Monte Carlo Calculations of Effective Surface Tension for Small Clusters*

Barbara N. Hale

Physics Department and Cloud and Aerosol Science Laboratory,
University of Missouri-Rolla, Rolla, MO 65401, USA.

Abstract

In this study we have calculated configurational Helmholtz free energy differences between n and $n-1$ molecule water clusters and n and $n-1$ atom argon clusters using classical effective atom–atom pair potentials and the Bennett–Metropolis Monte Carlo technique. When plotted versus $n^{-1/3}$ the slope of the free energy differences yields an effective surface tension, σ. It is found that these slopes display a universal (material independent) property related to the excess surface entropy/k per molecule (or atom), Ω. For most materials (in the bulk liquid state) the latter quantity is about 2. The results indicate that clusters as small as $n = 10$ display bulk surface free energy properties. The temperature dependence of the effective surface tension for the model water clusters is also investigated and is consistent with a simple scaled form, $\sigma/kT\rho_{\text{liquid}}^{2/3} \approx \Omega(T_c/T - 1)$, where $T_c = 647$ K and $\Omega = 1 \cdot 9$.

1. Introduction

The rate at which small clusters are formed from the vapour depends on the surface free energy of the critical clusters, the temperature T, and the ambient supersaturation ratio S (Abraham 1974). In many cases the critical cluster (that cluster which has equal probabilities of decay and growth) is small—of the order of 20 to 200 molecules (or atoms). It has long been of interest to determine whether the effective surface tension of such small clusters can be approximated by the surface tension σ of the bulk liquid. The nucleation rate J [that rate at which embryos of the new (liquid) phase are formed from the parent (vapour) phase] is exponentially dependent on $(\sigma/kT)^3$ (Becker and Döring 1935). A relatively small (15%) error in the surface tension can alter J by a factor of 10^{14}. Often the nucleation rate is evaluated at temperatures below which bulk liquid surface tension data are available and for which extrapolations must be used. It would be of great interest, consequently, to know both the magnitude and the temperature dependence of the small cluster 'effective' surface tension. The early considerations of the effect of surface curvature on surface tension (Tolman 1949) have been followed by many studies on the effects of size on surface tension, using both thermodynamic approaches and computer calculations of small cluster free energy (Mandell and Reiss 1975; Nishioka 1977; Rao *et al.* 19778; Vogelsbergber 1980; Sinanoglu 1981*b*; Falls *et al.* 1981, 1983; Natanson *et al.* 1983; Shreve *et al.* 1986; Nijmeijer *et al.* 1992).
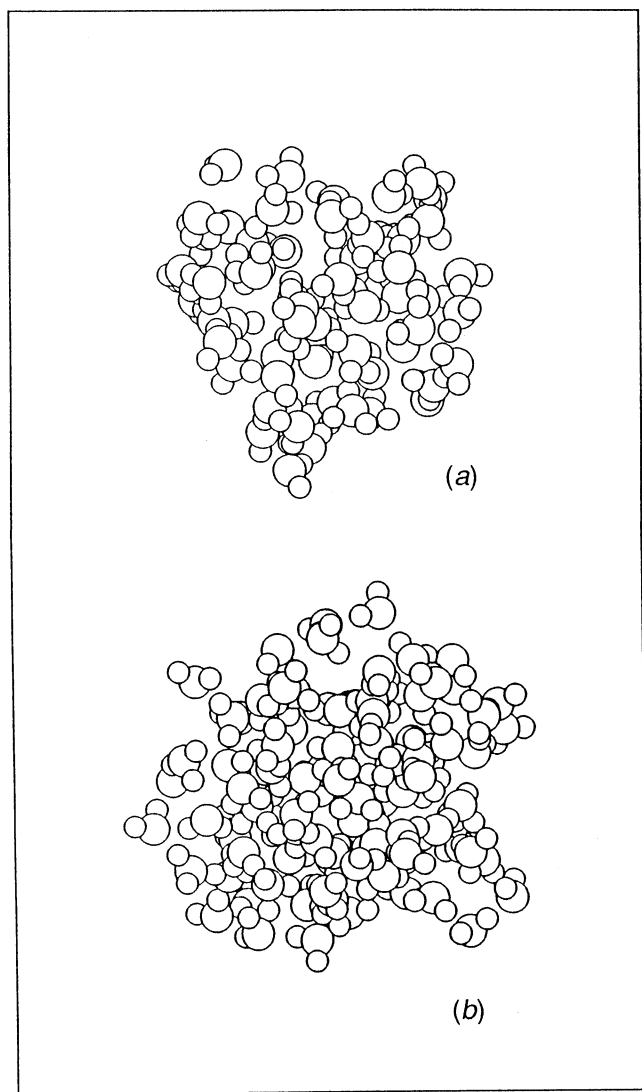
Fig. 1.   (*a*) Snapshot of 60 molecule water cluster at 263 K after 70 million steps; (*b*) snapshot of 96 molecule water cluster at 263 K after 143 million steps.

