Supersaturation, the Spinodal, and Their Prediction Using Equations of State

Jaime Wisniak[a]; Keren Galon[a]

[a] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

PLEASE SCROLL DOWN FOR ARTICLE

SUPERSATURATION, THE SPINODAL, AND THEIR PREDICTION USING EQUATIONS OF STATE

JAIME WISNIAK* and KEREN GALON

*Department of Chemical Engineering,
Ben-Gurion University of the Negev, Beer-Sheva, Israel*

The equations of state of Redlich-Kwong, Soave, BWR, Schmidt-Wenzel, and Harmens-Knapp have been tested and compared in their ability to predict the spinodal and the experimental limits of superheat of pure liquids. The results indicate that only the Peng-Robinson, Soave and BWR equations are capable of predicting reduced kinetic limits of supersaturation above the experimental ones.

Keywords: Supersaturation; spinodal; equations of state

1. INTRODUCTION

It is widely known that pure liquids can be cooled below their freezing temperature without solidification and that they can be heated above their boiling temperature without vaporization. The phenomenon of superheating is often observed in the laboratory in the bumping that occurs when a liquid is heated in a clean beaker. The phase transition phenomena that occur with a pure substance can be described using the *P-V* diagram given in Figure 1. When an unsaturated liquid (point a) is expanded at constant temperature it will become saturated when the pressure reaches its vapor pressure (point b), the pressure will remain constant along b−2−c, as long as two phases are present, and

---

*Corresponding author. e-mail: wisniak@bgumail.bgu.ac.il
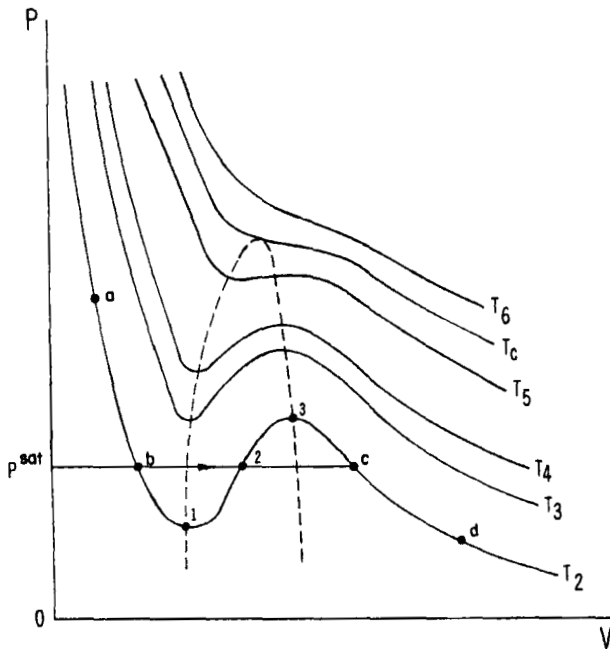
FIGURE 1   Phase transitions of a pure substance.

each intermediate state will be stable. After reaching state c the pressure will then continue to decrease (c−d). The figure shows that the passing from a homogeneous to a heterogeneous state is reflected in a discontinuity in the value of the derivative $(\partial P/\partial v)_T$ at points b (saturated liquid) and c (saturated vapor). A somewhat different picture arises when the phase transition process is described by an equation of state (EOS), particularly a cubic one. As long as the temperature is below the critical, the passing from unsaturated liquid to unsaturated vapor will now be described by a *continuous* curve (a−b−1−2−3−c−d). A given isotherm will now have three points of intersection with the isobar and, in addition, it will present a minimum and a maximum. The descending parts of the isotherm, b−1 and 3−c, correspond to processes of liquid supersaturation and vapor subcooling, which can be realized in practice if the expansion is performed carefully. Both superheated liquids and subcooled vapors constitute systems in *metastable* equilibrium and will evolve to the corresponding stable states if the system is altered in an appropriate form. In

addition, we realize that the portion $1-3$ corresponds to systems that are unstable because for them $(\partial P/\partial v)_T > 0$, a physical impossibility. Hence, we can conclude that all states located between $1-3$ are *intrinsically unstable* for the temperature in question.

The relative position of the actual isotherm and the one described by the EOS can be determined using the Maxwell relations. For a pure substance we have

$$dg = -sdT + vdP \qquad (1)$$

Since the process of evaporation occurs at constant temperature and pressure, it follows that along the horizontal line $b-2-c$ the Gibbs function remains constant while long the curve $b-1-2-3-c$ only T remains constant and therefore,

$$dg = vdP \qquad (2)$$

Integration of Eq. (2) between b and c yields the well-known Maxwell theorem of equal areas

$$g^G(c) - g^L(b) = \int_b^c vdP = 0 \qquad (3)$$

that is, the absolute values of areas $b-1-2-b$ and $2-3-c-2$ must be equal. In terms of reduced properties (P_r, v_r, T_r)

$$P_{rs}\left(v_r^G - v_r^L\right) = \int_L^G P_r(T_{rs}, v_r)dv_r \qquad (4)$$

where indexes s, G, L, represent the saturated state, the gas, and liquid phase respectively. If we use, for example, the van der Waals (vdW) EOS to represent the saturated states then Eq. (4) can be integrated to yield an expression for the reduced vapor pressure of the compound, P_{rs}

$$P_{rs} = \frac{8T_{rs}}{3(v_r^G - v_r^L)}\ln\left[\frac{3v_r^G - 1}{3v_r^L - 1}\right] - \frac{3}{v_r^G v_r^L} \qquad (5)$$

