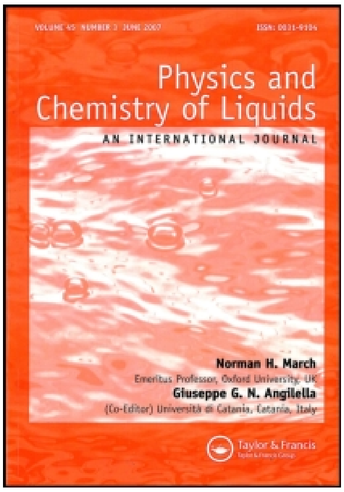

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On the Continuity of Isochore Slopes, and the Divergence of the Curvature of the Vaporization Curve at the Critical Point of a Simple Fluid†

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The role of the exponent inequality $\beta + \gamma > 1$ in the continuity of $(\partial P/\partial T)_v$ with the slope of the vaporization curve at the critical point is discussed. A connection between the divergence in the curvature of the vaporization curve and asymmetries in certain thermodynamic functions is established. It is shown, in the context of the scaling law equation of state, that the homogeneous phase specific heat $C_V^{(1)}$ on the liquid branch of the coexistence curve is slightly *lower* than on the gas branch, at the same temperature.

1 INTRODUCTION

In the first part of this paper we discuss the continuity of isochore slopes

$$\Gamma_v \equiv (\partial P/\partial T)_v \tag{1.1}$$

at the critical point of a simple fluid. In the context of the scaling law equation of state we observe that the exponent inequality $\beta + \gamma > 1$ is *sufficient* to ensure the continuity of isochore slopes with the slope of the vaporization curve, *irrespective* of the direction of approach to the critical point, but is *not necessary* for the continuity of the slope of the critical isochore Γ_{v_c} with the slope of the vaporization curve

$$\Gamma_\sigma \equiv (dP/dT)_\sigma \tag{1.2}$$

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§ On leave from the Physics Department, University of Alberta, Edmonton, Alberta, Canada at the critical point. These questions of continuity are also considered in generality via Clapeyron's equation, taking into account the requirements of thermodynamics.

In the second part of this paper we go on to discuss the origins of the divergence of the "curvature" of the vaporization curve $(d^2P/dT^2)_\sigma$, at the critical point, with particular reference to the small asymmetries which arise in the specific heat and certain other thermodynamic functions whose leading terms are perfectly symmetrical (or perfectly skew-symmetrical). We shall consider both the general consequences of thermodynamics, via Clapeyron's equation, and the specific formulae which come from the scaling law equation of state and from van der Waals' equation. In particular we shall show that, according to the scaling law, the value of the constant volume specific heat $C_v^{(l)}$ on the liquid branch of the coexistence curve is slightly lower than that of the gas at the same temperature.

Finally, we mention the rôle of Maxwell's construction, in spite of its dubious validity, in the continuity of Γ_v with Γ_σ, and in the divergence of $(d^2P/dT^2)_\sigma$ at the critical point.

2 CONTINUITY OF Γ_v AND THE EXPONENT INEQUALITY $\beta + \gamma > 1$.

Recently the question has arisen again as to why $(\partial P/\partial T)_v$ is continuous at the critical point of a simple fluid[1,2,3,4]. It is commonly stated that the critical isochore meets the vaporization curve σ at the critical point in the P-T phase diagram with the same slope. That is Γ_c and Γ_+ defined by

$$\Gamma_c \equiv \lim T \to T_c^- \Gamma_\sigma \tag{2.1}$$

and

$$\Gamma_+ \equiv \lim T \to T_c^+ \Gamma_{v_c} \tag{2.2}$$

are asserted to be equal. Experimental evidence on simple fluids is in favour of this equality. Indeed, sometimes the critical volume is measured by determining the density of the fluid at which this equality holds: that is, by finding which isochore joins smoothly onto the vaporization curve.[4] This equality is satisfied by van der Waals' equation, with the two-phase region being constructed in the usual way by Maxwell's equal-area rule. And it is built into the scaling-law equation of state, as formulated by Widom[5] and Griffiths[6,7,8].

Rice and Chang[1] have suggested that the equality of Γ_+ and Γ_c will follow if the coexistence curve exponent β and the isothermal compressibility exponent γ satisfy

$$\beta + \gamma > 1, \tag{2.3}$$

an inequality which will certainly hold if $\gamma > 1$ since $\beta > 0$. Their argument is based on the identity

$$(dP/dT)_\sigma = (\partial P/\partial T)^{(i)}_{V_{\ell,g}} + (\partial P/\partial V)^{(i)}_{T_{\ell,g}} (dV_{\ell,g}/dT), \tag{2.4}$$

where the subscripts ℓ, g denote the liquid or gas sides of the coexistence curve, and $i = 1, 2$ indicates that the partial derivative is evaluated from the i-phase side of the phase boundary, with $i = 1$ for the homogeneous phase, and $i = 2$ for the two-phase region. We denote the limiting values of Γ_V, evaluated on the phase boundary from the homogeneous phase side, by