The present work focuses on free energy differences between neighbouring sized clusters and on the scaling of these free energy differences with a universal temperature dependence (Hale 1986), $(T_c/T - 1)$, to examine the material independent features of the effective surface tension for small clusters. The classical nucleation rate formalism and some of the above small drop surface tension studies use the radius of the clusters r, rather than n, the number of molecules (or atoms). Clearly n accurately defines the small cluster size, whereas r necessitates assumptions about density and shape. Fig. 1 shows snapshots of the $n = 60$ and $n = 96$ molecule model water clusters at $T = 263$ K using the revised central force potential (RSL2) (Rahman and Stillinger 1978). The

water clusters consist of fluctuating five and six-membered rings and are in general non-spherical with ill-defined surface area. Our approach is to calculate configurational Helmholtz free energy differences $F_c(n) - F_c(n-1)$ and plot these differences versus $\delta(n^{2/3}) \approx \frac{2}{3} n^{-1/3}$. The slope of these data provides an effective surface tension for the small clusters. In this work results for model water clusters (RSL2 potentials) and model argon (Lennard-Jones) clusters are obtained using the Metropolis Monte Carlo procedure (Metropolis *et al.* 1953) and the Bennett (1976) method for calculating free energy differences. This method was first applied to argon (Lennard-Jones) clusters by Hale and Ward (1982). And some initial work was done on water clusters with non-fixed centre of masses (Kemper and Hale 1988; Kemper 1990); however, computer resources limited reliable results to clusters with $n \leq 24$. For purposes of comparison the present work extends the argon studies to larger cluster sizes, and concentrates primarily on the RSL2 water clusters.

2. Model and Calculational Procedures

The starting point for the present approach is the law of mass action for a (vapour) system with volume V, composed of a non-interacting mixture of ideal gases, with each cluster size constituting an ideal gas system. One further assumes that the Hamiltonian for an individual cluster has $3n$ independent degrees of freedom and that the potential energy is a function of only atomic position vectors. In this case the law of mass action gives the following classical statistical mechanical expression for the number of clusters with n atoms N_n, in terms of $Z(n)$, the canonical partition function for the n cluster:

$$\frac{N_n}{N_1^n} = \frac{Z(n)}{Z(1)^n} \tag{1}$$

$$= \frac{Z_T^n V^n Q(n)/n!}{[Z_T V Q(1)]^n} = \frac{Q(n)}{n! \, Q(1)^n} \, , \tag{2}$$

where $Z_T^n = (2\pi mkT/h^2)^{3n/2}$ is the kinetic energy contribution to the canonical partition function (arising from the integration over $3n$ atomic momentum coordinates) and $Q(n)$ is the unitless configurational integral given by

$$Q(n) \equiv V^{-n} \int \int \int ... \int \exp[-U(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, ... \boldsymbol{r}_n)/kT] \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}\boldsymbol{r}_3 ... \mathrm{d}\boldsymbol{r}_n . \tag{3}$$

The $\boldsymbol{r}_i$ is the position vector of the ith atom with mass m, U is the total interaction potential energy for the cluster, T is the temperature and k is the Boltzmann constant. Finally, after some algebra one obtains the following expression for N_n:

$$N_n = N_1 \exp \left[\sum_{n'=2,n} \ln \left(\frac{Q(n')}{Q(n'-1) \, Q_{n'}(1)} \right) - I_0 + \ln S \right] \tag{4}$$

$$\equiv N_1 \exp \left[\sum_{n'=2,n} -\delta F_c(n') - I_0 + \ln S \right] , \tag{5}$$

where $Q_n(1) \equiv Q(1)v_n/V = v_n/V$, $S \equiv N_1/N_1^0$, and $N_1^0/V \equiv \rho_{\text{vapour}}$ is the equilibrium monomer concentration,

$$-\delta F_c(n) \equiv \ln\left(\frac{Q(n)}{Q(n-1)\,Q_n(1)}\right), \qquad (6)$$

and

$$\ln\left(\frac{n/v_n}{N_1^0/V}\right) \approx \ln\left(\frac{\rho_{\text{liquid}}}{\rho_{\text{vapour}}}\right) \equiv I_0. \qquad (7)$$

