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Use of a Cubic Equation to Predict Surface Tension and Spinodal Limits

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The very general Shamsundar-Murali cubic equation is used to interpolate p–v–T *data into the metastable and unstable regions. This yields a spinodal line that closely matches the homogeneous nucleation limit predicted by an improved kinetic theory. Only the pressure, the saturated liquid and vapor volumes, and the liquid compressibility at saturation, as well as one compressed liquid data point, are needed to use the cubic equation for the interpolation process. The equation also yields an accurate prediction of the temperature dependence of surface tension when it is substituted in van der Waals' surface tension formula. Thus, by capitalizing on the inherent relation among the* p–v–T *equation, the spinodal prediction, and the surface tension – all three – it is possible to obtain each with high accuracy and minimal experimental data.*

Introduction

Surface tension is intimately related to the metastable and unstable fluid states, and to the $p-v-T$ equation that describes these states. The aim of this study is to use this interrelation to assist in the development of means for estimating and predicting both $p-v-T$ and surface tension data. We therefore begin by reviewing the character of this relationship.

Surface Tension and the Equation of State. It was shown in 1894 by van der Waals [1] that the temperature dependence of surface tension could be predicted precisely by the expression

$$\frac{\sigma}{\sigma_0}=f(T_r)=\int_{v_{r_f}}^{v_{r_g}}\frac{1}{v_r^{5/2}}\left[p_{r,\text{sat}}(v_r-v_{r_f})-\int_{v_{r_f}}^{v_r}p_r dv_r\right]^{1/2}dv_r \quad (1)$$

where σ is the surface tension; T_r, p_r, and v_r are the reduced[3] temperature, pressure, and volume: and where g and f denote saturated vapor and liquid values. The constant σ_0 is a reference value of the surface tension which van der Waals showed how to evaluate in terms of molecular properties. (No one to date has managed to make accurate evaluations of σ_0.)

Little has been done with equation (1) because its use requires a full knowledge of $p-v-T$ information throughout the metastable and unstable fluid regimes (see Fig. 1). van der Waals used his own famous equation of state in equation (1) and – without the aid of a computer – succeeded in making an approximation valid only near the critical point:

$$\lim_{T_r\to 1}\sigma=\frac{16}{\sqrt{6}}\sigma_0(1-T_r)^{3/2} \quad (2)$$

Recent studies (see, e.g., [2]) of the variation of σ with T_r near the critical point suggest that

$$\lim_{T_r\to 1}\sigma\propto(1-T_r)^{1.28 \text{ or } 1.29} \quad (3)$$

gives a more plausible temperature dependence for real fluids than equation (2). It is also known that a form of equation (2) with an exponent of 11/9, or 1.22, represents a wide variety of fluids pretty well at lower temperatures.

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[3]A "reduced" property is one divided by its thermodynamic critical value.
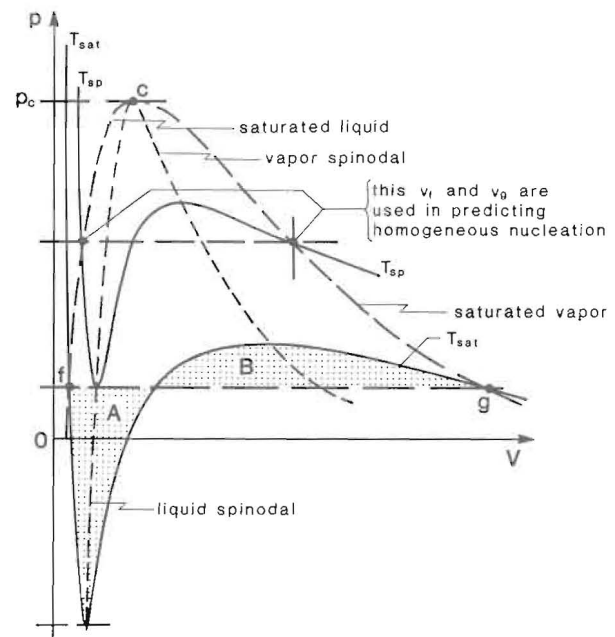
Fig. 1 Typical real-fluid isotherms

On Locating the Spinodal Line. A knowledge of the location of the liquid and/or vapor spinodal lines can be particularly helpful in the process of developing the $p-v-T$ equation of state that is needed to complete the integration of equation (1). In 1981, Lienhard and Karimi [3] provided molecular arguments that showed that the liquid spinodal limit[4] could be predicted quite accurately by homogeneous nucleation theory. They also showed that this was not true for the vapor spinodal limit [3, 4]. Vapor spinodal lines lie nowhere near the limit of homogeneous nucleation for vapors.