As we have mentioned before, all states located between the maximum and minimum points of the spinodal are intrinsically unstable and their actual location will depend on the particular value of the temperature. The locus of all the maximum and minimum points

constitutes a curve called *spinodal*. In the *P-V* plane the spinodal will be obviously located inside the saturation curve (binodal) and at the critical point both curves will converge and have a common horizontal tangent. We can summarize our findings and say that any state located within the mantle of the spinodal will be intrinsically unstable while every state located between both curves will be metastable. We should also realize that the thermodynamic limit of superheat (TLS, spinodal) does not represent the temperature at which boiling begins, it only provides a maximum upper limit beyond which the liquid phase is intrinsically unstable, *i.e.*, it cannot exist. Liquid to vapor transition will then occur in the temperature range between the boiling point at the system pressure, and the spinodal temperature for the pressure in question. Boiling will be marked by the formation of bubbles within the liquid phase, and it is usually accepted that these can form by one of two mechanisms; (a) heterogeneous nucleation where bubbles form from gases entrapped in surface imperfections, or (b) homogeneous nucleation where bubbles form by molecular activity in a liquid with no vapor phase. If the homogeneous system is not subject to initiating outside influences, the nucleus of the new phase will arise spontaneously because of thermal fluctuations and inter-molecular interaction. Homogeneous nucleation, and experimental information on the same are well reviewed in a paper by Avedisian [1]. The theory of homogeneous nucleation permits prediction of the so-called *kinetic limit of superheat* (KLS), and the paper by Avedisian quoted above, discusses the different techniques for measuring the same. Table I gives some representative values of KLS for pure compounds. It can be seen that superheating without boiling can reach high values, for example, at atmospheric pressure water can be heated almost 200 K (!) above its normal point without boiling. In addition, it is seen that the reduced limit of superheat varies approximately within the rather narrow margin of 0.88–0.91, that is, very close to the critical temperature.

From the above considerations we learn that an EOS that exhibits a loop as the one illustrated in Figure 1 (b–1–2–3–c, van der Waals loop), can be theoretically used to calculate the thermodynamic limit of supersaturation by simply imposing on it the mathematical conditions $(\partial P/\partial v)_T = 0$ and $(\partial^2 P/\partial v^2)_T > 0$. The pertinent procedure will be illustrated later.

TABLE I Measured limiting superheat and other properties of some liquids at 0.1 MPa. KLS data taken from [1]

	NBP	T_c	KLS	$RKLS_r$
Ethane	184.5	305.4	269.2	0.881
Propane	231.1	369.8	326.4	0.883
Propene	225.4	365	325.6	0.892
Propyne	250	402.4	356.8	0.887
2-Methylpropane	261.3	408.1	361	0.885
Butane	272.7	425.2	377.6	0.888
1-Butene	266.9	419.6	371	0.884
Pentane	309.2	479.8	426.2	0.888
Chloroform	334.3	536.4	466.2	0.869
Bromobenzene	429.2	670	534.2	0.797
Methanol	337.8	512.6	458.4	0.909
Ethanol	351.5	516.2	462.6	0.914
Acetone	329.4	508.1	454.5	0.911
Water	373.15	647	575	0.889

NBP = normal boiling point. T_c = critical temperature. TL = kinetic limit temperature. $RKLS_r$ = reduced kinetic limit temperature. All temperatures in K.

Metastable phase states are stable under small (continuous) variations in the thermodynamic parameters, but are unstable if a competing phase is formed in some way [2]. They have a fairly long life, since they are stable in themselves, but for transition into the stable state they must overcome a potential barrier, if no primer (like an impurity) is present. Inspection of Figure 1 indicates that the metastable state is achieved by passing through the equilibrium envelope without a phase change. Penetration into the metastable region may be very deep. States located on the spinodal represent the maximum penetration before a phase changed is forced on the system and their prediction requires an EOS applicable in the metastable state. The *binodal* represents the *limit of absolute stability* and the *spinodal* the *limit of significant instability*. The region of *metastable states* in quasistatic transitions is *between* the binodal and the spinodal. Figure 2 illustrates the different regions, as defined above [3]. The spinodal curve, when calculated with an EOS, provides the thermodynamic limit of superheat (TLS).