In these simulations the n cluster is defined (and thus approximated) as an n-molecule system contained in a spherical volume, $\alpha v_n = \alpha(n/\rho_{\text{liquid}})$, fixed on the centre of mass, $\alpha = 5$ and ρ_{liquid} is the experimental bulk liquid number density at the temperature T. Molecules are not allowed to move outside the constraining volume. This definition of the cluster has been used by Lee et $al.$ (1973) who found minimal effects on the Helmholtz free energy of the cluster due to variation in v_n when $\alpha \approx 5$. Too small a cluster volume produces the same effect as an external pressure and too large a volume allows the cluster to break up. The argon clusters are modelled with the Lennard-Jones potential using $\epsilon/k = 119 \cdot 4$ K and $\sigma = 3 \cdot 4$ Å and the water clusters are modelled with the RSL2 three point charge revised central force potential of Rahman and Stillinger (1978). The water molecules are rigid with $R_{\text{OH}} = 0 \cdot 958$ Å and H–O–H angle equal to $104 \cdot 5°$.

The standard Bennett technique allows one to determine configurational free energy differences between two ensembles with different interaction potentials. In the present work the goal is to calculate $-\delta F_c(n)$, as given by equation (6). Thus the two ensembles are defined as follows (Hale and Ward 1982): (1) the 'n ensemble' represents n molecules interacting normally in volume v_n; and (2) the '$n-1$ ensemble' represents n molecules in v_n with one molecule (the probe) having its total interaction energy reduced by a factor $\lambda \ll 1$. As $\lambda \rightarrow 0$, the '$n-1$ ensemble' becomes the $n-1$ cluster plus a monomer. One can show that corrections to δF_c due to non-zero λ include terms of the form $\lambda \mathrm{d}(\delta F_c)/\mathrm{d}\lambda$ and $\lambda^2 \mathrm{d}^2(\delta F_c)/\mathrm{d}\lambda^2$ and are negligible in the present simulations for $\lambda = 0 \cdot 01$. The $\delta F_c(n)$ then becomes the free energy difference between the n cluster and the $n-1$ cluster plus a monomer. Both systems have a fixed centre of mass and the same density. This density is the same for all cluster systems studied at the same T. In all cases the free energies $F_c(n)$ and $\delta F_c(n)$ have been divided by kT and are unitless.

The Bennett procedure is as follows. The simulations for each ensemble are carried out independently and in each ensemble a Fermi function average, $\langle f(\pm x)\rangle_m$, is calculated where $x = (1-\lambda)\Delta U_p + C$, $m = n$, $n-1$ and ΔU_p is the interaction potential energy of the probe molecule; C is a constant of the order of $-\delta F_c$. In the n ensemble every molecule is used as a probe and the Fermi functions for all molecules are averaged. In a Monte Carlo simulation the system is assumed to be in thermal equilibrium and the Z_T factors are known. Thus we are primarily concerned with the configurational part of the Helmholtz free energy, $F_c(n) \equiv -\ln[Q(n)/n\,!]$. Bennett's technique applied to this calculation

relates the constants C and the Fermi function averages as follows:

$$\frac{Q(n)}{Q(n-1)\,Q_n(1)} = \frac{\langle f(x)\rangle_{n-1}}{\langle f(-x)\rangle_n}\,\mathrm{e}^C\,. \tag{8}$$

The Fermi function averages are calculated for a range of C values with $\lambda = 0\cdot01$ and stored. At any step one can determine $-\delta F_c(n)$ from the value of $C \equiv C_n$ for which the Fermi function averages are equal, or apply equation (8) directly for a range of C values.

