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Liquid–Vapour Coexistence Curves from a Model Equation of State

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Using a model equation of state proposed by Chapman and March, which is sufficiently general to contain the models of van der Waals and Dieterici, the thermodynamics of the coexistence curve is set up. The requirement that the critical exponent is less than $\frac{1}{2}$ is shown to require a specific non-analytic behaviour of a function appearing in the model equation of state. In turn this provides a constraint having the nature of a relation between average density of liquid and vapour and temperature, transcending rectilinear diameters. Comparison between theory and experiment is made to the fluid alkali Cs and for some molecular fluids.

Key Words: Critical exponent; non-analyticity; rectilinear diameter.

1 INTRODUCTION

Considerable understanding now exists of the liquid–vapour coexistence curve very near to the critical point.¹ It is known that mean field theories such as van der Waals, while qualitatively useful, fail to describe the critical region in a quantitative manner. In particular, the order parameter $\rho_L - \rho_G$, with ρ_L and ρ_G the liquid and vapour densities respectively, varies along the coexistence curve according to a critical exponent β , such that

$$\rho_L - \rho_G = \text{constant}(T_c - T)^\beta \quad (1.1)$$

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with T_c the critical temperature. The value of β is known to be numerically near to $\frac{1}{3}$ from theory and experiment.² Van der Waals theory, on the other hand, yields $\beta = \frac{1}{2}$.

Here, while we add nothing new relating to critical exponents, we wish to investigate the way in which the liquid-vapour coexistence curve can be characterized over the whole range of density and temperature. This we shall do by invoking solely thermodynamics and phenomenology but, we stress, supplemented by the important knowledge that β in Eq. (1.1) is very near to $\frac{1}{3}$.

In Section 2, we shall therefore set up the theory of the liquid-vapour coexistence curve, using a model equation of state proposed by Chapman and March.³ This was set up specifically to embrace both the van der Waals and the Dieterici equations of state.⁴ An essential ingredient in the phenomenology presented below is to insist that $\beta = \frac{1}{3}$ and not $\frac{1}{2}$ as for van der Waals and Dieterici models. Then, in Section 3, in the light of this discussion, experimental data for a number of systems will be analyzed; in particular for fluid Cs⁵ and for C₂H₄.⁶ Section 4 consists of a summary of the main conclusions and points out directions for further studies.

2 LIQUID-VAPOUR COEXISTENCE CURVE FROM MODEL EQUATION OF STATE

The object of this section is to study the properties of the rather general equation of state³:

$$[p^* + f_1(T^*, \rho^*)][1 - \alpha\rho^*] = \frac{\rho^* T^*}{Z_c} f_2(T^*, \rho^*). \quad (2.1)$$

Here f_1 and f_2 are left general for the moment, while $p^* = p/p_c$ etc.; ie thermodynamic variables are scaled with the appropriate critical values. Finally, Z_c is the compressibility ratio $p_c/\rho_c k_B T_c$, while α is a constant.

From this Eq. (2.1), using $p = \rho^2(\partial F/\partial \rho)_T$ with F the Helmholtz free energy per particle, and the chemical potential $\mu = F + p/\rho$, one finds the equilibrium equations

$$\frac{T^*}{Z_c} \left\{ \frac{\rho_L^* f_2(T^*, \rho_L^*)}{1 - \alpha\rho_L^*} - \frac{\rho_G^* f_2(T^*, \rho_G^*)}{1 - \alpha\rho_G^*} \right\} = f_1(T^*, \rho_L^*) - f_1(T^*, \rho_G^*) \quad (2.2)$$

which comes from the equality of the pressures in the two phases and

$$T^* \ln \frac{\rho_G^*}{\rho_L^*} = T^* [F_2(T^*, \rho_L^*) - F_2(T^*, \rho_G^*)] + Z_c [F_1(T^*, \rho_L^*) - F_1(T^*, \rho_G^*)] \quad (2.3)$$

from the equality of the chemical potentials. Here the quantities F_1 and F_2 are defined by integrals on the isotherms as

$$F_1(T^*, \rho^*) = - \int^{\rho^*} \frac{d\rho^*}{\rho^*} \frac{\partial f_1(T^*, \rho^*)}{\partial \rho^*} \quad (2.4)$$

and

$$F_2(T^*, \rho^*) = - \int^{\rho^*} \frac{d\rho^*}{\rho^*} \left\{ 1 - \frac{\partial}{\partial \rho^*} \left[\frac{\rho^* f_2(T^*, \rho^*)}{1 - \alpha \rho^*} \right] \right\}. \quad (2.5)$$

To make these somewhat abstract equations concrete, we summarize in the Appendix explicit results for the cases of van der Waals and Dieterici equations of state.