Rapid formation of the vapor phase may result in a physical (thermohydraulic) explosion. The phenomenon of thermal explosions has been reported in the paper industry, in the spillage of molten metals into water (casting), and in the petroleum industry in connection with spills of natural gas. According to Avedisian [4] the energy
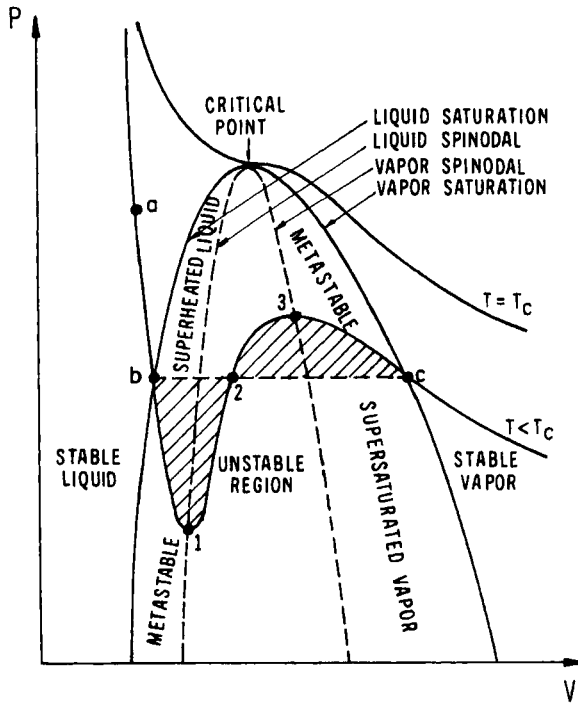
FIGURE 2   Regions of stability in the P-V plane [3].

released by a liquid at its limit of superheat is approximately equiva-
lent to the sensible heat about normal saturation. If a significant frac-
tion of this energy appears in the form of a thermal detonation wave,
or if bubbles grow at a rate that exceeds the ability of the surround-
ing liquid to acoustically respond, the resulting phase transition is
called a vapor explosion. This energy is several orders of magnitude
less than a typical chemical explosion, but enough to cause serious
damage. The reason for the explosion is assumed to be the rapid
growth of bubbles either within the volatile liquid or at the interface
between the volatile and nonvolatile liquid. According to Lienhard
et al. [5] the energy release is of the order of RT_c.

As a closing point we should mention that Skripov [6] has shown
that in the P-T plane the spinodal is the envelope of the isochores,

isentropic, and isenthalphs, that is

$$\left(\frac{dP}{dT}\right)_{spin} = \left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial P}{\partial T}\right)_s = \left(\frac{\partial P}{\partial T}\right)_h \tag{6}$$

Different workers have used equations of state to develop a thermodynamic expression for the spinodal. For example, Eberhart and Schnyders [3] compared KLS experimental data with TLS calculations based on the vdW, Berthelot, hard spheres, and hard cylinders EOS, and concluded that the vdW and hard spheres EOS yield TLS lower than the experimental data and hence were inadequate for limit of superheat predictions. On the other hand, the hard cylinder and Berthelot EOS gave TLS values larger than the experimental ones. Porteus and Blander [7] have also shown that the TLS values predicted by the Redlich-Kwong (R-K) EOS are below the experimental ones. Avedisian [4] has shown that the Peng-Robinson (P-R) EOS predicts values above the experimental ones. Others, like Avedisian and Sullivan [8], Lienhard and Karimi [9], Dong and Lienhard [10] and Lienhard [11], have used corresponding states methods for predicting the limits of superheat of liquids and their mixtures. Because of its industrial importance there have been many attempts to calculate the spinodal of water (see, for example, Thormahlen and Straub [12] and Kiselev *et al.* [13]). Two books [2, 14] give a detailed picture of the problem of metastable liquids.

It is the purpose of this work to test several equations of state and compare their ability to predict the limits of superheat of pure liquids.

2. RESULTS

Practical phase equilibrium calculation can be performed using equations of state. Here a single equation is used to represent all fluid phases. This is a powerful approach that provides a uniform representation of thermodynamics properties in both the one-phase and two-phase regions of the particular plane being investigated. All equations of state are developed under the assumption that each (P, T, V) state is a stable state. It is then important to realize that any attempt to use an EOS for predicting the spinodal, carries the implicit assumption

(unproved) that the EOS can be extrapolated into the metastable region. For a formulation to be acceptable, its spinodal must fall beyond the range of all measured stable and metastable data. An additional fact to consider is that although in the P-V plane the binodal and the spinodal seem to be coplanar, this is not so in the 3D space P-V-T, as shown in Figure 3.

We will now study the capability of some classical and more modern EOS to predict the spinodal and its relation to the thermodynamic superheat limit.

2.1. van der Waals and Berthelot EOS

The van der Waals and Berthelot EOS may be considered particular forms of a more general equation of state

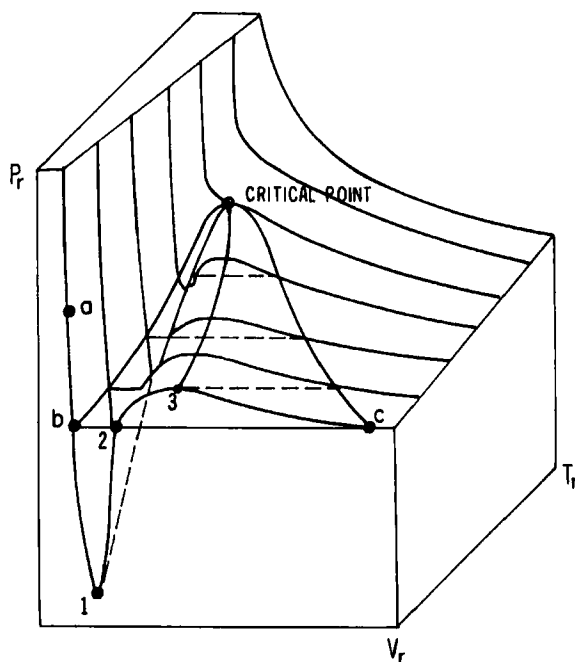$$\left(P + \frac{a}{T^n v^2}\right)(v - b) = RT \tag{7}$$