The $\delta F_c(n)$ is not quite $F_c(n) - F_c(n-1)$ but rather

$$\delta F_c(n) = F_c(n) - F_c(n-1) - \ln(\rho_{\mathrm{liquid}}\,V) \tag{9}$$

$$\approx -\ln\frac{Z(n)}{Z(n-1)} - \mu_{\mathrm{vapour}} - I_0\,. \tag{10}$$

If one takes the limit as $n \to \infty$,

$$\lim_{n \to \infty}\ \delta F_c(n) \approx \mu_{\mathrm{liquid}} - \mu_{\mathrm{vapour}} - I_0 + \frac{\rho_{\mathrm{vapour}}}{\rho_{\mathrm{liquid}}} \tag{11}$$

$$\approx -I_0 + 10^{-5}\,,$$

so that $-\delta F_c(\infty) \approx I_0 = \ln(\rho_{\mathrm{liquid}}/\rho_{\mathrm{vapour}})$. Finally, it is necessary to relate the $\delta F_c(n)$ to a theoretical model involving n dependence. We use the classical droplet model of Fisher (1967) and assume

$$-\delta F_c(n) = I_0 - \delta[An^{\frac{2}{3}} + \tau\,\ln(n) + \mathrm{constant}]$$

$$= I_0 - \delta[An^{\frac{2}{3}}] - \tau\,\ln\frac{n}{n-1} \tag{12}$$

$$\approx I_0 - \tfrac{2}{3}An^{-\frac{1}{3}}\quad\text{for large }n\,,$$

where in the classical liquid drop model $An^{\frac{2}{3}} \equiv 4\pi r_n^2\,\sigma/kT$ and σ is the liquid surface tension. Here τ is a parameter which near the critical point is $\approx 2\cdot2$. For T below the critical point τ is not known and for small n, τ could depend on n. Fortunately, the $\tau\ln[n/(n-1)]$ term is small for large n and should not affect strongly the slope of $-\delta F_c$ versus $n^{-1/3}$. In a previous study (Hale 1982, 1986) we noted that $\sigma \approx \sigma_0(T_c - T)$ and $\sigma_0/k\rho_{\mathrm{liquid}}^{2/3} \equiv \Omega \approx 2$ for most substances and proposed that a scaled (or 'law of corresponding states') form for A is given by

$$A = (36\pi)^{\frac{1}{3}}\,\Omega\left(\frac{T_c}{T} - 1\right)$$

$$\approx (36\pi)^{\frac{1}{3}}\,\sigma/(\rho^{\frac{2}{3}}kT)\,. \tag{13}$$

With this model for $\delta F_c(n)$, the slope of $-\delta F_c(n)$ versus $n^{-1/3}$ should give $\approx -\tfrac{2}{3}A$. Subsequently one can estimate an effective surface tension for small clusters and examine the results for consistency with the scaled form for A using Ω and T.
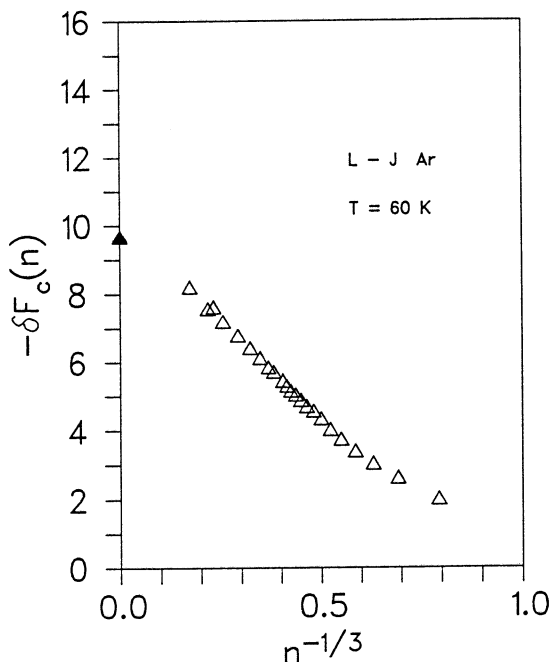
Fig. 2. Configurational Helmholtz free energy differences between n and $n-1$ atom argon (Lennard-Jones) clusters versus $n^{-1/3}$ at $T = 60$ K. The point at $n = \infty$ (filled symbol) is the experimental value of I_0 for argon. The points correspond to $n = 2$–15, 18, 20, 24, 30, 40, 60, 80, 96 and 192.