$$\Gamma_\ell \equiv \lim T \to T_c^- \Gamma_{V_\ell}, \tag{2.5}$$

and

$$\Gamma_g \equiv \lim T \to T_c^- \Gamma_{V_g}. \tag{2.6}$$

Then it is obvious from (2.4) that equality of both Γ_ℓ and Γ_g with Γ_c follows if and only if $\beta + \gamma > 1$ as in (2.3).[2] In order to complete the proof of equality of Γ_+ with Γ_c, which now equals Γ_ℓ and Γ_g when $\beta + \gamma > 1$, it would appear that one must make an additional assertion concerning the continuity of Γ_v at the critical point, in order to extend the domain of equality of limiting isochore slopes from the coexistence curve, when $\Gamma_\ell = \Gamma_g = \Gamma_c$ when $\beta + \gamma > 1$, round to the critical isochore in the homogeneous phase where $T \to T_c^+$. For example, if we make the extra assumption that isochore slopes increase with increasing density, so $\partial^2 P/\partial\rho\partial T > 0$, then the desired equality $\Gamma_+ = \Gamma_c = \Gamma_\ell = \Gamma_g$ follows at once. We remark that in deriving Libermann's inequality

$$\beta + \gamma \geqslant \beta\delta \tag{2.7}$$

one assumes that $\partial^2 P/\partial\rho\partial T > 0$ between the coexistence curve and the critical isotherm[9].

When the behaviour of the isothermal compressibility and the coexistence curve can be described purely by power laws with exponents γ and β, then the inequality $\beta + \gamma > 1$ is obviously a necessary condition for the continuity of Γ_v at the critical point. We are, however, querying whether this inequality on its own may not be sufficient to establish in general the complete continuity of Γ_v at the critical point irrespective of the direction of approach. In the very special context of the scaling law equation of state, this inequality is indeed sufficient to establish the complete continuity of Γ_v at the critical point.

The question of the continuity of the slope of the critical isochore $\Gamma_{v_c} = (\partial P/\partial T)_{v_c}$ with the slope of the coexistence curve Γ_σ requires separate investigation. The most obvious necessary and sufficient condition is that

$(\partial\mu/\partial T)_{v_c}$ be continuous along the critical isochore. This follows from the thermodynamic relations

$$\left(\frac{\partial P}{\partial T}\right)_v = \rho S + \rho\left(\frac{\partial \mu}{\partial T}\right)_v, \; T > T_c, \tag{2.8}$$

and

$$\left(\frac{dP}{dT}\right)_\sigma = \rho S + \rho\left(\frac{d\mu}{dT}\right)_\sigma, \; T < T_c, \tag{2.9}$$

in which the entropy S and the density ρ are continuous at the critical point. Below T_c, P and μ are functions of T only. The continuity of Γ_{v_c} is built into the scaling law equation of state by assumption, and consequently it is continuous even when $\beta + \gamma \ngtr 1$, as we show explicitly below. The inequality $\beta + \gamma > 1$ is therefore not necessary for continuity of $(\partial P/\partial T)_v$ along the critical isochore.

We summarize our conclusions in Table 1.

The queried general problem of the sufficiency of the inequality $\beta + \gamma > 1$ for the continuity of Γ_v merits further investigation. Also it would be interesting to discover whether more physically intuitive conditions exist for the continuity of Γ_{v_c} along the critical isochore, than the obvious one considered above.

3 CONTINUITY OF Γ_v AND THE SCALING-LAW EQUATION OF STATE

The question of the uniqueness of the limiting value of Γ_v at the critical point can readily be resolved in the context of the scaling-law equation of state, for which

$$\beta + \gamma = \beta\delta, \tag{3.1}$$

where δ is the critical isotherm exponent. In fact the condition that the homogeneous function of appropriate scaling variables representing Γ_v should have positive degree is just $\beta\delta > 1$. This requirement is immediately

TABLE I
Role of inequality $\beta + \gamma > 1$

Problem	General Case	Scaling Law
Complete continuity of Γ_v	Necessary, but not(?) sufficient	Necessary and sufficient
Continuity of Γ_{v_c} along critical isochore	Neither necessary, nor(?) sufficient	Not necessary and irrelevant for sufficiency

satisfied if $\gamma \geqslant 1$, since $\beta > 0$. Moreover, when $\gamma > 1$, $\partial^2 P/\partial\rho\partial T$ vanishes at the critical point, and is positive throughout the critical region,[3] as observed experimentally.

However, the condition $\beta\delta > 1$ is not necessary for the equality of Γ_+ with Γ_c which depends only on critical isochore properties, as discussed above. If we do set $\beta\delta = 1$, then we can have

$$\Gamma_\ell > \Gamma_+ = \Gamma_c > \Gamma_g. \tag{3.2}$$

The exponents α, β and δ can all take reasonable values, and there is no problem with $(\partial^2 P/\partial T^2)_v$. But difficulties arise over the behaviour of $(\partial^2 P/\partial\rho\partial T)$, which is no longer positive throughout the critical region, although it does retain the *same* (positive) sign along and close to the coexistence curve, as indeed it must, as we argue in the final paragraph of this section. Since $\beta > 0$, we must now have $\gamma < 1$, a condition which we feel is unlikely to occur in practice, as we discuss below. (The remainder of this section contains mainly technical details pertaining to the scaling law equation of state. Note that in scaling-law formulae we have set $P_c = \rho_c = T_c = 1$.)