FIGURE 3   The binodal and the spinodal in the P-V-T space [2].

where $n = 0$ for vdW and $n = 1$ for Berthelot. In the reduced form

$$\left(P_r + \frac{3}{T_r^n v_r^n}\right)\left(v_r - \frac{1}{3}\right) = \frac{8}{3}RT_r \tag{8}$$

Applying the condition for the spinodal, $(\partial P_r/\partial v_r)_{T_r} = 0$, we get

$$T_{r(i)}^{n+1} = \frac{(3v_r - 1)^2}{4v_r^3} \tag{9}$$

where index i represents either the liquid or the vapor branch of the curve. Equations (8) and (9) can be solved simultaneously, for given values of T_r, to give the corresponding values of P_r and v_r. For the particular case of vdW, substitution of T_r from Eq. (8) in Eq. (9) yields the alternative expression

$$P_r v_r^3 - 3v_r + 2 = 0 \tag{10}$$

The capability of the vdW EOS to describe the shape of the spinodal (two branches and a maximum) can be judged by calculating the slope predicted for the same. From Eqs. (9) and (10) we get

$$\left[\frac{\partial P_r}{\partial T_r} = \frac{3}{z_c(3v_r - 1)}\right]_{\text{spin}}^{i} \tag{11}$$

where z_c is the critical compressibility factor, which for vdW is 3/8. We know that $v_c = 3b$ where the vdW constant b (covolume) represents the minimum value that the gas can take. Hence, the minimum possible value of v_r is 1/3 and, from Eq. (11) $(\partial P_r/\partial T_r)_{\text{spin}}$ must be positive. Since $(v_r^L < v_r^G)_{\text{spin}}$ the slope of the liquid spinodal will be larger than that of the vapor spinodal, except at the critical point $(v_r = 1)$ where both will have a common tangent with slope 4.

Another interesting feature of both EOS is obtained by putting $P_r = 0$ in Eq. (8) and substituting the result in Eq. (9) to get $v_r = 2/3$. Replacing the latter value in Eq. (9) yields $T_r^{n+1} = 27/32$. In other words, for the vdW gas the isotherm $T_r = 0.844$ $(T_r = 0.919$ for the Berthelot gas) will have its minimum value at $v_r = 2/3$. For temperatures lower than $T_r = 0.844$ the vdW EOS predicts *negative* values of the pressure. This is not an unusual (nonphysical) behavior and is

well known in the flow of sap in trees; negative pressures of -50 to -80 atm are known to occur in desert plants [15]. If the tension is sufficient the liquid will break producing a phenomenon known as cavitation. Temperley [16, 17] has obtained a theoretical estimate of the tensile strength of a liquid that obeys a particular EOS. According to Temperley, the value of the ordinate at the minimum (negative) point, represents the limiting value of the tension the liquid can sustain at the particular temperatures.

Figure 4 illustrates in three different planes the binodal and spinodal curves, according to vdW.

For the following EOS we will discuss mainly their capability to describe the KLS. Numerical results will be calculated using the software *Mathematica 3*.
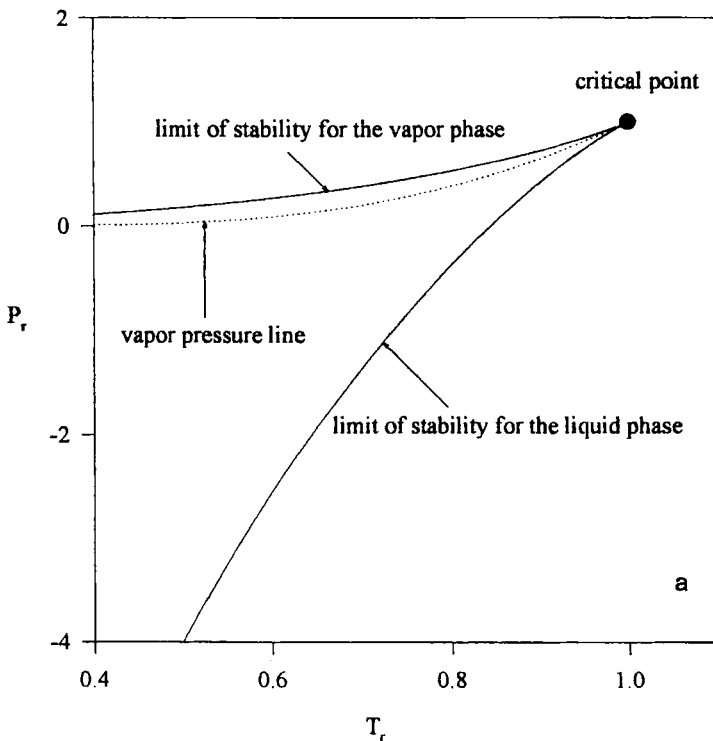