Drawing on the examples in the Appendix, it is straightforward for these cases to eliminate T^* and obtain a relationship between $\rho_L(T^*)$ and $\rho_G(T^*)$ along the coexistence curve. This is then a way of presenting experimental data; it will be touched on briefly again in Section 3.

2.1 Pressure on the Coexistence Curve

It will be useful next to construct from Eq. (2.1) the pressure on the coexistence curve as the average of the (equal) pressures in the liquid and in the gas. This "symmetrized" pressure, denoted by p_s , can then be conveniently written in terms of the average of $\rho_L(T)$ and $\rho_G(T)$ and of the order parameter $\rho_L - \rho_G$, which we denote respectively by ξ and η through

$$\xi = \frac{\rho_L^* + \rho_G^*}{2}; \eta = \rho_L^* - \rho_G^*. \quad (2.6)$$

The result is

$$p_s^*(\xi, \eta) = \frac{T^*}{2Z_c} \left\{ \frac{[\xi(1 - \alpha\xi) + \frac{1}{4}\alpha\eta^2]}{[(1 - \alpha\xi)^2 - (\frac{1}{4}\alpha\eta)^2]} [f_2(T^*, \xi + \frac{1}{2}\eta) + f_2(T^*, \xi - \frac{1}{2}\eta)] + \frac{\frac{1}{2}\eta}{[(1 - \alpha\xi)^2 - (\frac{1}{4}\alpha\eta)^2]} [f_2(T^*, \xi + \frac{1}{2}\eta) - f_2(T^*, \xi - \frac{1}{2}\eta)] \right\} - \frac{1}{2} \{ f_1(T^*, \xi + \frac{1}{2}\eta) + f_1(T^*, \xi - \frac{1}{2}\eta) \} \quad (2.7)$$

We proceed now to use the knowledge that $\beta = \frac{1}{3}$ by expanding Eq. (2.7) around the point $\eta = 0$. Since p_s is an even function of η , it might appear that this expansion should be solely as a series in η^2 . It is readily verified from the Appendix that this is true both for van der Waals and Dieterici examples. The important point to be made is that this leads inevitably to $\beta = \frac{1}{2}$ in Eq. (1.1), in disagreement with experiment.²

Therefore, the simplest possible assumption to be made is that any acceptable equation of state must lead to zero coefficient in the term of order η^2 . Evidently then, a non-analytic term (corresponding to $\beta \simeq \frac{1}{3}$) must be invoked in the η expansion; we shall argue below that this non-analyticity first enters $p_s^*(\xi, \eta)$ at order $|\eta|^3$.

To be quite specific, let us expand Eq. (2.7) around $\eta = 0$, assuming that f_2 has a Taylor expansion around $\eta = 0$, and that the non-analyticity enters solely through f_1 . We stress that this is an assumption: the motivation for it, however, is to note that the second square bracket involving f_2 in Eq. (2.7) must be odd in η . Therefore, all that need be added is that

$$\frac{1}{2}[f_1(T^*, \xi + \frac{1}{2}\eta) + f_1(T^*, \xi - \frac{1}{2}\eta)] = f_{10}(T^*, \xi) + f_{12}(T^*, \xi)\eta^2 + f_{13}(T^*, \xi)|\eta|^3 + \dots \quad (2.8)$$

