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A Relation Between Interfacial and Bulk Properties Along the Saturation Curve

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A liquid–vapor interface in thermal equilibrium was considered, where the pressure tensor depends upon the density $\rho(z)$ and the position z. The surface tension coefficient results are parametrized with the bulk compressibility, liquid–vapor density difference, and interfacial width along the saturation curve. Previous results at the triple and critical points reported by other investigators are verified. Also included is a plot of the computed results using the parametric equation and experimental data for different substances.

KEY WORDS: compressibility; interfacial properties; saturation curve; surface tension.

1. INTRODUCTION

The evaluation of the surface tension of pure fluids may be done through the use of semiempirical relations. Among the most important of these relations are those due to Macleod [1] and Sugden [2]. These relations correlate surface tension and bulk densities. Also, surface tension has been correlated with various other bulk properties such as refractive index, enthalpy of vaporization, viscosity, latent heat of vaporization [3], and compressibility [4]. Near the critical point, Rowlinson and Widom [5] found a relation using the scaling theory between surface tension and bulk quantities. Recently, Moldover [6] reviewed data to estimate the universal amplitude ratios relating the interfacial tension amplitude to the specific heat divergence and to the correlation length near the critical temperature.

In this work, we present an equation relating surface tension and bulk properties for the entire coexistence line. The relation has been derived

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assuming basically that the pressure tensor is an explicit function of the position and of the density profile. Then surface tension becomes related to local compressibility. An analysis near the critical and triple points is given in Section 3. In Section 4 we give a plot, using the experimental values for different substances, of the correlation found for different reduced temperatures.

2. SURFACE TENSION AND COMPRESSIBILITY

Let us analyze a flat liquid–vapor interface, at $z=0$ plane, in thermal equilibrium. Its surface tension, σ, may be defined as

$$\sigma=\int_{-\infty}^{\infty}[p-P_{\mathrm{T}}(z)]\,dz \tag{1}$$

where p is the equilibrium pressure and P_{T} is the tangential component of the pressure tensor $\bar{\bar{P}}$.

We assume from now on that $P_{\mathrm{T}}[z,\rho(z)]$ is an explicit function of the position z and the variable density $\rho(z)$ across the interface [7]. Then,

$$dP_{\mathrm{T}}=(\delta P_{\mathrm{T}}/\delta\rho)_z\,d\rho+(\delta P_{\mathrm{T}}/\delta z)_\rho\,dz$$

Using this equality and integrating Eq. (1) $n+1$ times by parts, we obtain

$$\begin{aligned}\sigma=&\sum_{n=0}^{N}\frac{(-1)^n}{(n+1)!}\int_{-\infty}^{\infty}\left[\frac{\delta^n}{\delta z^n}(\delta P_{\mathrm{T}}/\delta\rho)\right]\rho'\,dz\\&+\frac{(-1)^N}{(N+1)!}\int_{-\infty}^{\infty}z^{N+1}(\delta^{N+1}P_{\mathrm{T}}/\delta z^{N+1})\,dz\end{aligned} \tag{2}$$

It must be kept in mind that $P_{\mathrm{T}}[z,\rho(z)]$ approaches p for the bulk phases.

The surface tension given by Eq. (2) is functionally dependent upon $(\delta P_{\mathrm{T}}/\delta\rho)$ and $\delta^n/\delta z^n(\delta P_{\mathrm{T}}/\delta\rho)$ for $n\leqslant N$ as well as $(\delta^{N+1}P_{\mathrm{T}}/\delta z^{N+1})$.

Let us, now apply Eq. (2) to investigate the surface tension along the saturation curve. To do that, we assume the following behavior for $\rho(z)$ [8] and $(\delta P_{\mathrm{T}}/\delta\rho)$:

$$\rho(z)=a+bf_1(z/L) \tag{3}$$

$$(\sigma P_{\mathrm{T}}/\delta\rho)=A+Bf_2(z/L) \tag{4}$$

where

$$a=\frac{(\rho_{\mathrm{L}}+\rho_{\mathrm{V}})}{2},\qquad b=\frac{(\rho_{\mathrm{L}}-\rho_{\mathrm{V}})}{2}$$

