

## Liquid-vapour coexistence and correlations in the interface

by J. LEKNER

Physics Department, Victoria University, Wellington, New Zealand

and J. R. HENDERSON†

Cavendish Laboratory, Madingley Road, Cambridge, England

(Received 13 August 1979; revision received 27 October 1979)

From the derivative of the statistical mechanical definition of the number density (the first Yvon equation), we derive an infinite set of sum rules that must be satisfied by the density profile and the pair correlation function of a liquid-vapour system with pairwise central interactions. For a particular class of approximate pair correlation functions, the sum rules reduce to equations linking the pressure and temperature with the densities of the two bulk phases. Good agreement with experimental data is obtained.

### 1. INTRODUCTION

In this paper we will show that there is a direct link between the properties of two phases in coexistence and the correlations within the interface between these two phases. We shall discuss only simple monoatomic fluids, although it will be clear that generalizations to molecular and multicomponent fluids are possible.

Consider a system of  $N$  atoms confined to a box of sides  $2L_x, 2L_y, 2L_z$ . For suitable pressures and temperatures, there will be two phases, liquid and vapour, in equilibrium. In the presence of a gravitational field (which we take in the direction of negative  $z$ ), the phases will be separated by a flat liquid-vapour interface. It is convenient to take this to lie near the plane  $z=0$ . In the usual way, we assume that gravitational pressure gradients can be ignored, apart from their effect in creating a plane surface.

The calculations presented in this paper are based on an equation (the first of the hierarchy derived by Yvon [1]) which is obtained by differentiating the statistical mechanical definition of the number density

$$n(\mathbf{r}_1) = \frac{N \int d\mathbf{r}_2 \dots d\mathbf{r}_N \exp(-U/T)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp(-U/T)} \quad (1)$$

and using the definition of the pair density

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1) \int d\mathbf{r}_3 \dots d\mathbf{r}_N \exp(-U/T)}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp(-U/T)} \quad (2)$$

† Present address: Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, England.

(temperature is given the dimensions of energy). With  $U = \sum_{i < j} u(r_{ij})$ , the first Yvon equation reads

$$\nabla_1 n(\mathbf{r}_1) = \int_{-L_x}^{L_x} dx_2 \int_{-L_y}^{L_y} dy_2 \int_{-L_z}^{L_z} dz_2 n_2(\mathbf{r}_1, \mathbf{r}_2) \frac{r_{12}}{r_{12}^2} \phi'(r_{12}), \quad (3)$$

where we have written  $\phi$  for  $-u/T$ . It is convenient to use a generalized pair correlation function  $g(\mathbf{r}_1, \mathbf{r}_2)$  defined by

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2). \quad (4)$$

Deep inside either bulk phase,  $g(\mathbf{r}_1, \mathbf{r}_2)$  becomes the pair correlation function,  $g(r_{12})$ , of that phase. For the chosen geometry,  $n_2$  equals  $n(z_1)n(z_2)g(r_{12}, z_1, z_2)$  when atoms 1 and 2 are both away from the side walls. We let  $L_x$  and  $L_y$  tend to infinity, and reduce (3) by the transformations used in going from equation (24) to (25) in [2]. This gives, writing  $r$  for  $r_{12}$  and  $L$  for  $L_z$ ,

$$n'(z_1) = 2\pi n(z_1) \int_{-L}^L dz_2 n(z_2) z_{12} \int_{|z_{12}|}^{\infty} dr g(r, z_1, z_2) \phi'(r). \quad (5)$$

Note that  $\phi'$  is negligibly small except for  $r$  smaller than a few atomic diameters, so that contributions to the integral in (5) come only from small  $|z_{12}|$ .

## 2. MECHANICAL EQUILIBRIUM

Integration of (5) from a point  $z_1 = z_l$  deep inside the liquid, through the interface, to a point  $z_1 = z_v$  deep inside the vapour, gives

$$\begin{aligned} n_v - n_l &= 2\pi \int_{z_l}^{z_v} dz_1 n(z_1) \int_{-L}^L dz_2 n(z_2) z_{12} \int_{|z_{12}|}^{\infty} dr g(r, z_1, z_2) \phi'(r) \\ &= 2\pi \int_{z_l}^{z_v} dz_1 n(z_1) \left\{ \int_{-L}^{z_l} + \int_{z_l}^{z_v} + \int_{z_v}^L \right\} dz_2 n(z_2) z_{12} \int_{|z_{12}|}^{\infty} dr g(r, z_1, z_2) \phi'(r). \end{aligned} \quad (6)$$

Because of the 1, 2 antisymmetry of the integrand, the middle term is zero. In the first term, we can replace  $n(z_1)n(z_2)$  by  $n_l^2$  and  $g(r, z_1, z_2)$  by  $g_l(r)$ , since non-zero contributions come only from small  $|z_{12}|$ . The first term in (6) thus equals

$$2\pi n_l^2 \int_0^{\infty} d\zeta_1 \int_{-\infty}^0 d\zeta_2 \zeta_{12} \int_{\zeta_{12}}^{\infty} dr g_l(r) \phi'(r) = \frac{2\pi}{3} n_l^2 \int_0^{\infty} dr r^3 g_l(r) \phi'(r). \quad (7)$$

We recognize this integral as the contribution of interatomic forces to the pressure within the liquid: in a homogeneous system

$$p/T = n + \frac{2\pi}{3} n^2 \int_0^{\infty} dr r^3 g(r) \phi'(r). \quad (8)$$

Similarly, the last term in (6) can be expressed in terms of the pressure within the vapour. Thus (6) reduces to

$$p_l = p_v \quad (9)$$

(thermal equilibrium,  $T_l = T_v$ , has already been assumed in the defining equations). This method of integrating the Yvon equation thus reproduces the condition for mechanical equilibrium.