The scaling relations between exponents are

$$2 - \alpha = \beta(\delta + 1) = 2\beta + \gamma, \tag{3.3}$$

and (3.1). We require the specific heat exponent α to satisfy $0 \leqslant \alpha < 1$. If, as is usually the case, we assume $\gamma \geqslant 1$ (and $\beta > 0$, $\delta > 1$), then from (3.3) one finds that β, γ, δ are further restricted to the ranges

$$0 < \beta \leqslant \tfrac{1}{2},\ 1 \leqslant \gamma < 2,\ \delta \geqslant 3, \tag{3.4}$$

which correspond to values observed in practice. However, in the special case $\beta\delta = 1$ which we need now, the exponents are

$$\alpha = \gamma = 1 - \beta,\ \delta = 1/\beta, \tag{3.5}$$

so if $\beta < \frac{1}{3}$, α and δ can attain "reasonable" values, but $\gamma < 1$.

The discontinuous limiting behaviour of Γ_v when $\beta\delta = 1$ can readily be extracted from the scaling law equation of state, and the relevant expressions are collected in the Appendix, (A.19) to (A.22). We find

$$\Gamma_+ = \Gamma_c \equiv -da^*(T_c)/dT, \tag{3.6}$$

and

$$\Gamma_\ell = \Gamma_c + h'(-x_0),\ \Gamma_g = \Gamma_c - h'(-x_0), \tag{3.7}$$

where $h'(-x_0) > 0$, since the isothermal compressibility must be positive. More generally, if one approaches the critical point along a path of constant x, with $x = x_1 > -x_0$, say, then

$$\Gamma_v \to \Gamma_c + (\text{sign } \Delta\rho)h'(x_1),\ x = x_1. \tag{3.8}$$

On the other hand, along paths on which $x \to \infty$, so $|\Delta\rho| = o(\tau^{\beta})$, the leading term in the series part of (A.21) is $\Delta\rho\tau^{\gamma-1} = o(\tau^{\beta+\gamma-1}) = o(1)$, and we have

$$\Gamma_v \to \Gamma_c,\ x \to \infty. \tag{3.9}$$

So Γ_v is actually continuous for this latter class of paths, which *includes* the *linear* case.

When $\beta\delta = 1$, there are some difficulties associated with $h''(x)$. As $x \to \infty$

$$h''(x) = -\beta x^{\gamma-2}\sum_{n=1}^{\infty} c_n(2n-1)[\gamma - 2\beta(n-1)]x^{-2\beta(n-1)},\ (\beta\delta = 1), \tag{3.10}$$

which is negative. In spite of this, one must keep the constant C in (A.16) negative. Also when $\beta\delta = 1$,

$$\partial^2P/\partial\rho\partial T = \rho|\Delta\rho|^{\delta-1}(-x/\beta)h''(x). \tag{3.11}$$

On the coexistence curve $x = -x_0$ we have $h''(-x_0) > 0$, so $\partial^2P/\partial\rho\partial T$ is positive around the coexistence curve, and in its immediate neighbourhood. However, on the critical isotherm, $x = 0$ and $\partial^2P/\partial\rho\partial T$ vanishes. We may still take $h''(x) > 0$ for $-x_0 < x < 0$, so $\partial^2P/\partial\rho\partial T$ is positive between the coexistence curve and the critical isotherm. Just above T_c where $x > 0$, $\partial^2P/\partial\rho\partial T$ will be negative. But "close" to the critical isochore, in the sense that $x \to \infty$, $h''(x)$ is negative (3.10), and

$$\partial^2P/\partial\rho\partial T \sim c_1\gamma\tau^{\gamma-1} \tag{3.12}$$

is again positive, and diverges to $+\infty$, since $\gamma < 1$ when $\beta\delta = 1$. This erratic behaviour of $\partial^2P/\partial\rho\partial T$ has been discussed in order that one may appreciate the physical unacceptability of values of γ less than unity.

The necessity and sufficiency of the inequality $\beta + \gamma > 1$ for the complete continuity of Γ_v at the critical point follows straightforwardly from the general expressions for Γ_v in the Appendix, so we omit a detailed proof.