$$A=\frac{1}{2}\left(\frac{1}{\rho_{\mathrm{L}}\kappa_{\mathrm{L}}}+\frac{1}{\rho_{\mathrm{V}}\kappa_{\mathrm{V}}}\right),\qquad B=\frac{1}{2}\left(\frac{1}{\rho_{\mathrm{L}}\kappa_{\mathrm{L}}}-\frac{1}{\rho_{\mathrm{V}}\kappa_{\mathrm{V}}}\right)$$

and ρ_L, ρ_V, κ_L, and κ_V are the liquid and vapor densities and corresponding isothermal compressibilities, respectively. The functions f_1 and f_2 are such that

$$\lim_{z \to \pm\infty} f_1(z/L) = \lim_{z \to \pm\infty} f_2(z/L) = \pm 1$$

In the dimensionless functions f_1 and f_2 given by Eqs. (3) and (4), the temperature enters essentially only through the interfacial width L.

Substitution of Eqs. (3) and (4) into Eq. (2) gives

$$\sigma = bALI_{00} + bBL \sum_{n=0}^{N} \frac{(-1)^n}{(n+1)!} I_n + \frac{(-1)}{(N+1)!} \int_{-\infty}^{\infty} z^{N+1} \frac{\delta^{N+1} P_T}{\delta z^{N+1}} \, dz \tag{5}$$

where

$$I_{00} = \int_{-\infty}^{\infty} \frac{\delta f_1(\varepsilon)}{\delta \varepsilon} \varepsilon \, d\varepsilon$$

and

$$I_n = \int_{-\infty}^{\infty} \frac{\delta f_1(\varepsilon)}{\delta \varepsilon} \frac{\delta^n f_2(\varepsilon)}{\delta \varepsilon^n} \varepsilon^{n+1} \, d\varepsilon$$

Taking into account the condition of zero adsorption at the interface,

$$\int (\rho(z) - \rho_V) \, dz = \int [\rho_L - \rho(z)] \, dz$$

with the boundary condition

$$\lim_{z \to +\infty} [\rho_L - \rho(z)] z = \lim_{z \to -\infty} [\rho(z) - \rho_V] z = 0$$

then I_{00} vanishes (this condition is fulfilled by the Fisk–Widom, ERF, and hyperbolic tangent profiles).

If we assume that $P_T[z, \rho(z)]$ can be given by

$$P_T[z, \rho(z)] = \sum_{i=0}^{N} A_1[\rho(z)] z^1$$

then the last term in Eq. (5) becomes zero; then this equation can be rewritten as

$$\sigma = K(\rho\rho_L - \rho_V) \left(\frac{\rho_L}{\rho_L^2 \kappa_L} - \frac{\rho_V}{\rho_V^2 \kappa_V} \right) L \tag{6}$$

where

$$K = \frac{1}{4} \sum_{n=0}^{N} \frac{(-1)^n}{(n+1)!} I_n$$

This is the relation we sought. It relates surface to bulk properties along the whole saturation curve.

3. TRIPLE AND CRITICAL POINTS

We study, using Eq. (6), the two extreme points of the saturation curve, namely, the triple and the critical points.

Near the triple point ρ_V as well as $(\delta p/\delta \rho)_V$ is taken as zero. Then, Eq. (6) reduces to

$$\sigma \kappa_L = KL \tag{7}$$

This equation, relating the surface tension to the isothermal compressibility via the interfacial width, was obtained earlier [9–12]. Using experimental data, it is observed that this product is equal to a few tenths of an angstrom [9].

Now let us look at the critical region. As is known, many classical equations of state near the critical point (e.g., Van der Waals) have a symmetric behavior with respect to the product $\rho^2 \kappa$ at the coexistence curve, that is, $\rho_L^2 \kappa_L = \rho_V^2 \kappa_V$. Also, experimental observation [5] suggests the validity of the above relation. Then Eq. (6) becomes

$$\sigma = K \frac{(\rho_L - \rho_V)^2}{\rho_L^2} \frac{L}{\kappa_L} \tag{8}$$

Near the critical point, each one of the parameters entering in Eq. (8) scales with the reduced temperature: the density difference $\rho_L - \rho_V$ vanishes as $(T_c - T)^\beta$, the compressibility κ as $|T - T_c|^{-\gamma}$, the interfacial thickness diverges as $(T_c - T)^{-\nu'}$, and the surface tension σ vanishes as $(T_c - T)^\mu$. Replacing these relations in Eq. (8), the following scaling equation is obtained:

$$\mu = 2\beta - \nu' + \gamma \tag{9}$$

Now if the interfacial thickness [13, 14] scales linearly with the correlation length as $\xi_0 = (T - T_c)^{-\nu}$, then $\nu = \nu'$ and Eq. (9) becomes

$$\mu = 2\beta - \nu + \gamma \tag{10}$$

A full discussion of the validity of these equations can be found in the literature [5, 14–17].

The surface tension dependency on the density variation near the critical region is established by replacing Eq. (10) and the power temperature laws into Eq. (8), giving $\sigma=(\rho_L-\rho_V)^{\mu/\beta}$. This is the Macleod relation when $\mu/\beta=4$. The mean field theory predicts $\mu/\beta=3$, while experiments indicate $\mu/\beta=3.88$.

4. EXPERIMENTAL DATA ANALYSIS

Variation of the quantity KL obtained from Eq. (6) for different substances as a function of the reduced temperature $t=(T-T_t)/(T_t-T_c)$, where T_t is the temperature at the triple point, is shown in Fig. 1.

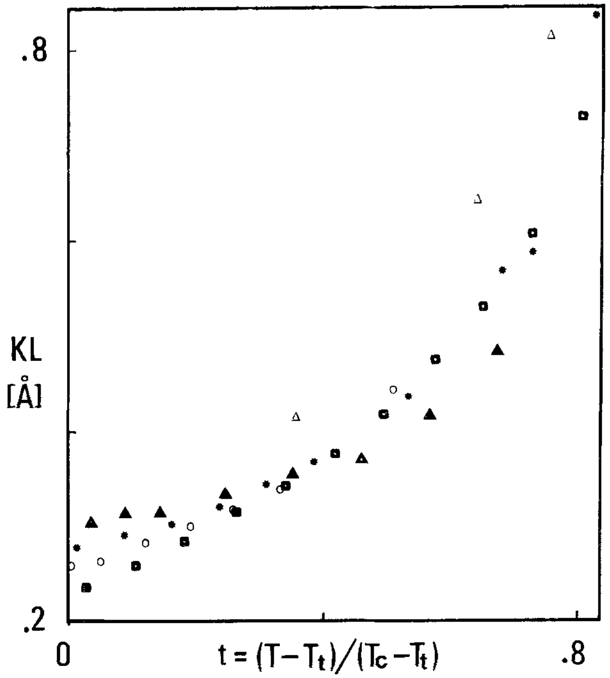

Fig. 1. Values of $KL=\sigma/[(\rho_L-\rho_V)(1/\rho_L\kappa_L-1/\rho_V\kappa_V)]$ for different fluids as a function of the reduced temperature from the triple to the critical points. Only some of the values near the triple point are included. A more extensive review of the experimental data for this region can be found in Refs. 4 and 9. The symbols represent the following substances: $*$, Ar; ●, Ne; ○, C_6H_6; ▲, Kr; △, CO_2.

The sources of the experimental data for the different substances are as follows.

Surface tension: argon and nitrogen [18], carbon dioxide [19], benzene [20, 21], and krypton [22].

Densities and compressibilities: argon [23–25], nitrogen [23, 26], carbon dioxide [27, 28]; benzene [23, 29]; and krypton [22, 25, 30].

5. COMMENTS

The theory proposed here provides a relation [Eq. (6)] between interfacial properties σ and L and bulk properties ρ and κ along the whole coexistence line. In the literature, relations between these variables are reported [4], at the triple point [9–12] and near the critical point [6, 8–13].

Near the critical point we found that the surface tension behavior is given by Eq. (8), from which the scaling laws follow [Eqs. (9) and (10)]. Moldover [6] found that the amplitude ratio, obtained from Eq. (8) with $K = 1/7$ [5], slightly overestimates the experimental data.

