

A simple theory for the densities of coexistent liquid and vapour through the transition region

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Abstract. The two-particle distribution function for a system of liquid and vapour in equilibrium is approximated by the product $n(z_1)n(z_2)g(|r_2 - r_1|)$, where the radial distribution function g is taken to be that of the liquid. The Born-Green-Yvon equation for the density $n(z)$ is solved, giving the form of the interface between liquid and vapour as well as a relation between their densities n_L and n_V .

The relation between the densities is shown to be consistent with experimental results. Further, when this relation is combined with the demand that the pressures in the two phases be equal, it is shown that the empirical scaling law $n_L - n_V \propto (T_C - T)^{1/3}$ is a consequence of a simple assumption about the approach of the liquid and vapour correlation functions towards equality near the critical temperature.

1. Introduction

Below the critical temperature a liquid can exist in equilibrium with its vapour, the two phases being separated by an interface which is exceedingly thin on a macroscopic scale.

Over a region comparable with atomic dimensions, however, time-averaged quantities, such as density, change smoothly from their liquid to their vapour values. The detailed form of the number density variation (the 'density profile') is important for the calculation of surface tension and other observable properties of the interface.

In this paper we begin (§ 2) by making a simple approximation for the form of the two-particle distribution function. This enables the appropriate statistical-mechanical equation to be solved for the density profile $n(z)$, starting from the liquid value n_L (at $z = -\infty$) and working through the interface (near $z = 0$) into the vapour phase (at $z = \infty$) where we predict the density n_V .

Next, in § 3, we examine more closely the relation between n_L and n_V , using first the additional empirical restriction that the density difference is proportional to $(T_C - T)^{1/3}$. Then we replace this restriction with the requirement that the pressures must be equal in the two phases. This leads to a formalism for the complete liquid-vapour coexistence curve if we regard the interatomic potential $\phi(R)$ and the liquid and vapour radial distribution functions $g_L(R)$ and $g_V(R)$ as given functions. The theory gives poor predictions for the pressure, which depends very sensitively on the precise form of the intermolecular correlations.

The final part of the article, § 4, is devoted to an examination of the coexistence curve near to the critical temperature T_C . We find that the simplest possible assumption concerning the temperature-dependence of g_L and g_V implies the well-established empirical law that the density difference $n_L - n_V$ is proportional to $(T_C - T)^{1/3}$. However, there appears to be no simple theoretical argument leading to the 'law of rectangular diameter' for $n_L + n_V$.

2. The density profile

We assume that the interface is situated near the plane $z = 0$, and we consider two points at \mathbf{r}_1 and \mathbf{r}_2 , separated by (figure 1)

$$\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1.$$

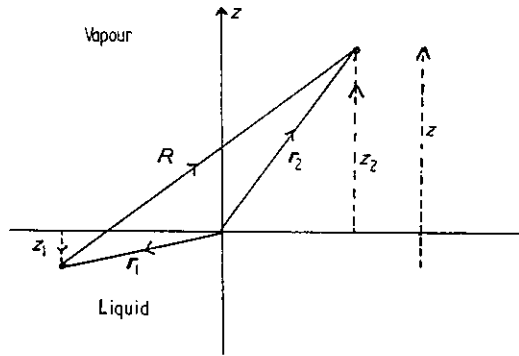


Figure 1. Basic geometry of interface.

Then the two-particle density distribution function, which depends not only on the separation of the two points but also on their position relative to the interface, can be denoted by $n_2(z_1, \mathbf{R})$. The Born–Green–Yvon (BGY) equation for the density $n(z)$, an exact relation derivable from equilibrium statistical mechanics (assuming only pairwise interactions between the molecules), is given by (Ono and Kondo 1960—equation (27.5))

$$kT \frac{dn(z_1)}{dz_1} = \int d\mathbf{R} \frac{z}{R} \phi'(R) n_2(z_1, \mathbf{R}) \quad (1)$$

where k is Boltzmann's constant, the primes denote differentiation of functions with respect to their arguments and z is the component of \mathbf{R} perpendicular to the interface.