In the course of their work, Lienhard and Karimi used the conventional homogeneous nucleation expression

$$j\frac{\text{nucleation events}}{\text{molecule collisions}}=e^{-\text{Gb}} \quad (4)$$

[4]The spinodal limit is the locus of points at which $(\partial p/\partial v)_T$ is zero (see Fig. 1).

where[5]
$j \equiv$ probability of nucleating a bubble in a given collision (5)
and

$$Gb \equiv Wk_{crit}/(kT \text{ or } kT_c) \tag{6}$$

and (see e.g. [5])

$$Wk_{crit} = \frac{16\pi\sigma^3}{3[p_{sat}(T_{sp}) - p]^2(1 - v_f/v_g)^2} \tag{7}$$

Notice that in equation (6) we suggest that the Gibbs number Gb should be a ratio of the critical work required to form a nucleus to either kT or kT_c. The conventional nucleation theory is based on the average kinetic energy of the surrounding molecules, which is on the order of kT. However, it was noted in [3] that the energy required to separate molecules from one another is on the order of kT_c. This seemed to be an equally plausible candidate for the characteristic energy of the system.

When equations (4), (6), and (7) are combined, we obtain the following expression for the homogeneous nucleation pressure p corresponding with a given temperature T_{sp}

$$-\ln j = \frac{16\pi\sigma^3}{3(kT \text{ or } kT_c)[p_{sat}(T_{sp}) - p]^2(1 - v_f/v_g)^2} \tag{8}$$

where v_f and v_g are to be evaluated at T_{sp}. Two issues remained: identifying the value of j that will give the spinodal limit, and deciding whether to use kT or kT_c.

Lienhard and Karimi next curve-fit cubic equations to the well-documented stable equilibrium states of water, constraining them to satisfy the "Gibbs–Maxwell" requirement that

$$\int_f^g v dp = 0 \tag{9}$$

which stipulates that the two regions between an isotherm and a horizontal line connecting f and g must be equal to one another in area (e.g., Area A in Fig. 1 equals area B). They chose the Himpan form [8] of cubic equation

$$p_r = \frac{A}{v_r - b} - \frac{a}{(v_r - c)(v_r + d)} \tag{10}$$

and evaluated all five constants using least squares fit. They re-evaluated the constants for each of many isotherms.

There were two weaknesses in this curve-fit procedure. The first is that equation (10) was not forced to fit the ideal gas law precisely at high temperatures. The second is that the Himpan form turns out to be slightly restrictive. We remedy these features subsequently.

Equation (10) with the five statistically fitted constants gave interpolated liquid spinodal pressures that showed some numerical data scatter. These pressures corresponded very

[5] Actually, it is more common (see Skripov [5, 6] and Avedisian [7]) to use J instead of j. J is equal to j multiplied by the rate of molecular collisions per cubic centimeter. For water, J is about 10^{39} times j in these units.

closely to the homogeneous nucleation pressures given by equation (8) with $j = 10^{-5}$ and with kT_c used as the characteristic energy. The interpolations *did not* come close to equation (8) when the conventional energy kT was used. (The minimal value of $j = 10^{-5}$ was not purely empirical. Molecular arguments in [3] fixed it within an order of magnitude or so.)

It is important to note that when these arguments are applied to the vapor spinodal [3] they show that the limit of homogeneous nucleation of droplets is far from the vapor spinodal limit.

A New Form of Cubic Equation for Fitting p-v-T Data. Shamsundar and Murali [9, 10] have recently made effective use of the following general form of cubic equation in fitting individual isotherms

$$\frac{p}{p_{sat}} = 1 - \frac{(v - v_f)(v - v_m)(v - v_g)}{(v + b)(v + c)(v + d)} \tag{11}$$

The quantities p_{sat}, v_f, v_m, v_g, b, c, and d all vary with temperature. This form has the advantage that it automatically satisfies critical point criteria, but it need not be tied to them. It is also prefactored to simplify fitting the constants.