We append a final remark concerning the sign of $\partial^2P/\partial T\partial V$. Quite generally, by differentiating (2.4),

$$\left(\frac{d^2P}{dT^2}\right)_\sigma = \left(\frac{\partial^2P}{\partial T^2}\right)_V + 2\left(\frac{\partial^2P}{\partial T\partial V}\right)\left(\frac{dV}{dT}\right)_\sigma + \left(\frac{\partial^2P}{\partial V^2}\right)_T\left(\frac{dV}{dT}\right)_\sigma^2 + \\ + \left(\frac{\partial P}{\partial V}\right)_T\left(\frac{d^2V}{dT^2}\right)_\sigma. \tag{3.13}$$

Now writing the expected signs and exponents (according to scaling) for all quantities except $\partial^2P/\partial T\partial V$ which is denoted by $(?)(-\tau)^{\gamma^*-1}$, this equation is asymptotically (to leading order, omitting amplitudes)

$$(-\tau)^{-\alpha} \sim (\text{sign } \Delta\rho)\left[(-\tau)^{-(\alpha+\beta)} + (?)(-\tau)^{\gamma^*+\beta-2} + (-\tau)^{\gamma+\beta-2} - (-\tau)^{\gamma+\beta-2}\right]. \tag{3.14}$$

In scaling with $\gamma^* = \gamma$, the four terms on the RHS all diverge like $(-\tau)^{-(\alpha+\beta)}$, and so must cancel. They will all change sign at the critical point, provided $\partial^2 P/\partial T \partial V$ retains the *same sign* around the coexistence curve. We are assuming that $(\partial^2 P/\partial V^2)_T$ has the intuitively obvious sign of $\Delta\rho$ in the vicinity of the critical point below T_c.

4 CONTINUITY OF Γ_v AND CLAPEYRON'S EQUATION

Clapeyron's equation for the slope of the coexistence curve is derived by requiring equality of chemical potentials of the saturated liquid and gas:

$$\left(\frac{dP}{dT}\right)_\sigma = \frac{S_g - S_l}{V_g - V_l} \tag{4.1}$$

By developing the numerator for the entropy difference between gas and liquid, one can investigate the continuity of Γ_v on the coexistence curve. We have

$$S_g - S_l = \int_l^g \left[\left(\frac{\partial P}{\partial T}\right)_v^{(1)} + \frac{C_v^{(1)}}{T}\left(\frac{dT}{dV}\right)_\sigma\right] dV \tag{4.2}$$

where partial derivatives are evaluated on the coexistence curve from the homogeneous phase side. Now one can describe the shape of the coexistence curve by

$$|V - V_c| \sim B_{l,g}(-\tau)^\beta, \tag{4.3}$$

allowing if necessary for different amplitudes B_l, B_g for the liquid and gas, but retaining the same exponent β. Similarly, the constant volume specific heat varies as

$$C_{vl,g}^{(1)} \sim (A_{l,g}/\alpha)(-\tau)^{-\alpha}. \tag{4.4}$$

And we adopt

$$(\partial P/\partial T)_v \sim \Gamma_c + E_{l,g}(\text{sign } \Delta\rho)(-\tau)^{\beta+\gamma^*-1} \tag{4.5}$$

with $E_{l,g} > 0$, as the form for Γ_v, where γ^* is an exponent which equals γ in the scaling theory. Such a form for Γ_v is to be expected since the temperature variation of Γ_v along the coexistence curve is described by

$$\begin{aligned}\left(\frac{d\Gamma_v}{dT}\right)_\sigma &= \frac{d}{dT}\left(\frac{\partial P}{\partial T}\right)_{vl,g}^{(1)} = \left(\frac{\partial^2 P}{\partial T^2}\right)_v + \left(\frac{\partial^2 P}{\partial T \partial V}\right)\left(\frac{dV}{dT}\right)_\sigma \\ &\sim (\text{sign } \Delta\rho)(-\tau)^{-\theta^*} + \left[-(-\tau)^{\gamma^*}\right]\left[(\text{sign } \Delta\rho)(-\tau)^{\beta-1}\right],\end{aligned} \tag{4.6}$$

where on the second line we indicate the signs and orders of magnitude of the various terms. In scaling theory $\theta^* = (\alpha + \beta)$ and $\gamma^* = \gamma$. Now Γ_v increases steadily with ρ around the coexistence curve, so the LHS of (4.6) has the same sign as $(-\Delta\rho)$. Consequently on the RHS the $(\partial^2 P/\partial T^2)_v$ term must be *completely* cancelled by part of the last term, and the exponent of the remainder must be $\gamma^* + \beta - 1$. This cancellation can be verified explicitly for the scaling law equation of state.

Inserting the above asymptotic forms in (4.2) we find that the entropy difference is

$$S_g - S_\ell \sim \Gamma_c(V_g - V_\ell) - \left[\frac{\beta E_{\ell,g} B_{\ell,g}(-\tau)^{\gamma^*+2\beta-1}}{(\gamma^* + 2\beta - 1)} + \frac{A_{\ell,g}^{(1)}(-\tau)^{1-\alpha}}{T\alpha(1-\alpha)}\right]_\ell^g. \tag{4.7}$$

If $\gamma^* + \beta > 1 > \alpha + \beta$ the second and third terms drop out, even after division by $(V_g - V_\ell) \sim (B_g + B_\ell)(-\tau)^\beta$. But if $\gamma^* + \beta = 1 = \alpha + \beta$, we have

$$\left(\frac{dP}{dT}\right)_\sigma \sim \left[\frac{\Gamma_g B_g + \Gamma_\ell B_\ell}{(B_g + B_\ell)}\right] - \left[\frac{A_g^{(1)} - A_\ell^{(1)}}{T\alpha(1-\alpha)(B_g + B_\ell)}\right], \tag{4.8}$$

where now

$$\Gamma_g = \Gamma_c - E_g,\ \Gamma_\ell = \Gamma_c + E_\ell. \tag{4.9}$$

(4.8) imposes a restriction on the amplitudes, since by definition of Γ_c in (2.1) the RHS must reduce to Γ_c, which it obviously does in the symmetrical case, as in scaling theory.