We now introduce our basic approximation: arguing that the densities $n(\mathbf{r}_1)$ and $n(\mathbf{r}_2)$ dominate the behaviour of the two-particle distribution function, and that most of the interactions which cause the correlations must occur in the liquid, we write

$$n_2(z_1, \mathbf{R}) = n(z_1) n(z_1 + z) g_L(R). \quad (2)$$

We assume that $g_L(R)$, and, later $g_V(R)$, depend only on T ; we are neglecting the dependence of these functions on the density along the isotherms near the coexistence curve. The relation (2) has also been suggested by Green (1960).

If we insert (2) into (1), and write the \mathbf{R} integration in terms of coordinates R , z and an azimuthal angle which integrates out to give a factor 2π , we get

$$kT \frac{d}{dz_1} \ln\{n(z_1)\} = 2\pi \int_{-\infty}^{\infty} dz n(z_1 + z) z \int_{|z|}^{\infty} dR \phi'(R) g_L(R). \quad (3)$$

This is a nonlinear integral equation for the density profile, involving the kernel

$$h(z) = \frac{2\pi z}{kT} \int_{|z|}^{\infty} dR \phi'(R) g_L(R) \quad (4)$$

which is an odd function of z and goes to zero when $|z|$ exceeds the range of the interparticle force. If we define the even function

$$k(z) = - \int_z^{\infty} h(z') dz' \quad (5)$$

our integral equation becomes

$$\begin{aligned} \frac{d}{dz_1} \ln\{n(z_1)\} &= \int_{-\infty}^{\infty} dz n(z_1+z) k'(z) \\ &= - \int_{-\infty}^{\infty} dz n'(z_1+z) k(z) \\ &\quad - \frac{d}{dz_1} \int_{-\infty}^{\infty} dz n(z_1+z) k(z) \end{aligned} \quad (6)$$

where we have integrated by parts. This can be integrated to give

$$C = \frac{1}{n(z_1)} \exp\left\{- \int_{-\infty}^{\infty} dz k(z)n(z_1+z)\right\} \quad (7)$$

where C is a constant independent of z .

Our basic relation between liquid and vapour densities will involve the constant

$$K_L(T) \equiv - \int_{-\infty}^{\infty} k(z) dz = \frac{4\pi}{3kT} \int_0^{\infty} dR R^3 \phi'(R) g_L(R) \quad (8)$$

where the last equality comes from (4) and (5) after a little reduction. K_L is positive because the interactions in the condensed liquid phase are dominated by the attractive forces, for which $\phi'(R)$ is positive. We now equate the asymptotic forms of the right-hand side of (7), to get

$$C = \frac{\exp(K_L n_L)}{n_L} = \frac{\exp(K_L n_V)}{n_V} \quad (9)$$

For a given temperature, we can plot $\exp\{K_L(T)n\}/n$ against n (figure 2), choose a liquid density n_L (which must exceed $1/K_L(T)$), and read off the corresponding vapour density n_V .

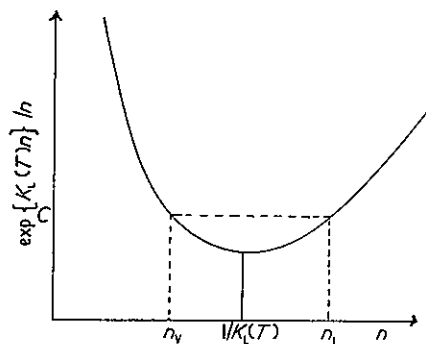


Figure 2. Construction relating liquid and vapour densities at a given temperature.