Three of the coefficients in equation (11) are the known temperature-dependent properties: p_{sat}, v_f, and v_g. Thus the most straightforward use of the equation is one in which it is fit to one isotherm at a time.

Murali simplified equation (11) by setting $c = d$ and thereby reducing the number of unknown coefficients to three. These three coefficients were determined by imposing the following three conditions on the equation: the ideal gas limit at low pressures, the Gibbs–Maxwell condition, and the measured isothermal compressibility of saturated liquid. He thus evaluated the coefficients of the equation directly (rather than statistically) using very few data.

The condition under which equation (11) reduces to the ideal gas law, by the way, is

$$\frac{RT}{p_{sat}} = b + c + d + v_f + v_m + v_g \tag{12}$$

This kind of temperature-by-temperature application of equation (11) yielded far higher accuracies [10] than any existing cubic equation, particularly in the liquid range. The equation also performs extremely well in the stable superheated vapor range. The key to this success is, of course, the fact that the coefficients do not have to obey any predetermined dependence on temperature.

An Illustrative Application of the Preceding Ideas. Information of the kind we have been describing can be used to expand existing knowledge. Karimi, for example, developed a new fundamental equation [11] for water, based in part on his interpolations. When this fundamental equation was used to generate p-v-T data for use in equation (1), the resulting values of σ/σ_0 lay within 4.3 percent of measured values over all but the lowest range of saturation temperatures. This was

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—————— Nomenclature ——————

A, a, b, c, d = undetermined constants in the various cubic equations
Gb = Gibbs number (see equation (6))
j = nucleation probability, equation (5)
J = j expressed as a rate per unit volume
k = Boltzmann's constant
p = pressure
T = temperature
v, v_f, v_g = specific volume, saturated liquid volume, saturated vapor volume
v_m = v at the root of a cubic p-v-T equation between v_f and v_g

σ, σ_0 = surface tension, undetermined reference value of σ
ω = the Pitzer acentric factor, $-1 - \log_{10} p_{r,sat}$ ($T_r = 0.7$)

Superscripts and Subscripts

c = a property at the critical point
f, g = saturated liquid or vapor properties
r = a "reduced" property ($X_r \equiv X/X_c$)
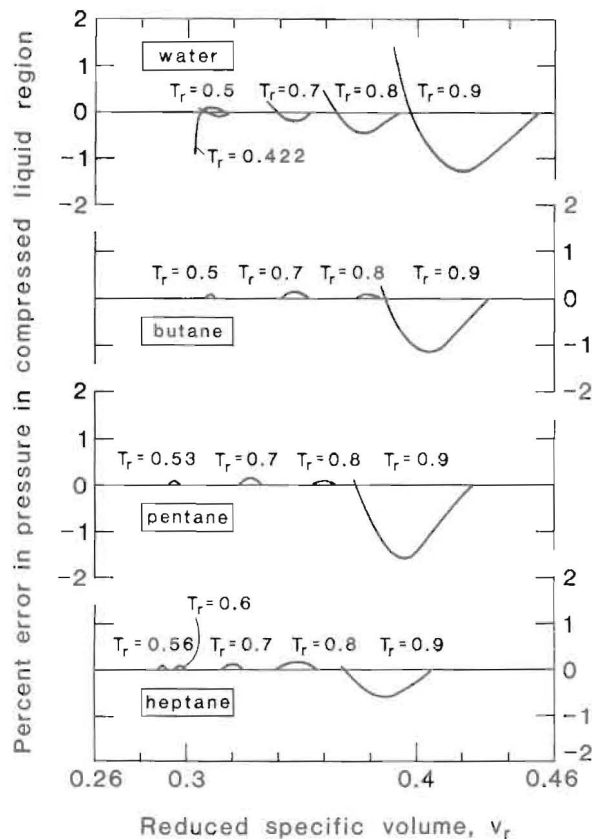sat = a property at a saturation condition
sp = a property at a spinodal point

Fig. 2 Typical values of the error in pressure as predicted by cubic p–v–T equation curve-fitted to four data points

Fig. 3 Comparison of the spinodal limit of water as predicted by homogeneous nucleation theory and by the general cubic equation

the first and only such use of the van der Waals surface tension theory to verify p–v–T information, to our knowledge, and it displays the potential interaction of σ and p–v–T information.