5 CURVATURE OF THE VAPORIZATION CURVE, AND ASYMMETRIES BETWEEN LIQUID AND GAS

The curvature of the vaporization curve $(d^2P/dT^2)_\sigma$ is related to the specific heat $C_v^{(2)}$ in the two phase region, and can further be expressed in terms of the differences between certain thermodynamic functions evaluated on the coexistence curve from the liquid and gas sides. One can therefore relate any divergence in the curvature of the vaporization curve to asymmetries in the specific heat in the one-phase region.

In general in the two-phase region at density ρ[10]

$$\left(\frac{d^2P}{dT^2}\right)_\sigma = \frac{\rho C_v^{(2)}}{T} + \rho\left(\frac{d^2\mu}{dT^2}\right)_\sigma. \tag{5.1}$$

Near the critical point let the vaporization curve curvature be described by

$$(d^2P/dT^2)_\sigma \sim (-\tau)^{-\theta}, \tag{5.2}$$

and let the specific heat along the critical isochore be

$$C^{(2)}_{V_c} \sim (A/\alpha)(-\tau)^{-\alpha}. \tag{5.3}$$

Then if $(d^2\mu/dT^2)_\sigma$ is non-singular (or sufficiently weakly singular) then

$$\theta = \alpha, \tag{5.4}$$

as is the case in scaling theory, in which $\mu(\rho_c, T)$ is presumed to be analytic in T. From (5.1), or from differentiation of Clapeyron's equation,

$$T\left(\frac{d^2P}{dT^2}\right)_\sigma = \left(\frac{\partial C_V}{\partial V}\right)_T = \frac{C^{(2)}_{Vg} - C^{(2)}_{V\ell}}{V_g - V_\ell}. \tag{5.5}$$

Now there is a (positive) jump discontinuity in the specific heat on entering the two-phase region, which is

$$\triangle \equiv C^{(2)}_V - C^{(1)}_V = (-)T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{dV}{dT}\right)^2_\sigma = \frac{T}{\rho^2}\left(\frac{\partial P}{\partial \rho}\right)_T\left(\frac{d\rho}{dT}\right)^2_\sigma. \tag{5.6}$$

Near the critical point the isothermal compressibility diverges like

$$K_T \equiv [\rho(\partial P/\partial\rho)_T]^{-1} \sim C_{\ell,g}(-\tau)^{-\gamma}, \tag{5.7}$$

so the jump $\triangle$ diverges like

$$\triangle \sim (B^2/C)(-\tau)^{-(2-2\beta-\gamma)} \tag{5.8}$$

By Rushbrooke's inequality $2 - 2\beta - \gamma < \alpha$,[11,12,13] so the divergence in the jump is at most as strong as the specific heat $C^{(2)}_{V_c}$ divergence in (5.3). From (5.5), when $(d^2P/dT^2)_\sigma$ is expressed in terms of homogeneous phase quantities, we have

$$T(d^2P/dT^2)_\sigma = [(C^{(1)}_{Vg} - C^{(1)}_{V\ell}) + (\triangle_g - \triangle_\ell)]/(V_g - V_\ell), \tag{5.9}$$

whence it is obvious that asymmetries in $C^{(1)}_V$ and $\triangle$ of order $(V_g - V_\ell)$ are involved.

In order to introduce the required asymmetries explicitly, let us write

$$(d\rho/dT)_\ell = (-)(d\rho/dT)_g[1 + d_1(\rho_\ell - \rho_g)/\rho_c + \ldots], \tag{5.10}$$

$$(\partial P/\partial\rho)_{T\ell} = (\partial P/\partial\rho)_{Tg}[1 + d_2(\rho_\ell - \rho_g)/\rho_c + \ldots], \tag{5.11}$$

$$C^{(1)}_{V\ell} = C^{(1)}_{Vg}[1 + d_3(\rho_\ell - \rho_g)/\rho_c + \ldots]. \tag{5.12}$$

We have retained linear asymmetric terms since these give the dominant contributions in (5.9). Any asymmetries in $(\partial P/\partial T)_V$ can be related to those in $(\partial P/\partial\rho)_T$ and $(d\rho/dT)_\sigma$ by (2.4). If a quasi-rectilinear diameter can be constructed in the form

$$\tfrac{1}{2}(\rho_\ell + \rho_g) \sim B_1(-\tau)^{1-\alpha} \tag{5.13}$$

with liquid and gas densities separately described by

$$\rho_l - \rho_c \sim B(-\tau)^\beta + B_1(-\tau)^{1-\alpha} \tag{5.14}$$
$$\rho_c - \rho_g \sim B(-\tau)^\beta - B_1(-\tau)^{1-\alpha},$$

with obvious generalizations if amplitude symmetry does not hold, then to leading orders

$$\left(\frac{d\rho_l}{dT}\right) \sim (-)\left(\frac{d\rho_g}{dT}\right)\left[1 + \frac{2(1-\alpha)B_1}{\beta B}\left(\frac{|\Delta\rho|}{B}\right)^{(1-\alpha-\beta)/\beta}\right] \tag{5.15}$$