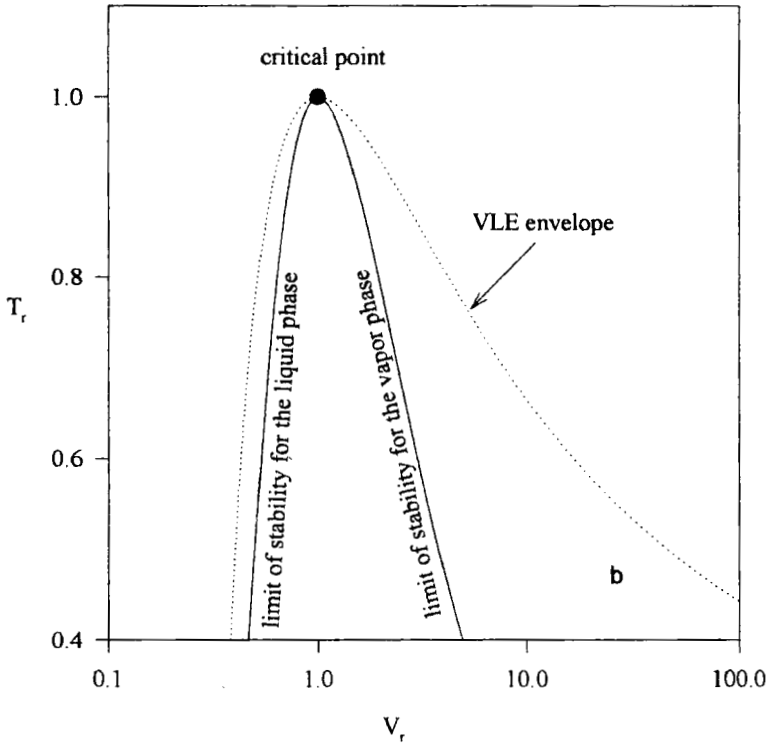FIGURE 4   The binodal and spinodal, according to vdW.

FIGURE 4 (Continued).

2.2. Redlich-Kwong (R-K) EOS

The reduced form of the EOS is

$$P_r = \frac{3T_r}{v_r - 0.25992} - \frac{3.8473}{T_r^{0.5}v_r(v_r + 0.25992)} \tag{12}$$

and the condition for the spinodal, $(\partial P_r/\partial T_r)_{\mathrm{spin}} = 0$, yields

$$T_r^{1.5} = 1.28243 \frac{(v_r - 0.25992)(2v_r + 0.25992)}{v_r^2(v_r + 0.25992)^2} \tag{13}$$

Equations (12) and (13) predict that the isotherm $T_r = 0.895$ will touch the *abscissa* $P_r = 0$ at $v_r = 0.6249$. For temperatures lower than $T_r = 0.895$ the Redlich-Kwong EOS predicts negative spinodal pressures.
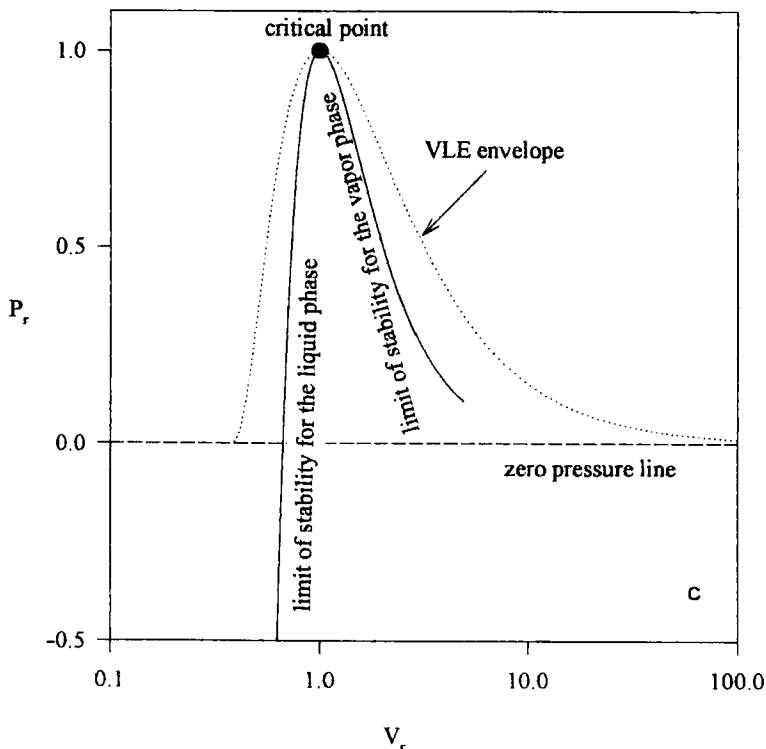
FIGURE 4   (Continued).

2.3. Soave (S) EOS

The reduced form of the EOS is

$$P_r = \frac{3T_r}{v_r - 0.2599} - \frac{3.8473\alpha}{v_r(v_r + 0.2599)} \qquad (14)$$

with

$$\alpha = [1 + (0.48508 + 1.55171\omega - 0.1561\omega^2)(1 - T_r^{0.5})]^2 \qquad (15)$$

where ω is the acentric factor.