At the triple point, we obtain Eq. (7), showing that the product of the surface tension and the liquid isothermal compressibility is proportional to the interfacial width. Egelstaff and Widom [9] previously an equation similar to Eq. (7), however, they derived it from an extension, to the triple point, of results obtained from a "squared density-gradient theory of surface tension valid only in the vicinity of the critical point," as has been pointed out by Present [12].

It must be mentioned that the equation $\sigma(\kappa/\rho)^{1/2} = \text{constant}$, derived in Ref. 4, appears to be an invariant for a variety of inorganic, organic, and polymer liquids. This equation seems to be different from Eq. (7), but it reduces to the latter when the interfacial width is introduced.

As can be seen from Fig. 1, the product KL may be expected to be a fundamental length characteristic of the liquid as has been assumed in Eqs. (3) and (4). Earlier, Egelstaff and Widom [9] proposed this idea for points near the triple point.

It can be observed that KL, for all the range of temperature variation for different substances, is of the same order of magnitude. However, for CO_2 the values of KL are significantly different from those for the others. This could be due to the fact that the molecular diameter of CO_2 is bigger than that of the others.

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REFERENCES

1. D. B. MacLeod, *Trans. Faraday Soc.* **19**:38 (1923).
2. S. Sugden, *J. Chem. Soc.* **125**:1177 (1924).
3. A. Sivaraman, J. Zegan, and R. Kobayashi, *Fluid Phase Equil.* **18**:225 (1984).
4. I. C. Sanchez, *J. Chem. Phys.* **79**:405 (1983).
5. J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clavendon Press, Oxford, 1982), Chap. 9.
6. M. R. Moldover, *Phys. Rev. A* **31**:1022 (1985).
7. J. K. Percus, *Chem. Phys. Lett.* **123**:311 (1986).
8. S. Fisk and B. Widom, *J. Chem. Phys.* **50**:3219 (1968).
9. P. A. Egelstaff and B. Widom, *J. Chem. Phys.* **53**:2667 (1970).
10. A. B. Batia and N. N. March, *J. Chem. Phys.* **68**:199 (1978).
11. A. B. Batia and N. N. March, *J. Chem. Phys.* **68**:4651 (1978).
12. R. D. Present, *J. Chem. Phys.* **61**:4267 (1974).
13. A. J. M. Yang, P. D. Fleming, and J. H. Gibbs, *J. Chem. Phys.* **64**:3732 (1976).
14. B. Widom, *Phase Transitions and Critical Phenomena, Vol. 2*, C. Domb and M. S. Green, eds. (Academic Press, New York, 1972), pp. 79–100.
15. B. Widom, *J. Chem. Phys.* **43**:3892 (1965).
16. P. G. Watson, *J. Phys. C* **1**:268 (1968).
17. O. K. Rice, *J. Phys. Chem.* **64**:976 (1960).
18. D. Stanfield, *Proc. Phys. Soc.* **72**:854 (1958).
19. *International Critical Tables* (McGraw–Hill, New York, 1928).
20. G. N. Muratov, *J. Phys. Chem.* **54**:1185 (1980).
21. N. B. Vargaftic, *Tables on the Thermodynamical Properties of Liquids and Gases*, 2nd. ed. (Hemisphere, Washington, D.C., 1975).
22. J. Amoros, J. R. Solana, and E. Villar, *Mater. Chem.* **7**:127 (1982).
23. J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed. (Butterworths, London, 1982).
24. A. Michels, J. M. Levelt, and W. De Graaf, *Physica* **24**:659 (1958).
25. R. D. Weir, I. W. Jones, J. S. Rowlinson, and G. Saville, *Trans. Faraday Soc.* **63**:1020 (1967).
26. S. Angus, B. Armstrong, and K. M. de Reuck, IUPAC Project Centre, *International Thermodynamic Tables of the Fluid State—5* (Pergamon Press, Elmsford, N.Y., 1976).
27. C. A. M. Michels-Veraart, *Some Physical Properties of Compressed Carbon Dioxide* (University of Amsterdam, Amsterdam, 1937).
28. Ref. 26 for carbon dioxide.
29. American Petroleum Institute, Research Project No. 44 (Texas A&M University, College Station).
30. C. Gladun and F. Menzel, *Cryogenics* **10**:210 (1970).