Present Objectives. The availability of Shamsundar and Murali's new method for interpolating isotherms gives means for substantially improving upon the work in [3] and for reopening the two questions: (1) "Is kT_c a better characteristic energy than kT?" (2) "What minimum value of j gives the spinodal limit when it is used in equation (8)?"

We therefore address these matters using van der Waals' surface tension prediction as a hitherto little-used validity check.

Isothermal Curve Fits

We altered two of Murali's assumptions: We did not use the assumption that $c = d$. This increased the number of unknown coefficients by one, but stood to improve the accuracy of the resulting equation. The second alteration dealt with the restrictive form of the denominator of equation (11) $(v + b)$ • $(v + c)$ $(v + d)$. In this form the equation is restrictive if b, c, and d are to be real. This implication was relaxed by writing the denominator in the form $(v + a)$ $(v^2 + fv + g)$ where $f = b + c$ and $g = bc$ [9]. This form allows b and c to be complex without using complex numbers explicitly.

To complete the curve fit we needed one more condition than Murali did since we chose not to set $c = d$. For this we selected a high-pressure liquid point. We identified the pressure that made the isotherm best fit the available data for stable liquid and vapor states by trying several pressures until we found the one that worked best. For water this pressure proved to be about 800 bars, or a reduced pressure of about 3.7, although substantially higher or lower values worked almost as well. Data from the IFC Formulation for Scientific Use [12] were used to do this.
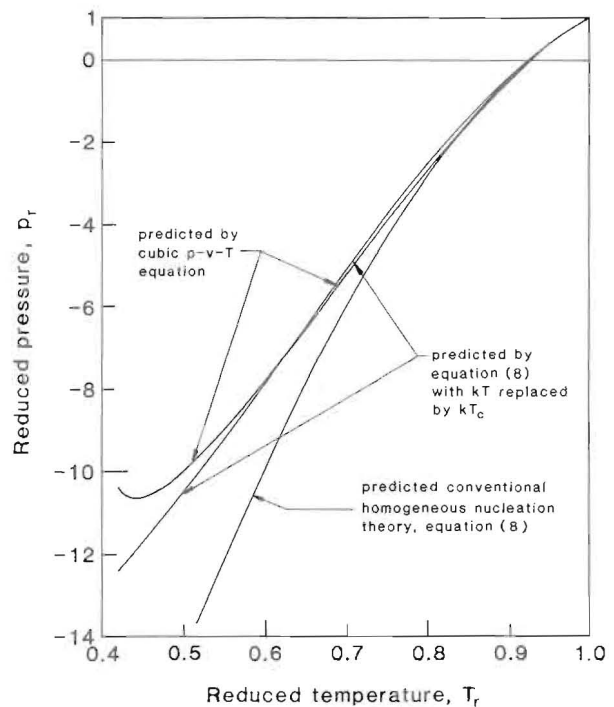
When the four conditions were applied to the cubic equation (11) they yielded four nonlinear equations which we solved using the method of successive substitutions and linear interpolation.

We made sets of isothermal curve fits for water and for several straight-chain hydrocarbons. For the straight-chain hydrocarbons, we used the data of Starling [13] as curve-fitted by Reynolds [14], where we could. (However, in a few cases the Starling data for liquids disagreed with API data [15] or the data of Vargaftik [16].) These were the only substances for which we could readily obtain reliable p–v–T and surface tension data [15, 16, 17] over broad ranges of temperature. In all cases, the high-pressure p–v–T data point used in the curve fit was the value at $p_r = 5$.

We also looked at ammonia, argon, benzene, carbon dioxide, methane, hydrogen, oxygen, and nitrogen for which we did not have complete data over large ranges. In these cases curve fits were only made at one temperature each. The data sources for these cases were [16, 17, 18].