The condition for the spinodal, $(\partial P_r/\partial T_r)_{\text{spin}} = 0$, yields

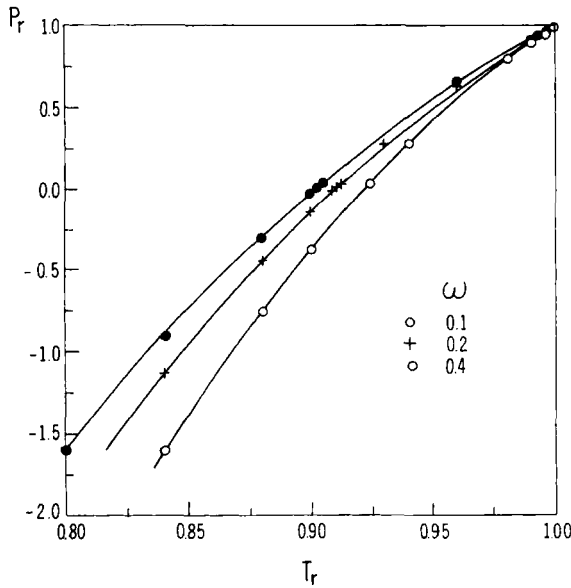$$\frac{T_r}{\alpha} = 1.28243 \frac{(v_r - 0.25992)(2v_r + 0.25992)}{v_r^2(v_r + 0.25992)^2} \qquad (16)$$

FIGURE 5   The binodal and spinodal, according to Soave: (a) $w = 0.2$, (b) variation of the liquid spinodal with the acentric factor.

In this case the value of T_r for which the P_r of the spinodal is zero will depend on the particular value of ω, although it will occur always at the *same* value of v_r ($= 0.6249$) of the Redlich-Kwong EOS. Thus, from Eq. (16) we have that the ratio T_r/α will have the constant value 0.847. For example, for $\omega = 0.1$ we get $T_r = 0.901$. Figure 5 illustrates the spinodal, according to Soave for various values of the acentric factor; it is seen that for a given value of P_r the corresponding values of T_r increase as ω increases.

2.4. Bennedict-Webb-Rubin (BWR) EOS

The EOS is

$$P = \frac{RT}{v} + \frac{B_0 RT - C_0/T^2 - A_0}{v^2} + \frac{bRT - a}{v^3}$$
$$+ \frac{c(1 + c_1/v^2)\exp(-c_1/v^2)}{T^2 v^3} + \frac{aa_1}{v^6} \tag{17}$$

where A_0, B_0, C_0, a, b, a_1, and c_1, are constants, characteristics of the gas in question. As an example, Table II gives the values of the

TABLE II   Values of the reduced coordinates of the spinodal for butane, according to the BWR EOS

	Liquid spinodal			Gas spinodal	
v_r^L	T_r^L	P_r^L	v_r^G	T_r^G	P_r^G
0.305	0.235	− 273	14.4	0.470	0.0582
0.324	0.282	− 156	11.1	0.517	0.0829
0.349	0.352	− 77.3	8.72	0.564	0.114
0.389	0.470	− 30.0	7.00	0.611	0.152
0.406	0.571	− 21.6	7.71	0.658	0.199
0.422	0.564	− 15.8	4.71	0.705	0.256
0.439	0.611	− 11.7	3.92	0.752	0.323
0.456	0.658	8.56	3.28	0.799	0.404
0.476	0.705	− 6.18	2.75	0.846	0.500
0.497	0.752	− 4.31	2.28	0.893	0.616
0.521	0.799	− 2.79			
0.550	0.846	− 1.55			
0.587	0.893	− 0.538			
0.619	0.923	0.0046			
0.620	0.923	0.0159			
0.621	0.925	0.0341			
0.643	0.939	0.281			

spinodal for butane, using the constants reported by Walas [15], and Figure 6 compares the theoretical limit of liquid superheat against the experimental one (taken from Avedisian [1]).

2.5. Schmidt-Wenzel (S-W) EOS

The EOS is

$$P_r = \frac{T_r}{v_r - b_1} - \frac{a_1}{v_r^2 + (1 + 3\omega)b_1 v_r - 3\omega b_1^2} \tag{18}$$

where

$$a_1 = \left[1 - \frac{1 - \beta_c}{3(1 + \beta_c \omega)}\right]$$
$$\left\{1 + [5T_r - 1 - 2(0.465 + 1.347\omega - 0.528\omega^2)]^2 \left(\frac{1 - \sqrt{T_r}}{70}\right)\right\}^2 \tag{19}$$