Knowing the two limiting densities, the profile $n(z)$ can be found by iterating equation (7). Starting from a zeroth approximation where the density changes suddenly from n_L to n_V at $z = 0$, namely

$$n^{(0)}(z) = n_L\theta(-z) + n_V\theta(z) \quad (10)$$

(where $\theta(z)$ is the unit step function), we calculate the m th approximation from

$$n^{(m)}(z) = n_L \exp\left\{-K_L n_L - \int_{-\infty}^{\infty} dz' n^{(m-1)}(z+z') k(z')\right\} \quad (11)$$

which behaves correctly at $z = \pm \infty$. For a simple analytical approximation it is probably sufficient to take the first iteration,

$$n^{(1)}(z) = n_L \exp\left\{\int_{-\infty}^z dz' k(z')(n_L - n_V)\right\}. \quad (12)$$

According to our theory, the thickness of the transition layer between liquid and vapour is comparable with the range of the kernel $k(z)$, i.e. with the range of the interatomic forces. This result should hold right up to the critical point (the broadening of the interface to macroscopic dimensions, observed in experiments near the critical point, can be interpreted as a gravitational effect—Heller 1967).

3. The liquid-vapour coexistence curve

From our equation (9) it is possible to calculate n_V from a given n_L , but a second equation is necessary in order to determine the single n_L for which liquid and vapour can coexist at a given temperature. One such relation is the empirical law (Guggenheim 1945)

$$\frac{n_L - n_V}{n_C} = \frac{7}{2} \left(1 - \frac{T}{T_C}\right)^{1/3} \quad (13)$$

which is satisfied down to about half the critical temperature for a range of substances. The combination of (13), (9), and (16) (which we shall prove presently) leads to

$$\left. \begin{aligned} n_L(T) &= \frac{7n_C(1 - T/T_C)^{1/3}}{2[1 - \exp\{-7\{K_L(T)/2K_C\}(1 - T/T_C)^{1/3}\}]} \\ n_V(T) &= \frac{7n_C(1 - T/T_C)^{1/3} \exp\{-7\{K_L(T)/2K_C\}(1 - T/T_C)^{1/3}\}}{2[1 - \exp\{-7\{K_L(T)/2K_C\}(1 - T/T_C)^{1/3}\}]} \end{aligned} \right\} \quad (14)$$

where subscripts denote quantities which are evaluated at the critical point. These two densities are plotted against T in figure 3, together with the curve (Guggenheim 1945) which best fits the experimental results; we assume for simplicity that the liquid radial distribution function is independent of temperature, so that $K_L(r) \propto 1/T$ (cf. equation (8)). It is seen that the curves differ markedly only near (but not, of course, at) the critical point, probably because we cannot neglect the T dependence of g_L in this region.

An alternative procedure to using the empirical relation (13) to supplement our equation (9) is to demand that the densities n_L and n_V obey the basic equilibrium

condition that the liquid and vapour must have the same pressure. In any homogeneous phase, the pressure is given by (Egelstaff 1967)

$$p(n, T) = nkT \left\{ 1 - \frac{n}{2} K(T) \right\}. \quad (15)$$

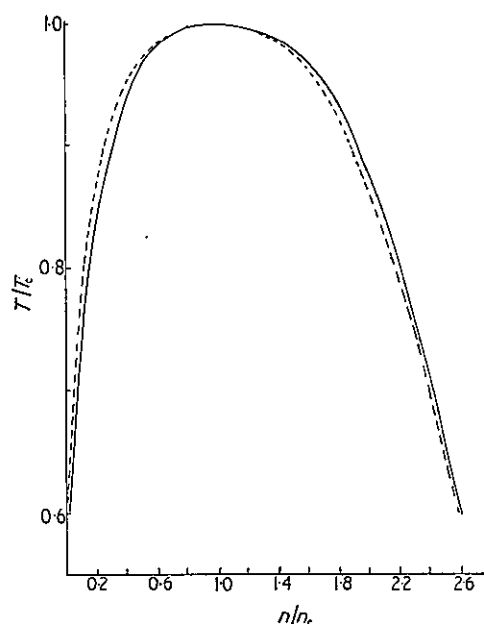


Figure 3. Comparison of theoretical densities (full line) with experiment (broken line).