The fluids considered here resolve roughly into two classifications: those for which we are confident of the accuracy (water, oxygen, hydrogen, nitrogen, butane, heptane, pentane, and propane) and those for which we found some level of unresolvable disagreement in the relevant properties (ammonia, argon, benzene, carbon dioxide, ethane, hexane, methane, and octane). In the subsequent discussions we take care to base our conclusions only on the results obtained in the former fluids.

Figure 2 shows the resulting errors of the cubic interpolations for several typical fluids. These plots of error in the predicted pressure, at selected values of T_r in the liquid range, reflect a very severe test of the curve fits. They consistently show errors substantially less than one percent, at reduced temperatures below 0.9.

Liquid Spinodal Limits

Figure 3 compares the spinodal limit of water as predicted by our cubic equation with the predicted spinodal limit based on equation (8). The NBS surface tension recommendation [19] was used in this calculation. (The value of j used in Fig. 3
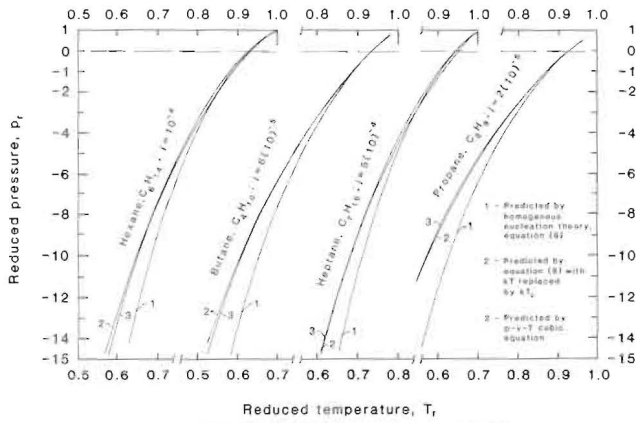
Fig. 4 Comparison of the spinodal limit of several fluids as predicted by homogeneous nucleation theory and by the general cubic equation

Fig. 5 Comparison of the values of $\sqrt{-\ln(j)}$ for which equations (8) and (11) agree exactly

was 2×10^{-5}. We return to the question of specifying j below.) The agreement is very good when kT_c is used in place of kT in the equation, except at such low temperatures and high liquid tensile stresses that both theories are being pushed to the edge of their limits of applicability. The choice between kT and kT_c makes little difference in the region of positive pressure, and this is the only region in which nucleation experiments have ever been made for large j. At lower pressures the two diverge very strongly.

Our suggestion that kT be replaced with kT_c is largely based on this kind of extrapolation. This kind of demonstration was made less conclusively (with the less flexible Himpan equation) in [3]. The present evidence is very compelling indeed.

Several other such comparisons are given in Fig. 4 for butane, heptane, hexane, and propane. (Since surface tension data were not available for butane and propane over the entire range of temperature, the missing values had to be filled in with the help of equation (1) in these cases.) In each case, we have used a limiting value of j that best fits the extrapolation. These j's do not all match the value of 2×10^{-5} used for water.

The four fluids selected for display in Fig. 4 were chosen because they embrace a wide range of j values. By the same token, the four fluids shown in Fig. 2 were selected because they typified the error of the many fluids that have been fitted.

The results of an inverse kind of calculation are shown in Fig. 5. Values of $\sqrt{-\ln(j)}$, which is inversely proportional to the pressure difference between saturation and the liquid spinodal line, were calculated at each point using equation (8), with kT_c, and the pressure difference predicted by equation (11).

Figure 5 strongly suggests that a "best value" of j for the spinodal limit – if one truly exists – is one slightly in excess of 10^{-5}, in preference to 10^{-5} which was previously suggested [3]. It is clear that these j limits are fairly sensitive to the accuracy of the data upon which they are based. Thus, in choosing the appropriate limiting value, one must be guided strongly by water and the other very well-documented fluids.

One must also consider whether or not these j values were obtained in regimes in which the cubic equation is truly very accurate. Figure 2 makes it clear that the general cubic equation interpolations begin to lose precision at very high temperatures – typically before $T_r = 0.9$. It also becomes apparent in the subsequent section that, although it interpolates stable properties very accurately at low temperatures, equation (11) probably fails to represent metastable and unstable properties with very high accuracy at low temperatures. This is evident in its failure to predict the temperature dependence of surface tension with high accuracy below $T_r \cong 0.5$.