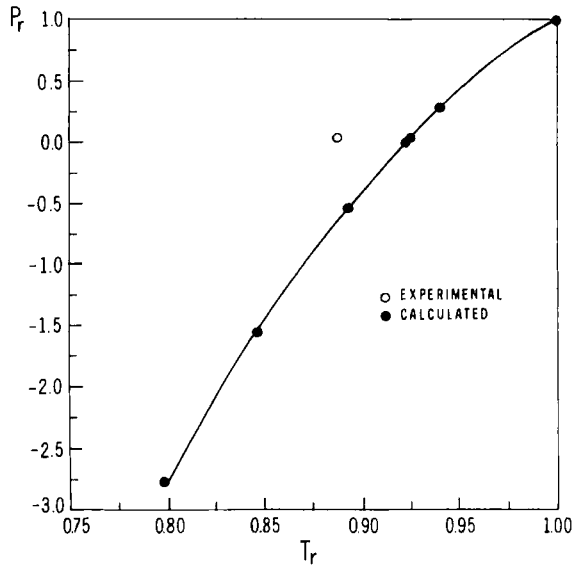$$b_1 = \frac{\beta_c}{3(1 + \beta_c \omega)} \tag{20}$$

FIGURE 6   The binodal and spinodal of butane according to BWR.

$$\beta_c = 0.25989 - 0.0217\omega + 0.00357\omega^2 \tag{21}$$

The equation of the spinodal is

$$T_r = a_1 \frac{(v_r^2 - b_1)^2 [2v_r + (1 + 3\omega)b_1]}{[v_r^2 + (1 + 3\omega)b_1 v_r - 3\omega b_1^2]^2} \tag{22}$$

Figure 7 illustrates the spinodal curve calculated according to Soave for various values of the acentric factor; it is seen that for a given value of P_r the corresponding values of T_r increase as ω increases.

2.6. Harmens-Knapp (H-K) EOS

The EOS is

$$P_r = \frac{T_r}{v_r - \Omega_a} - \frac{\alpha\Omega_a}{v_r^2 + \Omega_b\left(1 + \frac{1-3\zeta}{\beta\zeta}\right)v_r - \Omega_b^2 \frac{1-3\zeta}{\beta\zeta}} \tag{23}$$
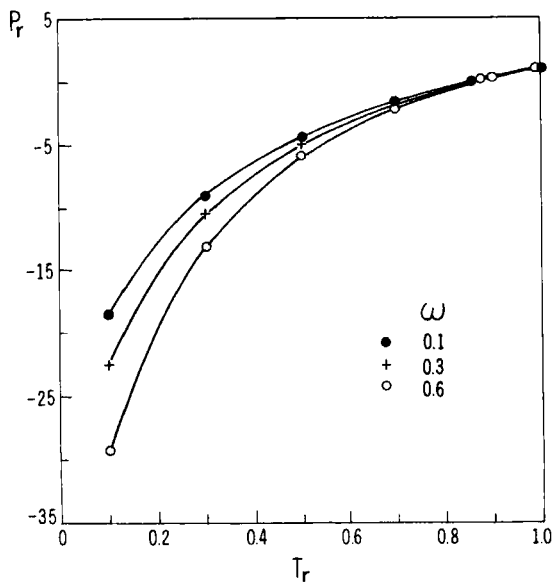
FIGURE 7   The binodal and spinodal, according to Schmidt and Wenzel: (a) $w = 0.2$, (b) variation of the liquid spinodal with the acentric factor.

where

$$\alpha = [1 + A(1 - T_r^{0.5}) - B(1 - T_r^{-1})]^2 \qquad (24)$$

$$\beta = 0.1077 + 0.76405\zeta - 1.24282\zeta^2 + 0.96210\zeta^3 \qquad (25)$$

$$\zeta = 0.3211 - 0.080\omega + 0.0384\omega^2 \qquad (26)$$

$$\Omega_a = 1 - 3\zeta + 3\zeta^2 + \beta\zeta(3 - 6\zeta + \beta\zeta) \qquad (27)$$

$$\Omega_b = \beta\zeta \qquad (28)$$

When $\omega \le 0.2$

$$A = 0.50 + 0.27767\omega + 2.17225\omega^2 \qquad (29)$$

$$B = -0.022 + 0.338\omega - 0.845\omega^2 \qquad (30)$$

and when $\omega > 0.2$

$$A = 0.41311 + 1.14657\omega \tag{31}$$

$$B = 0.0118 \tag{32}$$

The equation of the spinodal is

$$\frac{T_r}{\alpha} = \frac{\Omega_a\left[2v_r + \Omega_b\left(1 + \frac{1-3\zeta}{\beta\zeta}\right)\right] +}{\left[v_r^2 + \Omega_b\left(1 + \frac{1-3\zeta}{\beta\zeta}\right)v_r - \Omega_b^2\frac{1-3\zeta}{\beta\zeta}\right]^2} \tag{33}$$

Figure 8 illustrates the spinodal curve calculated according to Harmens-Knapp for various values of the acentric factor; it is seen that for a given value of P_r the corresponding values of T_r increase as ω increases.

