvdW theory offers not only ease of computation but also greater physical insight into the ingredients of the theory. This, we believe—and previous and ongoing work supports this notion—will make it possible to extend the range of applications to include systems and phenomena hitherto considered too complicated for accurate statistical mechanical methods.

It must, of course, be noted that the present calculations leave several important aspects of simple fluid interfaces still to be considered. Apart from the detailed correlation effects that we have had to leave out to achieve the main simplification of the GvdW theory there are surface and bulk density fluctuations and quantum effects to be accounted for. It is for example, well known[25] that the behavior of the interface for temperatures very close to T_c reflects long-range correlation effects not likely to be found in theories such as ours which focus on short-range interactions. There are also many-particle effects on the potential of interaction even in a simple fluid such as argon. These have been previously considered in this context by Lee et al.[26] Thus there is much scope for further development of our present calculations.

Finally, we shall make an attempt to put our GvdW theory of interfaces as developed here in perspective. Its many deep-seated deviations from other current theories are important but perhaps not so readily appreciated. Let us first recall that the GvdW theory is a continuum theory conceptually related to, e.g., the famous Boltzmann equation of kinetic theory. It can be understood as a development of the theory described by van Kampen.[27] The major difference is that while van Kampen introduced a lattice of semimacroscopic cells the cell volume has in the GvdW theory decreased to the point where there is one and only one particle per cell. Thus we have, in principle, constructed a single occupation cell theory. The lattice is, however, not rigid but flexible so as to allow nonuniform structure to be resolved. Because only those configurations are accounted for which are consistent with the optimal cell structure the theory is based on a maximal contribution assumption and would, for example, neglect the communal entropy of the ideal fluid. Although this assumption introduces

some error it allows the free energy functional to be estimated on the basis of simple microscopic considerations. Long-range collective phenomena such as occur around the critical point can then be studied separately.

The extreme simplicity of the free-energy functionals that are used in the GvdW theory is difficult to understand from the point of view of the currently dominant pair correlation approach to dense fluid theory. There is, however, as discussed by Lebowitz and Waisman[28] in a recent review of van der Waals theories of fluids, much evidence of the lack of sensitivity to short-range correlations. We would put the case as follows. The pair correlation function for Lennard-Jones fluids is dominated by hard-sphere packing effects. Their effects on the free energy, given that we use an appropriate definition for the hard-sphere diameter, is nearly purely entropic and can be estimated with good accuracy by simple excluded volume arguments. The attraction between particles is not greatly affected by correlation effects (beyond hard-sphere exclusion) for temperatures above the triple point. These are the characteristics of the problem which allow us to circumvent the full force of the pair correlation problem in the GvdW theory. They are also drawn upon in the construction of successful reference fluid perturbation theories.[5,6]

The most successful theories of gas/liquid interfaces previously developed, so far as we know, are extensions of the reference fluid–perturbation theory to nonuniform fluids. Toxvaerd[23] started from the Barker–Henderson theory[5] and created a free-energy functional wherein the energy is nonlocal. He obtained predictions of very good accuracy. Subsequently the derivations have become more sophisticated.[29,24,30,9,10] The modified van der Waals theory of Bongiorno and Davis[29] differs little from Toxvaerd's method with respect to basic principle but the implementation is based on the use of the Weeks–Chandler–Anderson perturbation theory.[31] The calculations by McCoy and Davis[32] show this theory to be capable of good accuracy. The theories of Ebner et al.[24] and Evans[10,33] are based on approximations to the direct correlation function in the nonuniform fluid. They are capable of high accuracy. In all cases these theories construct free-energy functionals in terms of the average particle density and are therefore, to some degree, mean field theories. They introduce pair correlations obtained from the uniform fluid at some average density. Thus they differ conceptually and computationally from the GvdW theory. The precise nature of these differences and their consequences for the predictions of the theories is a worthy topic of further research. In this context we also take note of the very recent work of Varea et al.[34] on the interface in a fluid mixture where the limit of infinite ranged attractions is studied, and the analysis of Percus[35] based on a one-dimensional analogy.

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