3. Results of the Monte Carlo Simulations and Estimates of Ω and T_c

The free energy differences $-\delta F_c(n)$ are calculated for n values ranging from 2 to 192 using the experimental values for ρ_{liquid} to determine v_n. Note that while we calculate the free energy differences for a volume αv_n, the plotted values in Figs 2 and 3 are $[-\delta F_{\text{calc}} + \ln(\alpha)]$ corresponding to $-\delta F_c$ as defined in (6). In practice one has to run for more than $n \times 10^6$ steps to obtain a reliable C_n value; and with the model water clusters it is necessary to make runs with a number of initial configurations and average the C_n values. The present calculations were done on an HP 735 workstation and took $\approx 1 \cdot 3$ hours per million steps for two ensembles with $n = 60$.

The calculated $-\delta F_c(n)$ values for the model argon Lennard-Jones clusters at $T = 60$ K clusters are plotted versus $n^{-1/3}$ in Fig. 2. At $n = \infty$ the filled symbol indicates the experimentally predicted intercept, $\ln[\rho_{\text{liquid}}/\rho_{\text{vapour}}] = 9 \cdot 6$. There is a slight curve in the results for $n < 6$. We note that $\tau \ln[n/(n-1)]$ corrections cannot be ruled out in this range. If one applies (12) and (13) and the experimental $T_c = 150$ K for argon to the larger cluster data ($n > 10$), a value of $\Omega = 2 \cdot 1$ is obtained. The experimental bulk liquid value for argon is $2 \cdot 17$ and we see that even clusters as small as 6 to 10 appear to fall on a line with the same slope as the larger clusters. The predicted effective surface tension for these clusters (as well as those for $n > 10$) could thus be well approximated by $\Omega = 2 \cdot 17$ extracted from the bulk liquid surface tension.
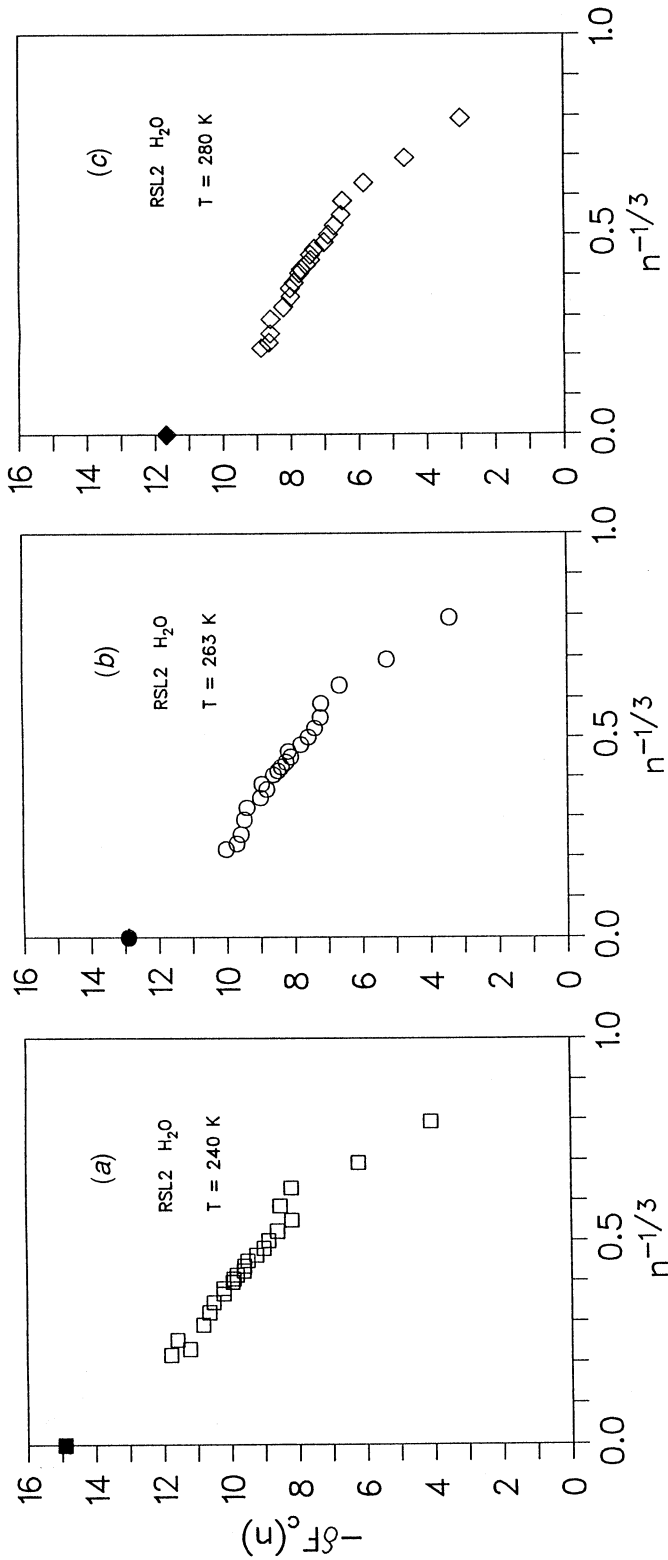
Fig. 3. Configurational Helmholtz free energy differences between n and $n-1$ molecule water (RSL2) clusters versus $n^{-1/3}$ at: (a) $T = 240$ K, (b) $T = 263$ K and (c) $T = 280$ K. The point at $n = \infty$ (filled symbol) is the experimental value of I_0 for water at 240, 263 and 280 K respectively. The points correspond to $n = 2$–15, 18, 20, 24, 30, 40, 60, 80 and 96.