Inserting these assumptions for f_1 and f_2 into Eq. (2.7) we are led to the small η expansion of the "symmetrized" pressure as

$$p_s^*(\xi, \eta) = p^*\left(T^*, \frac{\rho_L^* + \rho_G^*}{2}\right) + \eta^2 P_2(T^*, \xi) - |\eta|^3 f_{13}(T^*, \xi) + \dots \quad (2.9)$$

where

$$P_2(T^*, \xi) = \frac{T^*}{2Z_c(1 - \alpha\xi)^2} \left[\frac{\frac{1}{4}\alpha f_{20}}{1 - \alpha\xi} + \xi(1 - \alpha\xi)f_{22} + f_{21} \right] - f_{12}. \quad (2.10)$$

Here f_{nm} is again a function of T^* and ξ , the notation being for the "coefficients" in the η expansions of f_1 and f_2 . As to models we note that provided $f_1(\xi + \frac{1}{2}\eta) - f_1(\xi - \frac{1}{2}\eta)$ as a function of η has a Fourier transform with inverse power decay in the transformed variable γ , starting with a power γ^{-6} at sufficiently large γ , then the $|\eta|^3$ non-analyticity follows in leading order.

As emphasized above, any acceptable equation of state must lead to $P_2(T^*, \xi) = 0$; a result which clearly yields:

$$\frac{\rho_L + \rho_G}{2\rho_c} = g(T/T_c). \quad (2.11)$$

The simplest non-trivial form of the function g corresponds to the so-called law of rectilinear diameters. This, however, is known not to be valid for the heavy fluid alkali metals from the experiments of Jüngst *et al.*⁵

To press this a little further, the form of Eq. (2.10), though involving as yet unknown functions, is already suggestive of a generalization of the law of rectilinear diameters if it is assumed that the f_{nm} 's are not functions of temperature.

3 COMPARISON WITH EXPERIMENT FOR FLUID METAL Cs AND FOR SOME MOLECULAR FLUIDS

Here we shall take advantage of the availability of recent data on the fluid alkali metal Cs,⁵ and on the molecular fluid C₂H₄,⁶ to make contact between the above discussion and experiment.

Figure 1 shows a conventional plot of the coexistence curves in the (T, ρ) plane. Besides the two fluids referred to already, data for Ne⁷ has been added, together with the representation of the coexistence curve proposed by Guggenheim,⁴ and given explicitly in Eqs (4.1) and (4.2) below. The latter gives an excellent fit of the data for Ne, but there are marked deviations from this fit for both Cs and C₂H₄. The van der

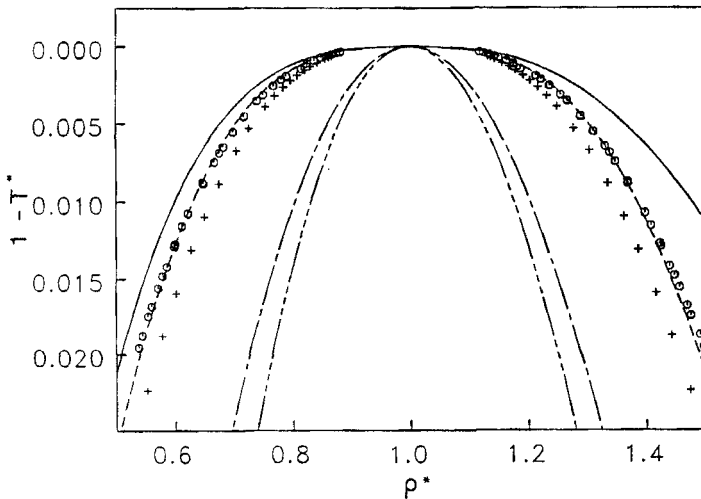


Figure 1 Liquid vapour coexistence curves. \circ Neon; $+$ Ethylene; $-$ Caesium. For comparison with the experimental data the following models are shown: $---$ Guggenheim formulae (4.1) and (4.2); $---$ Van der Waals; $- \cdot - \cdot -$ Dieterici.

