Spinodal Curves of Monatomic Fluids from Model Equations of State

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Letter

Spinodal Curves of Monatomic Fluids from Model Equations of State

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Using a model equation of state which embraces, but transcends, those of van der Waals (W) and Dieterici (D), the equations determining the spinodal curves of monatomic fluids are set up. To exemplify the results, the spinodal curves for the W and D models are given explicitly. Finally, a schematic account is presented of the way a correct critical exponent β can be expected to reflect itself in the spinodal properties.

Key Words: critical exponent; coexistence curve.

In a recent paper,[1] the liquid–vapour coexistence curve was discussed on the basis of a model equation of state.[2] The purpose of this Letter is to set down the thermodynamic equations for the spinodal curves of monatomic fluids, starting from the same model.

The spinodal curve is normally defined as corresponding to zero second derivative of the Helmholtz free energy F with respect to density ρ. Using the expression $p = \rho^2(\partial F/\partial \rho)_T$ where p is the pressure, this condition can be posed as $(\partial p/\partial \rho)_T = 0$. This is used in conjunction with the model equation of state

$$[p^* + f_1(T^*, \rho^*)][1 - \alpha\rho^*] = \frac{T^*\rho^*}{Z_c} f_2(T^*, \rho^*) \qquad (1)$$

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where $p^* = p/p_c$, etc. while $Z_c = p_c/\rho_c k_B T_c$. The functions f_1 and f_2 and the constant α will later be made explicit in the examples of van der Waals and Dieterici models.

From Eq. (1) $(\partial p^*/\partial \rho^*)_T = 0$ yields

$$\frac{T^*}{Z_c}\left[\frac{f_2(T^*, \rho^*)}{1 - \alpha\rho^*} + \rho^*\left(\frac{\partial f_2(T^*, \rho^*)}{\partial \rho^*}\right)_{T^*}\right] = (1 - \alpha\rho^*)\left(\frac{\partial f_1(T^*, \rho^*)}{\partial \rho^*}\right)_{T^*} \quad (2)$$

The solution of Eq. (2) gives T^* as a function of ρ^*, and substituting in Eq. (1) one finds the equation of the spinodal curve in the (p^*, ρ^*) plane as

$$p^*(\rho^*) = \frac{T^*(\rho^*)}{Z_c}\frac{\rho^* f_2(T^*(\rho^*), \rho^*)}{1 - \alpha\rho^*} - f_1(T^*(\rho^*), \rho^*). \quad (3)$$

At the critical density ρ_c one evidently has $(dp^*(\rho^*)/d\rho^*)_{\rho^*=1} = 0$, with similar conditions on p^* from Eq. (3) and T^* from Eq. (2).

While these equations define the spinodal curve for general functions f_1 and f_2, we shall merely illustrate the use of Eqs (1) to (3) by taking in turn the Dieterici and then the van der Waals models. For the Dieterici equation of state, one has explicitly:

$$f_1(T^*, \rho^*) = 0, f_2(T^*, \rho^*) = \exp(-2\rho^*/T^*),$$
$$\alpha = \tfrac{1}{2}, Z_c = 2\exp(-2) \quad (4)$$

Equations (2) and (3) then become

$$T^*(\rho^*) = \rho^*(2 - \rho^*) \quad (5)$$

and

$$p^*(\rho^*) = \rho^{*2}\exp\left[2\frac{1 - \rho^*}{2 - \rho^*}\right] \quad (6)$$

From Eq. (5), the relation between density and temperature on the spinodal curve is

$$\rho^* = 1 \pm (1 - T^*)^{1/2} \quad (7)$$

For the case of van der Waals,

$$f_1(T^*, \rho^*) = 3\rho^{*2}, f_2(T^*, \rho^*) = 1, \alpha = \tfrac{1}{3}, Z_c = \tfrac{3}{8} \quad (8)$$

Equations (2) and (3) now take the form

$$T^*(\rho^*) = \tfrac{1}{4}\rho^*(3 - \rho^*)^2 \quad (9)$$

and

$$p^*(\rho^*) = \rho^{*2}(3 - 2\rho^*) \quad (10)$$

The two physically acceptable solutions of Eq. (9) for the density-temperature relation on the spinodal curve are

$$\rho^*(T^*) = [2 - \cos(\tfrac{1}{3}\ \text{arctg}\ \tau)] \pm \sqrt{3}\ \sin(\tfrac{1}{3}\ \text{arctg}\ \tau) \qquad (11)$$

where

$$\tau = [4T^*(1 - T^*)]^{1/2}/(2T^* - 1) \qquad (12)$$

On approaching the critical point ($T^* \to 1$), Eqs (11) and (12) yield

$$\rho^* \to 1 \pm \frac{2\sqrt{3}}{3}(1 - T^*)^{1/2} \qquad (13)$$

We know, from critical exponent theory, that both van der Waals and Dieterici models give an incorrect description of the coexistence curve near the critical point. The relevance of this to the present discussion is that, in the (T^*, ρ^*) plane, the spinodal forms (7) and (13) have the same exponents as for these same models of the coexistence curve. We anticipate that such behaviour will be erroneous near T_c for
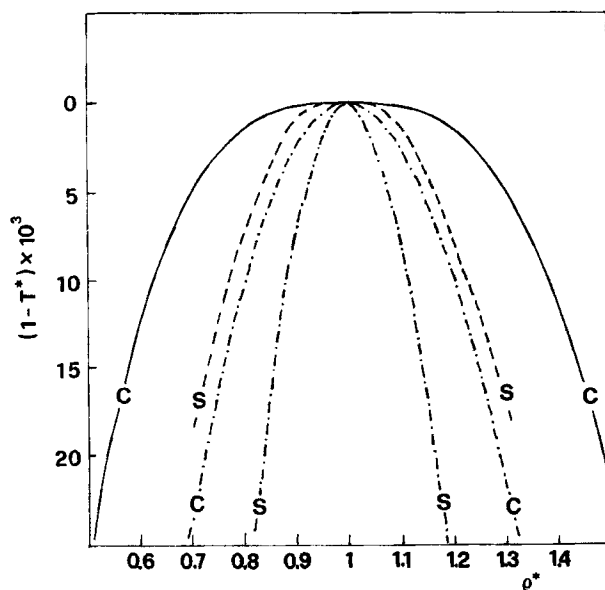
Figure 1 Schematic form representing relation anticipated between liquid–vapour coexistence curve (C) and spinodal behaviour (S) for a simple fluid near the critical temperature (full and dashed lines, respectively). The full curve reproduces a realistic fit presented by Guggenheim[3] for experimental data on liquid–vapour coexistence in molecular fluids. The dash-dot lines show the results of the van der Waals model.

spinodal properties also, but we must stress that, to date, we are not aware of experiments on monatomic fluids which are decisive on this point.

Nevertheless, it seemed of interest to show in the Figure a schematic plot of the way spinodal and coexistence curves might relate to one another in a more general model. In particular, a critical exponent β, known to be very near to $\frac{1}{3}$ for the coexistence curve, can be expected to have relevance for the spinodal behaviour near the critical point. As discussed in the earlier work[1] on the coexistence curve using the model equation of state (1), the function f_1 is general enough to permit the inclusion of non-analytic behaviour near the critical point, leading to $\beta = \frac{1}{3}$.

Acknowledgements

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