The model water cluster results at $T = 240$, 263 and 280 K are shown in Fig. 3. The experimentally predicted intercepts (solid symbols at $n = \infty$) are surprisingly consistent with the calculated data. For the model RSL2 water clusters care must be taken concerning T_c, as the RSL2 potentials could produce a different critical temperature. (A rough estimate of $T_c^{RSL2} \approx 755 \pm 100$ K can be extracted from the present small cluster results.) But with $-\delta F_c$ at three temperatures, one can test for consistency with the temperature dependence of A in (13) and examine how well the experimental value for $T_c = 647$ K fits the data. The following analysis is motivated by the success of the scaled form for A in predicting nucleation rates (Hale 1982, 1986, 1988, 1992a, 1992b; Hale and Kemper 1989; Hale and Kelly 1992) and is justified in part by the observation that the experimental intercepts I_0 are also nearly proportional to $(T_c^{exp}/T - 1)$. For example, at $T = 240$, 263 and 280 K (where the experimental values of I_0 are $14 \cdot 9$, $12 \cdot 9$ and $11 \cdot 7$ respectively) the values of $I_0/(T_c^{exp}/T - 1)$ reduce to $8 \cdot 79$, $8 \cdot 84$ and $8 \cdot 89$ respectively. So one expects that both the intercept and the slope in (12) are proportional to $(T_c/T - 1)$. In Fig. 4 the results for all three temperatures for the model water clusters are plotted as $-\delta F_c/(T_c/T - 1)$ using the experimental T_c. The calculated values appear to collapse onto a single set of scaled free energy differences, suggesting a universal T dependence similar to
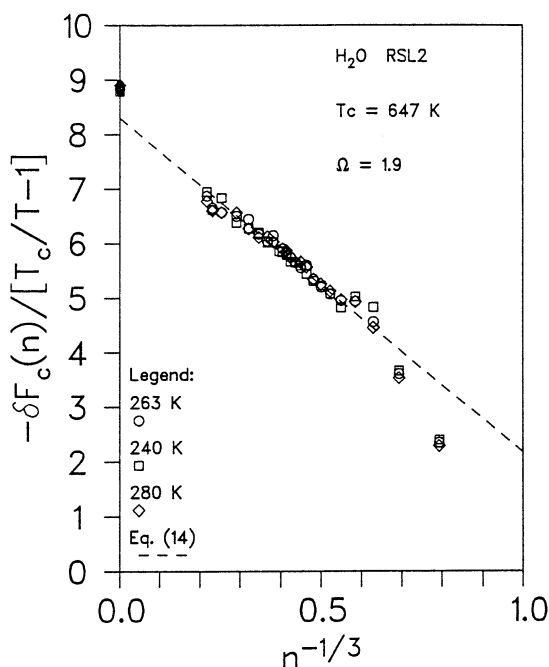

Fig. 4. Configurational Helmholtz free energy differences between n and $n-1$ molecule water (RSL2) clusters scaled with $(T_c^{exp}/T - 1)$ versus $n^{-1/3}$ at $T = 240$, 263 and 280 K. The dashed line is $8 \cdot 8 - \frac{2}{3}(36\pi)^{1/3}\Omega n^{-1/3}$, where $T_c^{exp} = 647$ K and $\Omega = 1 \cdot 9$. The points at $n = \infty$ (filled symbols) are the experimental values of $I_0/(T_c^{exp}/T - 1)$ for water.