Table III compares the TLS values of the various EOS, against the experimental KLS, it is seen that only the EOS of Peng-Robinson, BWR, and Soave predict values of RKLS above the measured ones.
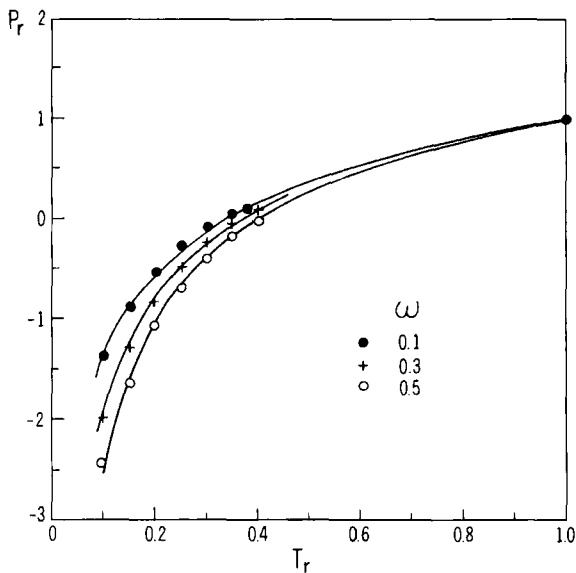
FIGURE 8   The binodal and spinodal, according to Harmens and Knapp: (a) $w = 0.2$, (b) variation of the liquid spinodal with the acentric factor.

TABLE III   Comparison between experimental RKLS and the value predicted by different EOS (at 101.3 kPa)*

Substance	RKLS*	Predicted RTLS (EOS)						
		vdW	P-R**	R-K	BWR	Soave	S-W	H-K
n-Pentane	0.888	0.848	0.918	0.898	0.924	0.915	0.866	0.375
n-Heptane	0.914	0.849	0.924	0.898	0.925	0.921	0.870	0.393
n-Octane	0.903	0.849	0.923	0.898	0.925	0.924	0.871	0.402
Methanol	0.909	0.845	0.931	0.896	0.923	0.929	0.873	0.413
Ethanol	0.914	0.846	0.934	0.896	0.923	0.933	0.875	0.426
Water	0.889	0.844	0.921	0.895	0.923	0.919	0.866	0.379
Acetone	0.911	0.846	–	0.897	0.924	0.918	0.867	0.379
Chloroform	0.869	0.846	–	0.896	0.924	0.912	0.864	0.365
Benzene	0.90	0.846	–	0.897	0.924	0.912	0.864	0.365
Hexafluorobenzene	0.906	0.848	–	0.898	0.924	0.923	0.870	0.397

* Values in italics exceed RKLS.
** From [1].

3. CONCLUSIONS

The phenomenon of supersaturation has been analyzed from the viewpoint of thermodynamic stability. The equations of state of Redlich-Kwong, Soave, BWR, Schmidt-Wenzel, and Harmens-Knapp have been tested and compared in their ability to predict the spinodal and the experimental limits of superheat of pure liquids. The results indicate that only the Peng-Robinson, Soave and BWR equations are capable of predicting reduced kinetic limits of supersaturation above the experimental ones.

References

[1] Avedisian, C. T. (1985). *J. Phys. Chem. Ref. Data*, **14**, 695.
[2] Skripov, V. P. (1974). *"Metastable Liquids"*, J. Wiley & Sons, New York.
[3] Eberhart, J. G. and Schnyders, H. C. (1973). *J. Phys. Chem.*, **77**, 2730.
[4] Avedisian, C. T. (1986). "Bubble Growth within Superheated Liquid Droplets", *Encyclopedia of Fluid Mechanics*, Vol. 3, Chapter 8, pp. 130–190, Gulf Publishing Co.
[5] Lienhard, J. H., Shamsundar, N. and Biney, P. O. (1986). *Nuclear Engineering and Design*, **95**, 297.
[6] Skripov, V. P. (1966). *Teplofizika Vysokih Tem.*, **4**, 816.
[7] Porteus, W. and Blander, M. (1975). *AIChEJ*, **21**, 560.
[8] Avedisian, C. T. and Sullivan, J. R. (1984). *Chem. Eng. Science*, **39**, 1033.
[9] Lienhard, J. H. and Karimi, A. H. (1978). *ASME Journal of Heat Transfer*, **100**, 492.
[10] Dong, W.-G. and Lienhard, J. H. (1986). *Can. J. Chem. Eng.*, **64**, 158.
[11] Lienhard, J. H. (1982). *ASME Journal of Heat Transfer*, **104**, 492.

[12] Thormahlen, I. and Straub, J. (1984). 252, *Proceedings of the 10th International Conference on the Properties of Steam*, Sytchev, V. V. and Aleksandrov, A. A., Editors, Moskow, pp. 252–262.

[13] Kiselev, S. B., Levelt Sengers, J. M. H. and Zheng, Q. (1994). *Proceedings of the 12th International Conference on the Properties of Water and Steam*, White, H. J., Sengers, J. V., Neumann, D. B. and Bellows, J. C., Editors, pp. 378–385.

[14] Debenedetti, P. G. (1996). *"Metastable Liquids"*, Princeton University Press, Princeton.

[15] Salisbury, F. B. (1985). *"Plant Physiology"*, 3rd. edition, Wadsworth Publications, Belmont, California.

[16] Temperley, H. V. N. (1947). *Proc. Phys. Soc.*, **59**, 199.

[17] Temperley, H. V. N. and Trevena, D. H. (1978). *"Liquids and Their Properties"*, Ellis Horwood Ltd., Chichester.

[18] Walas, S. M. (1985). *"Phase Equilibria in Chemical Engineering, Butterworth"*, Boston.