The function $K(T)$, given by (8), is dependent on density n via the radial distribution function $g(R)$, but our basic assumptions include the neglect of this dependence. To test the approximation thus involved, we investigate the critical point, for which

$$0 = \left(\frac{\partial p}{\partial n}(n_c, T_c) \right)_T = kT_c - n_c k T_c K(T_c)$$

i.e.

$$n_c K(T_c) = 1. \quad (16)$$

It is encouraging that this is exactly the relation which must hold for n_L and n_V to be equal according to our theory (equation (9)). For the critical pressure, however, we obtain

$$p_c = n_c k T_c \left(1 - \frac{1}{2} \right) = \frac{1}{2} n_c k T_c \quad (17)$$

whereas the experimental results have 0.292 instead of $\frac{1}{2}$ for a wide variety of substances (Guggenheim 1945). This poor result is an indication of the extreme sensitivity of pressure to different assumptions about the interparticle correlations.

If we equate the vapour and liquid pressures, we get

$$n_V \left\{ 1 - \frac{1}{2} n_V K_V(T) \right\} = n_L \left\{ 1 - \frac{1}{2} n_L K_L(T) \right\}. \quad (18)$$

This equation would be exact if K_V and K_L were calculated using g_V and g_L for the

densities n_v and n_L on the coexistence line at temperature T , but is actually approximate since we are treating $K_v(T)$ and $K_L(T)$ as independent of density. The equations (9) and (18), with K_v and K_L assumed given functions of T , constitute a theory from which the densities of coexistent liquid and vapour can be calculated for any temperature.

To emphasize that our theory should not be used to calculate pressures, we eliminate K_L in (18) by means of (9), to give

$$p = n_L kT \left\{ 1 - \frac{n_L}{2(n_L - n_v)} \ln \left(\frac{n_L}{n_v} \right) \right\}. \quad (19)$$

This predicted pressure is negative whenever

$$\frac{n_L}{n_v} > \exp \left\{ 2 \left(1 - \frac{n_L}{n_v} \right) \right\} \simeq e^2 \quad (20)$$

a value far exceeded by the ratio of densities commonly observed for coexistent liquid and vapour.

We shall now use the theory defined by equations (9) and (18) to investigate conditions near the critical point.

4. The critical region

It is convenient, when exploring the critical region, to define the dimensionless density variables

$$\left. \begin{aligned} y_L(T) &\equiv \frac{K_L(T) n_L(T)}{K_C n_C} \\ y_V(T) &\equiv \frac{K_L(T) n_V(T)}{K_C n_C} \end{aligned} \right\} \quad (21)$$

in terms of which our density and pressure equations (9) and (18) become

$$\frac{e^{y_L}}{y_L} = \frac{e^{y_V}}{y_V} \quad (22)$$

and

$$y_L(1 - \frac{1}{2}y_L) = y_V(1 - \frac{1}{2}\gamma(T)y_V) \quad (23)$$

where

$$\gamma(T) \equiv \frac{K_V(T)}{K_L(T)} = \frac{\int_0^\infty dR R^3 \phi'(R) g_V(R, T)}{\int_0^\infty dR R^3 \phi'(R) g_L(R, T)} \quad (24)$$

and equation (16) has been used.

Near to the critical point, where $y_L = y_V = 1$, the curve e^y/y can be replaced by a parabola rendered asymmetrical by the addition of a cubic term, and (22) becomes

$$\frac{1}{2}(y_L - 1)^2 - \frac{1}{3}(y_L - 1)^3 = \frac{1}{2}(y_V - 1)^2 - \frac{1}{3}(y_V - 1)^3. \quad (25)$$

Also, the liquid and vapour correlation functions approach one another, so that

$$\gamma(T) = 1 + \epsilon(T) \quad (26)$$

where $\epsilon(T)$ is a function of unknown form which vanishes at T_C . We can expect ϵ to

be positive, because an examination of the factors in the integrands of (24) shows that in the integral involving g_V the negative (repulsive) region of the force curve is less weighted, and the positive (attractive) region more weighted; this means that $K_V > K_L$ and $\gamma > 1$, since K_L is positive (figure 4). Combining (25), (26) and (23), and letting ϵ tend to zero, we obtain, after some careful reduction, the following expressions for the dimensionless densities near the critical point:

$$\left. \begin{aligned} y_L - y_V &= 2\left(\frac{3}{4}\epsilon\right)^{1/3} \\ \frac{1}{2}(y_L + y_V) &= 1 + \frac{1}{4}\left(\frac{4}{3}\right)^{1/3}\epsilon^{2/3} \end{aligned} \right\} \quad (27)$$