We accordingly restrict the plots in Fig. 5 to the range $0.5 < T_r < 0.85$, or to a smaller range in which reliable data are
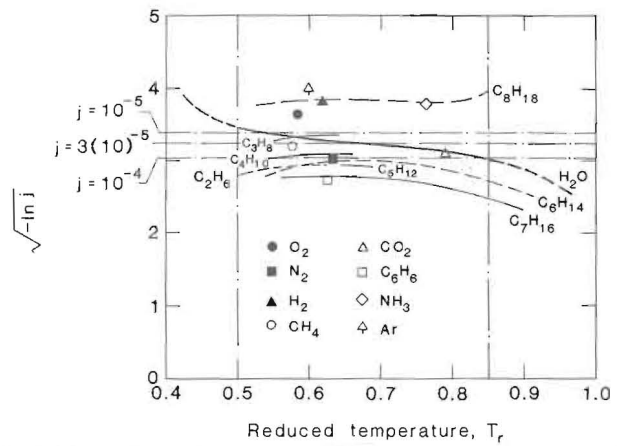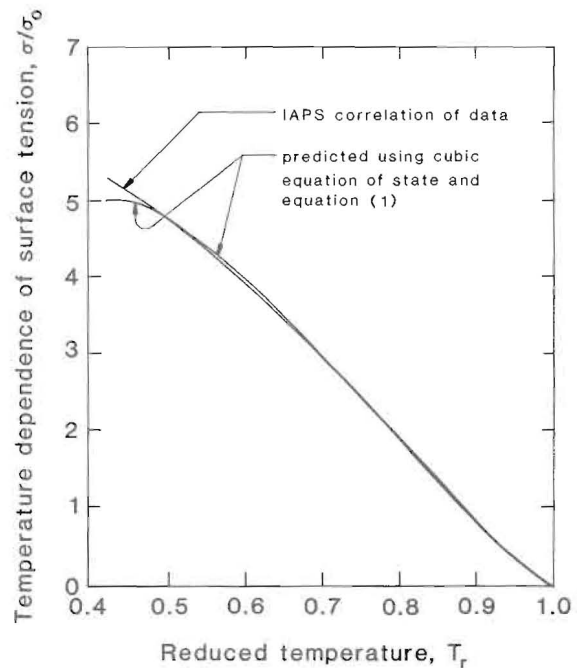

Fig. 6 Predicted and measured temperature dependence of the surface tension of water

available. Furthermore, we suggest that the middle temperature range in Fig. 5 is the most reliable. We have averaged the ordinate values of the more reliable data in Fig. 5, giving water double weight, to obtain the recommendation that

$$j_{\text{spinodal}} \cong 3 \times 10^{-5}$$

This is just a little higher than the values of (1 or 2) $\times 10^{-5}$, used previously. However this must be accompanied by the warning that we might eventually have to admit some dependence of the limiting j on T_r and the fluid. (Of course 3×10^{-5} is an approximation that one would only want to use if better information about j were unavailable.)

Notice, too, that replacing kT with kT_c was a pretty revolutionary suggestion. The modification of j by even so much as an order of magnitude, on the other hand, is far less important because most calculations based on j are very insensitive to its value.

Prediction of Surface Tension

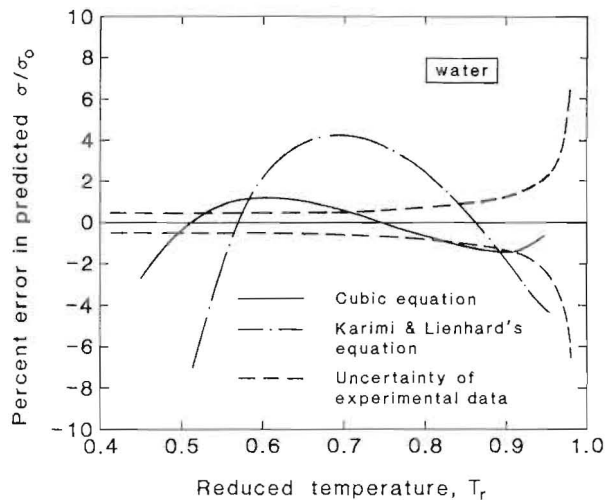The acid test of any p–v–T equation that purports to predict