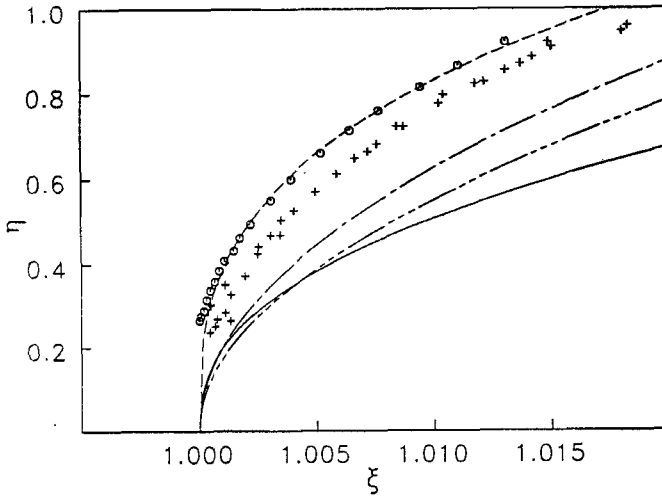


Figure 2 Order parameter $\eta = \rho_L^* - \rho_G^*$ versus mean density $\xi = \frac{1}{2}(\rho_L^* + \rho_G^*)$. Labelling of curves is identical to that in Figure 1.

Waals and Dieterici models fail to account for the data, as is already known.

We have also explored the plot of $\rho_L(T)$ versus $\rho_G(T)$ referred to in Section 2, and though a cubic relation of the Guggenheim form (4.3) is a reasonable fit of the data, deviations are again apparent for Cs, though this is a less sensitive plot of differences in data than the other plots explored. Therefore we shall not reproduce the ρ_L versus ρ_G plot here.

Finally, in Figure 2, the order parameter $\eta = \rho_L - \rho_G$ has been plotted against the mean density $(\rho_L + \rho_G)/2$ as also proposed in Section 2. This does seem a more illuminating plot; the same curves are shown as in Figure 1 in these different coordinates. The fluid metal is plainly very different from both Ne and C_2H_4 ; we return to this point briefly below.

4 DISCUSSION AND SUMMARY

In this section, we shall first pursue a little further the discussion of the coexistence curve in thermodynamic and/or phenomenological terms, and then turn to enquire what might be the microscopic origin of the non-analytic effects discussed earlier.

First of all, it is worth reiterating that the description of the coexistence curve, by elimination of the temperature, as a relation

between ρ_L and ρ_G , might eventually be best treated in terms of a differential equation. Specifically, a second-order differential equation is attractive since, in addition to the critical point boundary condition that $\eta = 0$ at $\xi = 1$, one could then build in, say, the density of the liquid at the triple point as the second boundary condition.

To illustrate this, we note that while Eqs (A5) and (A12) give the ρ_L versus ρ_G relation for van der Waals and Dieterici equations of state respectively, it is more fruitful to start from Guggenheim's empirical representation⁴ for molecular fluids, already used in Figures 1 and 2, namely

$$\xi = 1 + \frac{3}{4} \left(1 - \frac{T}{T_c} \right) \quad (4.1)$$

and

$$\eta = \frac{7}{2} \left(1 - \frac{T}{T_c} \right)^{1/3}, \quad (4.2)$$

this latter Eq. (4.2) contrasting with the van der Waals result $\eta = 4(1 - T/T_c)^{1/2}$ (see Appendix). Eliminating T between Eqs (4.1) and Eq. (4.2) yields

$$\xi = 1 + \frac{6}{243} \eta^3. \quad (4.3)$$

This is readily shown to satisfy the second-order differential equation for η in terms of ξ :

$$\eta \frac{d^2 \eta}{d\xi^2} + 2 \left(\frac{d\eta}{d\xi} \right)^2 = 0. \quad (4.4)$$

This non-linear form, while undoubtedly oversimplified, displays at least some of the structure we expect to appear in a definitive theory of the coexistence curve.

Turning to microscopic aspects, one does not have far to seek for reasons why a discussion like that of Osman and Silbert,⁸ closely related to that of van der Waals, becomes inappropriate in the immediate vicinity of the critical point. The reason we focus on here is the use of $c(r) = -\phi(r)/k_B T$, with $c(r)$ the Ornstein-Zernike direct pair correlation function and $\phi(r)$ the pair potential. While this asymptotic form is valid near the triple point, it breaks down as the critical point is approached since eventually the range of the correlations exceeds the range of the forces. Any equation of state which is describing the coexistence curve realistically must give due attention to such particle correlations. Though different from this discussion, earlier work has referred to three-body forces as responsible for the shape of the

coexistence curve near the critical point. Also relevant in the present context is the study of Lekner and Henderson⁹ on the connection between correlations in the interface and the coexistence curve.