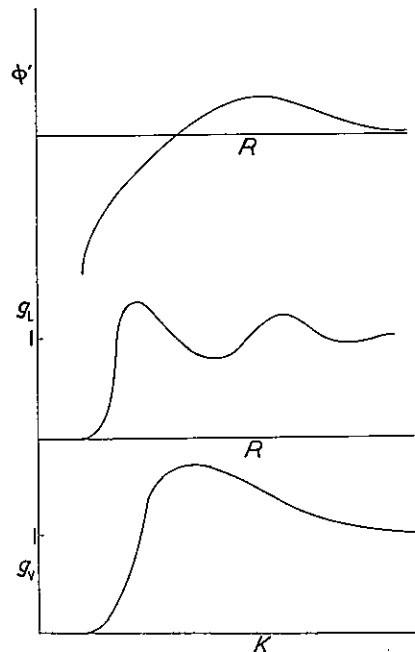


Figure 4. Qualitative behaviour of factors in integrals for $\gamma(T)$.

When we convert back to actual densities using (21), the first equation in (27) is not altered in form near T_C by the variation of $K_C/K_L(T)$, and we have

$$n_L(T) - n_V(T) = 2n_C \left\{ \frac{3}{4}\epsilon(T) \right\}^{1/3}.$$

If we take the simplest possible variation of $\epsilon(T)$, namely a linear increase with temperature below the critical point—a procedure for which there is at present no theoretical justification—we obtain precisely the law (13), which is very well confirmed experimentally (see Heller 1967).

The question of the variation of the 'diameter' $(n_L + n_V)/2$ is more subtle, but a simple case occurs if the factor $K_C/K_L(T)$ departs from unity more slowly than $\epsilon^{2/3}$ as we move away from T_C . Then the second equation of (27) has the leading terms

$$\frac{1}{2}(n_L + n_V) = n_C \left\{ 1 + \frac{1}{4}\left(\frac{4}{3}\right)^{1/3}\epsilon(T)^{2/3} \right\}. \quad (28)$$

If ϵ is linear in $T_C - T$, as (13) implies, then the diameter departs from the constant value n_C according to a $(T_C - T)^{2/3}$ power law, which contradicts the often-quoted

'law of rectilinear diameter' (Guggenheim 1945). The $\frac{2}{3}$ power law fits the experimental data for Argon (Michels *et al.* 1958) over the range $0.75T_C$ up to T_C less well than a linear law. In fact, the maximum deviations from experiment were four times greater than the deviations produced by the law of rectilinear diameter, and of opposite sign (which suggests that the exponent in the law of the diameter is slightly greater than unity).

5. Conclusions

We have shown that the BGY equation (1) of statistical mechanics can be solved, using the simple approximation (2) for the two-particle density function, to give the density profile for a liquid in equilibrium with its vapour. Our theory differs considerably from the 'quasi-thermodynamic' method of Hill (1952), and work is in progress aimed at comparing the density profiles produced by the two formalisms. This can only be done indirectly, by calculating such quantities as surface tension.

The relation (9), between liquid and vapour densities, almost reproduces the experimental coexistence curve when supplemented with the empirical relation (13) for the temperature dependence of the density difference between liquid and vapour.

The theory based on the approximation (2) yields poor predictions for pressures, but the necessary condition (18) that the vapour and liquid pressures be equal, combined with (9), gives some insight into the two empirical laws governing the coexistence curve near the critical point. The $(T_C - T)^{1/2}$ law of (13) emerges as a consequence of the liquid and vapour radial distribution functions approaching equality linearly with $T_C - T$, but the 'law of rectilinear diameter' seems to have no such simple origin.

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