Fig. 7 Accuracy of the predicted temperature dependence of the surface tension of water, based on the present cubic interpolations of p-v-T data, and upon Karimi's fundamental equation
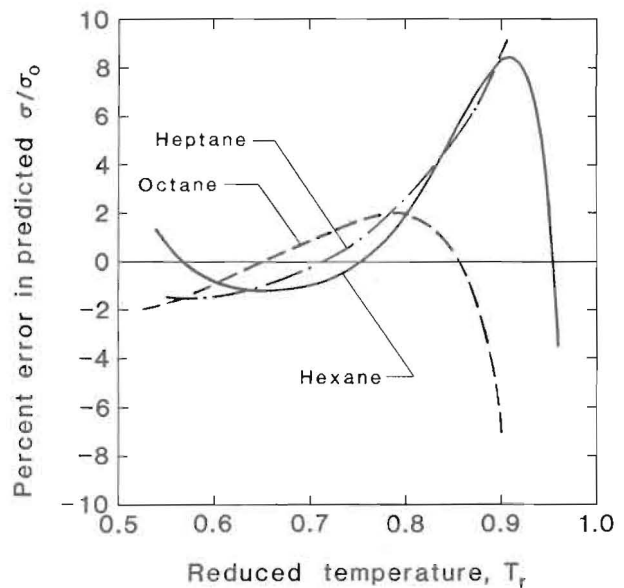

Fig. 9 Accuracy of the predicted temperature dependence of the surface tension of three fluids, based upon the present cubic interpolations of p-v-T data
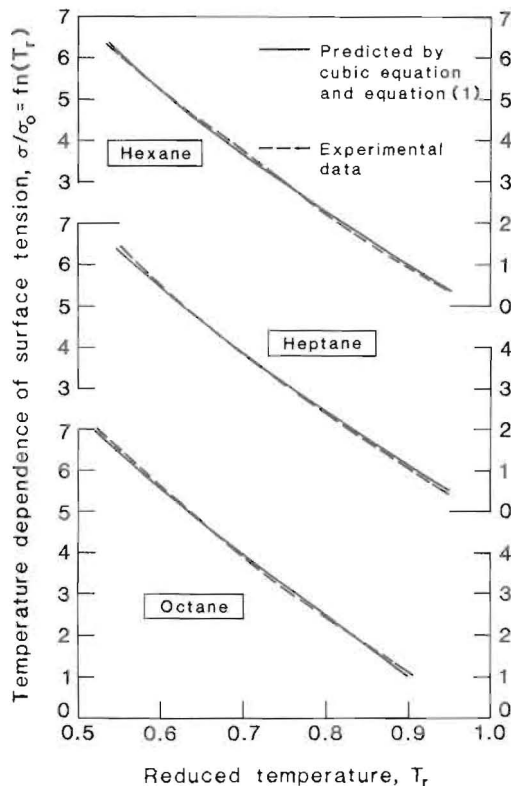

Fig. 8 Predicted and measured temperature dependence of the surface tension of three fluids

Fig. 10 Corresponding states correlation of the surface tension lead constant

metastable and unstable properties is whether or not it correctly predicts the temperature dependence of surface tension when it is used in van der Waals' equation (1). We have subjected our cubic equations for water to this test at each temperature, and the results are shown in Fig. 6.