But the exponent $(1 - \alpha - \beta)/\beta$ in (5.15) is greater than unity when $\gamma > 1$, since, at least in scaling theory, $1 - \alpha - 2\beta = \gamma - 1 > 0$, and is exactly unity for van der Waals' equation. So the coefficient d_1 is zero in practice, except for van der Waals' equation. In scaling theory, complete symmetry of the coexistence curve is assumed, and then d_1 is automatically zero.

Substituting in (5.9), we obtain

$$\left(\frac{d^2P}{dT^2}\right)_\sigma \sim (-)\frac{d_3\rho_c C^{(1)}_{v_g}}{T} + \frac{1}{\rho_c}\left(\frac{\partial P}{\partial\rho}\right)_{T_g}\left(\frac{d\rho_g}{dT}\right)^2[2 - 2d_1 - d_2]. \tag{5.16}$$

This equation displays explicitly how the curvature of the vaporization curve acquires the same asymptotic divergence as $C_v^{(1)}$ (and $\triangle$), and yet depends on asymmetries in these quantities. From experiment, we know that the vaporization curve of a simple fluid bends upwards in the P-T phase diagram, so $(d^2P/dT^2)_\sigma > 0$. Therefore the terms on the RHS of (5.16) must combine to give a positive result. This is achieved in scaling theory since then $d_1 = 0$, $d_2 = 1$ and $d_3 < 0$, as we shall show below. Moreover if $\alpha > 2 - 2\beta - \gamma$, then the $C_v^{(1)}$ term is dominant, and we must have $d_3 < 0$. But this means that close to the critical point $C^{(1)}_{v_g} > C^{(1)}_{v_l}$, and the liquid has a *lower* specific heat than the gas (on the coexistence curve at the same temperature), even though both specific heats are divergent. This is somewhat surprising since one generally expects the liquid to have a greater specific heat than the gas. This result is confirmed by the scaling-law theory, and merits checking out experimentally.

6 CURVATURE OF THE VAPORIZATION CURVE, AND SCALING THEORY

According to scaling theory, the curvature of the vaporization curve is

$$(d^2P/dT^2)_\sigma = -d^2a^*(T)/dT^2 - (2-\alpha)(1-\alpha)(-\tau/x_0)^{-\alpha}a_\alpha(-x_0)/x_0^2, \tag{6.1}$$

where $a_\alpha(-x_0) < 0$ so the specific heat $C_{v_c}^{(2)}$ is positive. This divergence can now be related to $C_V^{(1)}$ and Δ. On the coexistence curve

$$\rho C_V^{(1)}/T = -d^2a^*(T)/dT^2 - \rho d^2\mu(\rho_c,T)/dT^2 - (-\tau/x_0)^{-\alpha}a''_\alpha(-x_0), \quad (6.2)$$

where the final singular term is assumed to be positive for thermodynamic stability. The specific heat difference between liquid and gas is now

$$C_{V_\ell}^{(1)} - C_{V_g}^{(1)} = T(V_g - V_\ell)[d^2a^*(T)/dT^2 + (-\tau/x_0)^{-\alpha}a''_\alpha(-x_0)], \quad (6.3)$$

which is *negative* and vanishes like $(-\tau)^{\beta-\alpha}$ at the critical point.

In scaling, the coexistence curve and the derivative combination $(\partial P/\partial\rho)_T/\rho$ are *completely symmetrical* in liquid and gas about the critical point, with

$$(\partial P/\partial\rho)_T/\rho = (\rho^2K_T)^{-1} = (-\tau/x_0)^\gamma(x_0/\beta)h'(-x_0). \quad (6.4)$$

Now it is obvious that $d_1 = 0$, $d_2 = 1$, and $d_3 < 0$ in (6.3). Combining the specific heat difference and the jump difference, both of which are *positive* and are *entirely linear* in $(V_g - V_\ell)$, we obtain

$$(d^2P/dT^2)_\sigma = -d^2a^*(T)/dT^2 + (-\tau/x_0)^{-\alpha}[(\beta/x_0)h'(-x_0) - a''_\alpha(-x_0)], \quad (6.5)$$

which may be shown to be equivalent to (6.1) by use of the differential equation (A.13) for $a_\alpha(x)$ when $x = -x_0$.

7 RÔLE OF MAXWELL'S CONSTRUCTION

We shall show briefly how Maxwell's tangent construction, or "equal-area" rule can be used to derive the continuity of Γ_σ with Γ_V when the equation of state expresses the pressure P as an analytic function P^* of V and T, as it is in the case of van der Waals' equation, for example.