Thus far, the paper has focussed solely on theory appropriate to neutral fluids; eg the condensed rare gases and molecular fluids like C_2H_4 . We want to add here a different line of argument which we believe is especially appropriate to expanded fluid metals. This is to emphasize the need to consider carefully, in any definitive theory, the nature of the interface between bulk liquid and vapour phases because of charge transfer across the interface. In particular, in an alkali metal with positive ions and electrons, an interfacial dipole layer will result and this will contribute to the equilibrium conditions on the pressure and the chemical potential. To attempt to make this concrete in an admittedly oversimplified example, let us consider at this point the one-component plasma. Charge transfer in this model creates a "Maxwell" pressure which balances a difference between the bulk thermodynamic pressures in phases at different densities. Similarly a difference in bulk thermodynamic chemical potentials can be balanced by a drop in the electrostatic potential through the interface.¹⁰

In summary, what has been demonstrated here, from a model equation of state of sufficient generality to embrace van der Waals and Dieterici models, is that insistence that $\beta < \frac{1}{2}$ requires a definite relation between T/T_c and the mean density $(\rho_L + \rho_G)/2$. This, we interpret in its most elementary form as the origin of the (approximate) law of rectilinear diameters.

On this point of rectilinear diameters, it is worth referring again to the fact that such behaviour will inevitably occur for analytic equations of state near the critical point. Thus, from the Appendix, it follows that both van der Waals and Dieterici models give $\frac{1}{2}(\rho_L^* + \rho_G^*) = 1 + \frac{2}{3}t + \dots$ where $t = 1 - T^*$, though they differ in giving $\frac{1}{2}(\rho_L - \rho_G) = 2t^{1/2}$ and $\sqrt{3}t^{1/2}$ respectively. The occurrence of a term $t^{1-\alpha}$ seems to be supported by experiment, though the amplitude of this term is particularly large for Cs. This arises, of course, from the non-analytic part of the Helmholtz energy density, while Goldstein and Ashcroft¹¹ have related the large amplitude for Cs to the strong state dependence of the potential.

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Appendix Coexistence curves for van der Waals and for Dieterici equations of state

In this Appendix we shall record a complete set of thermodynamic formulae for the van der Waals equation of state, as a limiting case of the model equation of state treated in the main text. For the equation of state of Dieterici, the main results needed to construct the coexistence curve will also be given.

VAN DER WAALS EQUATION

Relating to the main text, we have the explicit functions:

$$f_1(T^*, \rho^*) = 3\rho^{*2} \quad (\text{A1})$$

$$f_2(T^*, \rho^*) = 1, \quad (\text{A2})$$

together with $\alpha = \frac{1}{3}$ and $Z_c = \frac{3}{8}$.

The explicit form of the chemical potential is then

$$\frac{\mu}{k_B T_c} = \frac{\mu_{\text{ideal}}}{k_B T_c} - T^* \ln(1 - \frac{1}{3}\rho^*) + \frac{T^*}{(1 - \frac{1}{3}\rho^*)} - \frac{9}{4}\rho^*. \quad (\text{A3})$$

The liquid-vapour equilibrium conditions $\mu = \text{constant}$ and $p = \text{constant}$ then lead to:

$$T^* = \frac{1}{8}(\rho_L^* + \rho_G^*)(3 - \rho_L^*)(3 - \rho_G^*) \quad (\text{A4})$$

and

$$\ln \left[\frac{\rho_G^* 3 - \rho_L^*}{\rho_L^* 3 - \rho_G^*} \right] = 3 \frac{\rho_L^* - \rho_G^*}{(3 - \rho_L^*)(3 - \rho_G^*)} \left[1 - \frac{6}{\rho_L^* + \rho_G^*} \right]. \quad (\text{A5})$$

Equation (A5) yields the relation between ρ_L^* and ρ_G^* which is also plotted in Figure 1.