Figure 6 makes it quite clear that, except at the very lowest temperatures, this prediction has been extraordinarily successful. Nevertheless, it is this evidence that suggests that, while the cubic fits the low-temperature stable points with great accuracy, it is probably less accurate than we would wish in the metastable-unstable range. Of course, this observation is based on water — the only substance for which we had full data below $T_r = 0.5$, but one which is also known for its strange behavior at low temperatures.
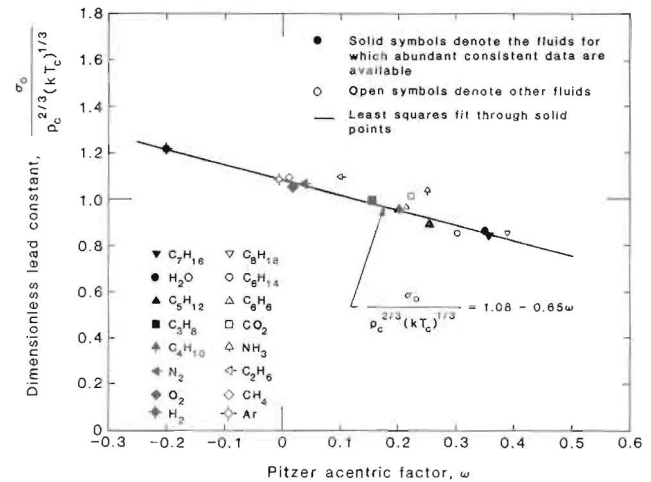
Figure 7 shows the error in the predicted temperature dependence of surface tension, for water. The prediction is very nearly within the reported accuracy of the NBS surface tension data [19] for $T_r \geq 0.5$. The accuracy of Karimi's prediction is also included for comparison.

Figure 8 includes a comparable set of curves for heptane, hexane, and octane, the only fluids besides water for which convincing surface tension data were available over a wide range of temperature [16]. These curves again show that the cubic interpolations give very good predictions of the temperature dependence of surface tension when they are substituted in equation (1). Figure 9 shows the percent error in σ/σ_0 for these fluids. Once again the results are very accurate for $T_r \leq 0.85$.

While equation (1) only predicts σ/σ_0, we would like to be able to predict σ_0 as well. To make the comparisons in Figs. 6 and 8, it was necessary to calculate the average value of σ_0 for each substance, based on the surface tension data. We also computed some values of σ_0 at single points for fluids for which reliable p-v-T and σ data were not available over ranges of temperature.

In 1955, Brock and Bird [20] showed that the appropriate corresponding states nondimensionalization of σ was

$\sigma_0/p_c^{2/3}(kT_c)^{1/3}$. Figure 10 presents the correlation of our σ_0 values as a function of the Pitzer factor ω using this non-dimensionalization.[6] The points based upon the data in which we have high confidence are presented as solid symbols. They define the following correlation

$$\sigma_0/p_c^{2/3}(kT_c)^{1/3} = 1.08 - 0.65\omega \qquad (13)$$

with a correlation coefficient of 0.995. The remaining data are somewhat more widely scattered, but they do not significantly alter the correlation.

Others, starting with Hakim et al. [23], have formed corresponding states correlations for σ that include expressions for σ_0. These can be very useful, but they are normally based on assumed forms of the temperature dependence of σ/σ_0, that differ from that given by van der Waals' integral. Yet, even though these σ_0 expressions might also be linear in ω (as is true in [23]), they do not and should not match equation (13). Equation (13) gives the lead constant specifically for the van der Waals integral.

One can thus predict surface tension with acceptable accuracy for many applications, using p-v-T data alone, with the help of equations (1) and (13). As a matter of academic interest, we can predict a dimensionless σ_0 for the van der Waals equations (for which $\omega = -0.302$). The value is 1.276.

Conclusions

1   It appears possible to interpolate p-v-T data with great accuracy and a minimum of experimental data, using equation (11). The accuracy of such predictions has proven to be best (for the 16 fluids studied) in the range $0.5 < T_r < 0.85$.

2   The limiting value of j for which the homogeneous nucleation theory, equation (8), gives the spinodal limit, is on the order of 3×10^{-5}. However, it might ultimately show some variation from fluid to fluid, or from one saturation condition to another.

3   Further compelling support is provided for the idea (suggested in [3]) that kT_c should be used in equation (8) in place of kT.

4   Equation (1) provides convincing support for the present predictions of metastable and unstable p-v-T data.

5   The lead constant σ_0 in equation (1) is given by equation (13).

6   The Shamsundar–Murali cubic equation has only been used for individual isotherms here. We strongly recommend that the problem of developing general corresponding states correlations to represent the temperature dependence of its coefficients be undertaken in the future.

Acknowledgments

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[6]The Pitzer acentric factor [21], $\omega \equiv -1 - \log_{10} p_{r,\text{sat}} \ (T_r = 0.7)$, is probably the best choice of molecular parameter available for correcting Corresponding States correlations. See, e.g., [22] for a further discussion of recent applications.