Suppose quite generally that

$$P = P^*(V, T). \quad (7.1)$$

In order to locate the coexistence curve at temperature T, set

$$P_\sigma = P^*(V_g, T) = P^*(V_\ell, T), \quad (7.2)$$

and apply the equal area rule

$$P_\sigma(V_g - V_\ell) = \int_{V_\ell}^{V_g} P^*(V, T)\,dV. \quad (7.3)$$

Differentiating with respect to temperature, one obtains

$$(V_g - V_\ell)\left(\frac{dP}{dT}\right)_\sigma = \int_{V_\ell}^{V_g}\left(\frac{\partial P^*}{\partial T}\right)_V dV. \quad (7.4)$$

Letting $T \to T_c$, one find that Γ_c, defined in (2.1) as the limiting slope of the vaporization curve, equals the unique limiting value of $\Gamma_v = (\partial P/\partial T)_v$.

The singular behaviour of $(d^2 P/dT^2)_\sigma$ also follows by a further differentiation with respect to temperature:

$$(V_g - V_l)\left(\frac{d^2 P}{dT^2}\right)_\sigma = \frac{\Delta_g - \Delta_l}{T} + \int_{V_l}^{V_g}\left(\frac{\partial^2 P^*}{\partial T^2}\right)_v dV \tag{7.5}$$

where Δ_g and Δ_l are the specific heat jumps. For van der Waals' equation $(\partial^2 P/\partial T^2)_v \equiv 0$, so the discontinuous behaviour of $(d^2 P/dT^2)_\sigma$ arises in this case entirely from the specific heat jumps. Equation (7.5) may be compared with (5.9), and the asymmetries may be introduced explicitly as in (5.10) to (5.12) if desired, to give a formula analogous to (5.16).

Of course, the well-known undesirable feature of the Maxwell construction – that it employs the analytic continuation of the pressure into the two-phase region in order to locate the coexistence curve – persists in the above formulae. Our previous results such as (5.9) and (5.16) are of quite general validity.

Appendix

We summarize here the scaling law equation of state for a simple fluid, and derive expressions for the various derivatives referred to in the text. We employ a system of units in which the critical values of pressure, molar density, and temperature are unity: $P_c = \rho_c = T_c = 1$. Also $V = 1/\rho$. The chemical potential $\mu(\rho, T)$ as a function of ρ and T is expressed in terms of the deviation from its value $\mu(\rho_c, T)$ on the critical isochore as follows:

$$\Delta\mu \equiv \mu(\rho, T) - \mu(\rho_c, T) = (\mathrm{sign}\ \Delta\rho)|\Delta\rho|^\delta h(x), \tag{A.1}$$

where

$$\begin{aligned} x &= \tau/|\Delta\rho|^{1/\beta},\\ \tau &= (T - T_c)/T_c,\\ \Delta\rho &= (\rho - \rho_c)/\rho_c. \end{aligned} \tag{A.2}$$

$\Delta\mu$ is antisymmetric in $\Delta\rho$. Also $\mu(\rho_c, T)$ is taken to be analytic in T, so that $\Delta\mu$ will be analytic in ρ and T throughout the homogeneous phase (one-phase region). h(x) vanishes on the phase boundary (coexistence curve) where $x = -x_0 < 0$. The equation of the coexistence curve is then

$$|\Delta\rho| = (-\tau/x_0)^\beta. \tag{A.3}$$

In the neighbourhood of the critical isotherm h(x) is assumed to have the expansion

$$h(x) = \sum_{n=0}^{\infty} h_n x^n. \tag{A.4}$$

In the neighbourhood of the critical isochore h(x) is assumed to have the expansion

$$h(x) = \sum_{n=1}^{\infty} c_n\, x^{\beta(\delta+1-2n)} = x^{\gamma} \sum_{n=1}^{\infty} c_n\, x^{-2\beta(n-1)}, \tag{A.5}$$

where we have set

$$\gamma = \beta(\delta - 1). \tag{A.6}$$

This ensures that for $T > T_c$, $\Delta\mu$ can be expanded as a power series in $\Delta\rho$ containing only odd powers. γ will be the exponent for the isothermal compressibility, as may easily be seen from

$$(\rho^2 K_T)^{-1} = (\partial\mu/\partial\rho)_T = |\Delta\rho|^{\delta-1}[\delta h(x) - (x/\beta)h'(x)] \tag{A.7a}$$

$$= \tau^{\gamma} \sum_{n=1}^{\infty} c_n\,(2n - 1)x^{-2\beta(n-1)}, \tag{A.7b}$$

which must be positive, for stability. On the coexistence curve

$$(\rho^2 K_T)^{-1} = (-\tau/x_0)^{\gamma}(x_0/\beta)h'(-x_0). \tag{A.8}$$

A further differentiation gives

$$\frac{\partial^2 P}{\partial\rho\partial T} = \rho|\Delta\rho|^{(\gamma-1)/\beta}[(\beta\delta - 1)h'(x) - xh''(x)]/\beta \tag{A.9a}$$

$$= \rho\tau^{\gamma-1} \sum_{n=1}^{\infty} c_n\,(2n - 1)[\gamma - 2\beta(n - 1)]x^{-2\beta(n-1)}. \tag{A.9b}$$

If we set

$$2 - \alpha = \beta(\delta + 1) = 2\beta + \gamma, \tag{A.10}$$

α will be the specific heat C_v exponent, which must be less than unity so the entropy is finite. We consider only cases with $0 < \alpha < 1$.