equation (13). The scaled form for the $\delta F_{\mathrm{c}}(n)$ is shown in (14) from which (with $T_{\mathrm{c}} = 647$ K) one can extract $\Omega = 1 \cdot 9$, a value close to that for argon,

$$-\delta F_{\mathrm{c}} \approx I_0 - \tfrac{2}{3}(36\pi)^{\frac{1}{3}}\Omega\left(\frac{T_{\mathrm{c}}}{T} - 1\right)n^{-\frac{1}{3}}. \tag{14}$$

The predicted effective surface tension for the small clusters is $\approx 99 \ \mathrm{mN\,m^{-1}}$ at $T = 283$ K. If the $-\delta F_{\mathrm{c}}$ for $n > 192$ follow the pattern in Fig. 4 and approach the experimental value of the intercept at $n = \infty$, one would estimate a bulk liquid surface tension for RSL2 water of $\approx 99 \ \mathrm{mN\,m^{-1}}$ at $T = 283$ K. The experimental value is $74 \ \mathrm{mN\,m^{-1}}$. Unfortunately, other calculated values for the surface tension of model RSL2 water are not available for comparison. In any case the results presented in Figs 2 and 3 indicate that the small cluster slope of $-\delta F_{\mathrm{c}}$ (or Ω value) should be close to the larger (approaching bulk) cluster value.

4. Comments and Conclusions

The configurational free energy differences for both model argon and model RSL2 water clusters indicate that an effective surface tension for the small clusters can be approximated from $\sigma/kT\rho_{\mathrm{liquid}}^{2/3} \approx \Omega(T_{\mathrm{c}}/T - 1)$ and that clusters down to about 10 molecules (atoms) appear to be well approximated by the bulk (large) cluster values. The data for the model RSL2 water clusters are consistent with $\Omega = 1 \cdot 9$ and a critical temperature close to the experimental value, 647 K. These results suggest in part a theoretical corroboration of the scaling law, $\ln S_{\mathrm{crit}} \approx 0 \cdot 53 \left[\Omega(T_{\mathrm{c}}/T - 1)\right]^{3/2}$, where $S_{\mathrm{crit}} \equiv P/P_0$ is the onset supersaturation ratio for formation of liquid embryos from the vapour (Hale 1982, 1986). Here P is the ambient pressure and P_0 is the equilibrium vapour pressure at temperature T. The fact that the smallest clusters display a fairly uniform representation in terms of $A = (36\pi)^{1/3}\Omega(T_{\mathrm{c}}/T - 1)$ indicates that one should be able to apply this surface energy term in the calculation of nucleation rates down to clusters of the order of 10 molecules or atoms. The effective surface tension for the small RSL2 water clusters is $\approx 99 \ \mathrm{mN\,m^{-1}}$ at 283 K. This value is larger than the experimental bulk liquid surface tension for water, $74 \ \mathrm{mN\,m^{-1}}$. The RSL2 potential has no quadrupole moment and (consisting as it does of three point charges) a tendency to produce less order in the surface layer and in the bulk. This effect could increase the value of Ω (and hence the surface tension). Some preliminary calculations using the ST2 potential (Stillinger 1975) which has a quadrupole moment indicate that the Ω values are smaller. Similar calculations of small cluster effective surface tension are in progress using TIP4P (Jorgensen et al. 1983), another four site water–water potential. The RSL2 potential is also known to produce too large an internal pressure at a density of $1 \ \mathrm{g\,cm^{-3}}$. If this increase in pressure is also found for the RSL2 vapour pressure our data should predict an intercept, as $n \to \infty$, smaller than the experimental value. In Fig. 4 one can see that this is the case for the RSL2 clusters. If all of the discrepancy were attributed to the vapour pressure it would imply that the vapour pressure for the RSL2 potentials is about a factor of 2 larger than the experimental value for both 263 and 280 K. Finally, it is interesting to note that the Ω parameter is nearly the same for both the Lennard-Jones argon clusters $(2 \cdot 1)$ and the RSL2 water clusters $(1 \cdot 9)$.

Acknowledgments

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