To complete the results of the van der Waals model, we record the "symmetrized" pressure, in units of the critical value, defined by

$$p_s^* = \frac{1}{2p_c} [p(T^*, \rho_L^*) + p(T^*, \rho_G^*)]. \quad (\text{A6})$$

In terms of ξ and η this takes the alternative forms

$$p_s^* = 8T^* \frac{\xi(3 - \xi) + \frac{1}{4}\eta^2}{(3 - \xi)^2 - \frac{1}{4}\eta^2} - 3(\xi^2 + \frac{1}{4}\eta^2) = (3 - 2\xi)(\xi^2 - \frac{1}{4}\eta^2), \quad (\text{A7})$$

the last step following from Eq. (A4). As anticipated in the main text, this depends on η^2 ; ie it is analytic at $\eta = 0$. To prove that $\beta = \frac{1}{2}$, one way is to return to Eq. (A5) and expand around $\xi = 1$ and $\eta = 0$.

A recent study of Osman and Silbert is also relevant here. They plot the coexistence curve for argon: below we indicate the modifications that occur using their treatment instead of van der Waals. The equation of state underlying the work of Osman and Silbert can be written

$$p = \frac{6}{\pi\sigma^3} \left[\frac{1 + \delta + \delta^2}{(1 - \delta)^3} k_B T + \frac{1}{2} K \delta^2 \right], \quad (\text{A8})$$

where the packing fraction δ is given in terms of the number density ρ and the hard core diameter σ as $\delta = \frac{1}{6}\pi\rho\sigma^3$. Writing again the appropriate equilibrium conditions one finds for the "symmetrized" pressure p_s :

$$p_s = \frac{3K}{\pi\sigma^3} \left[\frac{\delta_G^2(1 + \delta_L + \delta_L^2)(1 - \delta_G)^3 - \delta_L^2(1 + \delta_G + \delta_G^2)(1 - \delta_L)^3}{(1 + \delta_L + \delta_L^2)(1 - \delta_G)^3 - (1 + \delta_G + \delta_G^2)(1 - \delta_L)^3} \right] \quad (\text{A9})$$

The same defect of analyticity around the critical point is present in Eq. (A9), just as in the van der Waals form (A7). This is reflected in Figure 1 of the paper by Osman and Silbert.

DIETERICI'S EQUATION

Again making reference to the main text, one has the explicit forms:

$$f_1 = 0, f_2 = \exp(-2\rho^*/T^*), \alpha = \frac{1}{2}, Z_c = 2e^{-2}, \quad (\text{A10})$$

The equality of the pressure in the two phases yields first:

$$\frac{2(\rho_G^* - \rho_L^*)}{T^*} = \ln \left[\frac{\rho_G^*(2 - \rho_L^*)}{\rho_L^*(2 - \rho_G^*)} \right] \quad (\text{A11})$$

Equating chemical potentials, which is equivalent to Maxwell's "equal areas" construction, and then eliminating T^* , yields

$$\int_{\rho_G^*}^{\rho_L^*} d\rho^* \frac{\theta^{\rho^*/\eta}}{\rho^*(2 - \rho^*)} = \frac{\theta^{\rho_G^*/\eta}}{2 - \rho_G^*} - \frac{\theta^{\rho_L^*/\eta}}{2 - \rho_L^*} \quad (\text{A12})$$

where

$$\theta = \frac{\rho_G^*(2 - \rho_L^*)}{\rho_L^*(2 - \rho_G^*)}. \quad (\text{A13})$$

Relation (A12) has also been plotted in Figure 1.

The reduced symmetrized pressure p_s^* can again be found as

$$p_s^* = T^* \exp\{2(1 - \xi/T^*)\} \frac{[\xi(2 - \xi) + \frac{1}{4}\eta^2] \cosh(\eta/T^*) - \eta \sinh(\eta/T^*)}{(2 - \xi)^2 - \frac{1}{4}\eta^2} \quad (\text{A14})$$

which again is a function of η^2 .