The Helmholtz free energy per unit volume takes the form

$$a(\rho, T) = a^*(T) + \rho\mu(\rho_c, T) + |\Delta\rho|^{\delta+1}a_\alpha(x), \tag{A.11}$$

where a*(T) is an unknown "background" free energy, presumed to be an analytic function of T. Since

$$(\partial a/\partial\rho)_T = \mu, \tag{A.12}$$

the function $a_\alpha(x)$ must satisfy the differential equation

$$-xa'_\alpha(x) + (2-\alpha)a_x(x) = \beta h(x). \tag{A.13}$$

The solution which is analytic near $x = 0$ is unique, and may be written in the form

$$a_\alpha(x) = \beta\left[\frac{h(x)}{(2-\alpha)} + \frac{xh'(x)}{(2-\alpha)(1-\alpha)} - x|x|^{1-\alpha}\int_0^x \frac{h''(y)|y|^{\alpha-1}}{(2-\alpha)(1-\alpha)}dy\right] \tag{A.14}$$

The solution for $x > 0$ is

$$a_\alpha(x) = Cx^{2-\alpha} + \beta x^{2-\alpha}\int_x^\infty h(y)y^{\alpha-3}dy, \tag{A.15}$$

where the constant C is determined by matching the two forms of the solution for large x:

$$C = -\beta\int_0^\infty \frac{h''(y)y^{\alpha-1}}{(2-\alpha)(1-\alpha)}dy. \tag{A.16}$$

C must be negative so that the specific heat is positive.A suffficient condition for this is $h''(x) > 0$ for $0 < x < \infty$. By differentiation, we can now obtain the specific heat at constant volume $C_V^{(1)}$:

$$\left(\frac{-\rho C_V^{(1)}}{T}\right) = \frac{d^2a^*(T)}{dT^2} + \rho\frac{d^2\mu(\rho_c, T)}{dT^2} + |\Delta\rho|^{-\alpha/\beta}a''_\alpha(x). \tag{A.17}$$

All three terms on the RHS are presumed to be negative.

An explicit formula for the pressure may be derived via the thermodynamic relation $P = \mu\rho - a$:

$$P(\rho, T) = -a^*(T) + (\text{sign } \Delta\rho)|\Delta\rho|^\delta h(x) + |\Delta\rho|^{\delta-1}[h(x) - a_\alpha(x)]. \tag{A.18}$$

The critical value of the pressure is $P_c \equiv P(\rho_c, T_c) = -a^*(T_c)$. Setting $x = -x_0$, we obtain the equation of the vaporization curve, and its slope and curvature:

$$P_\sigma = -a^*(T) - a_\alpha(-x_0)(-\tau/x_0)^{2-\alpha}, \tag{A.19a}$$

$$\Gamma_\sigma \equiv (dP/dT)_\sigma = -da^*(T)/dT + (2-\alpha)a_\alpha(-x_0)(-\tau/x_0)^{1-\alpha}/x_0, \tag{A.19b}$$

$$(d^2P/dT^2)_\sigma = -d^2a^*(T)/dT^2 - (2-\alpha)(1-\alpha)a_\alpha(-x_0)(-\tau/x_0)^{-\alpha}/x_0^2. \tag{A.19c}$$

We presume that $a_\alpha(-x_0)$ is negative in order that the specific heat $C_V^{(2)}$ in the two-phase region be positive. The curvature of the vaporization curve is then positive in (A.19c).

A partial derivative of the pressure with respect to temperature gives the isochore slopes

$$\begin{aligned}\Gamma_v \equiv (\partial P/\partial T)_v = -da^*(T)/dT + (\mathrm{sign}\ \Delta\rho)|\Delta\rho|^{\delta-1/\beta}h'(x) \\ + |\Delta\rho|^{\delta+1-1/\beta}[h'(x) - a'_\alpha(x)],\end{aligned} \tag{A.20}$$

where $a'_\alpha(x)$ is given by the differential equation (A.13). Near the critical isochore

$$\begin{aligned}\Gamma_v = -da^*(T)/dT - C(2-\alpha)\tau^{1-\alpha} \\ + \Delta\rho\tau^{\gamma-1}\sum_{n=1}^{\infty} c_n\left[1 + \Delta\rho\left(1 - \frac{1}{2n}\right)\right][\gamma - 2\beta(n-1)]x^{-2\beta(n-1)},\end{aligned} \tag{A.21}$$

and on the coexistence curve

$$\begin{aligned}\Gamma_{v_{l,g}} = -da^*(T)/dT + (\mathrm{sign}\ \Delta\rho)(-\tau/x_0)^{\beta\delta-1}h'(-x_0) \\ + (-\tau/x_0)^{1-\alpha}[h'(x) - a'_\alpha(x)].\end{aligned} \tag{A.22}$$

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