3. SUM RULES

There are many other ways of integrating (5). For example, we can divide by  $n(z_1)$  before integrating between the limits  $z_1 = z_l$  and  $z_1 = z_v$ . This gives

$$\log \frac{n_v}{n_l} = \frac{p}{T} \left( \frac{1}{n_l} - \frac{1}{n_v} \right) + 2\pi \int_{z_l}^{z_v} dz_1 \int_{z_l}^{z_v} dz_2 n(z_2) z_{12} \int_{|z_{12}|}^{\infty} dr g(r, z_1, z_2) \phi'(r), \quad (10)$$

which can be written in a more symmetric form by an interchange of the variables of integration :

$$\log \frac{n_l}{n_v} = \frac{p}{T} \left( \frac{1}{n_v} - \frac{1}{n_l} \right) + \pi \int_{z_l}^{z_v} dz_1 \int_{z_l}^{z_v} dz_2 [n(z_1) - n(z_2)] z_{12} \int_{|z_{12}|}^{\infty} dr g(r, z_1, z_2) \phi'(r). \quad (11)$$

More generally, multiply (5) by  $n^{s-1}(z_1)$  before integrating. The result is

$$(1 - s^{-1})(n_l^s - n_v^s) = \frac{p}{T} (n_l^{s-1} - n_v^{s-1}) + \pi \int_{z_l}^{z_v} dz_1 \int_{z_l}^{z_v} dz_2 n(z_1) n(z_2) \times [n^{s-1}(z_1) - n^{s-1}(z_2)] z_{12} \int_{|z_{12}|}^{\infty} dr g(r, z_1, z_2) \phi'(r). \quad (12)$$

[(11) can be obtained from (12) by using  $\lim_{s \rightarrow 0} s^{-1}(x^s - 1) = \log x$ .] Thus we have obtained an infinite set of equations relating  $n_l$ ,  $n_v$  and  $p/T$  to integrals over the density profile and the generalized pair correlation function. The bulk contributions to these sum rules have been evaluated in terms of  $p/T$ ; the last term in (12) is manifestly an interface contribution. The only assumptions made so far have been the neglect of gravitational pressure gradients and the restriction to central pairwise interactions.

4. APPROXIMATIONS FOR  $g(r, z_1, z_2)$

The pair correlation function within the interface has not been determined by experiment, and computer studies are still at a preliminary stage [3-5]. This lack of knowledge about  $g(r, z_1, z_2)$  (or  $c(r, z_1, z_2)$ ) is a problem common to most theories of liquid-vapour interface properties; analytic progress is made by approximating the pair correlation function. Often,  $g(r, z_1, z_2)$  has been approximated by a pair correlation function at some average density, or by a combination of such functions; for example [6]

$$g \left( r, n \left( \frac{z_1 + z_2}{2} \right) \right), \quad g \left( r, \frac{n(z_1) + n(z_2)}{2} \right), \quad \frac{1}{2} [g(r, n(z_1)) + g(r, n(z_2))]. \quad (13)$$

The above expressions are in terms of pair correlation functions of hypothetical homogeneous fluids, with non-physical densities (i.e. neither  $n_l$  nor  $n_v$ ). We prefer to develop an approximation in terms of pair correlation functions of the actual coexisting bulk phases, namely  $g_l$  and  $g_v$ . Also, for mathematical simplicity, we approximate  $g(r, z_1, z_2)$  by  $g(r, \bar{z})$ ,  $\bar{z} = (z_1 + z_2)/2$ . The simplest expression for  $g(r, \bar{z})$  in terms of  $g_l$ ,  $g_v$  and the density profile  $n(z)$  is linear in the profile (c.f. [7, 8])

$$g(r, \bar{z}) = \frac{1}{2} [g_l(r) + g_v(r)] - \frac{1}{2} [g_l(r) - g_v(r)] \theta(\bar{z}), \quad (14)$$

where  $\theta$  is defined by

$$n(z) = \frac{1}{2}[n_l + n_v] - \frac{1}{2}[n_l - n_v]\theta(z) \quad (15)$$

(for our geometry,  $\theta(\pm\infty) = \pm 1$ ). A generalization of (14) is

$$g(r, \bar{z}) = \frac{1}{2}[g_l(r) + g_v(r)] - \frac{1}{2}[g_l(r) - g_v(r)]\theta(\bar{z}) + f_l(\bar{z})g_l(r) + f_v(\bar{z})g_v(r), \quad (16)$$

where  $f_{l,v}(\pm\infty) = 0$ . As  $r \rightarrow \infty$ ,  $g(r, \bar{z}) \rightarrow 1$ , so  $f_l + f_v = 0$  for all  $\bar{z}$ . Thus (16) simplifies to

$$g(r, \bar{z}) = \frac{1}{2}[g_l + g_v] - \frac{1}{2}[g_l - g_v]\theta(\bar{z}) + (g_l - g_v)F, \quad (17)$$

where  $F$  is an unknown function of  $\bar{z}$  or  $\theta(\bar{z})$ , which goes to zero deep in either phase.

### 5. COEXISTENCE CURVE EQUATIONS

Using our approximations for  $g$ , we are able to investigate the consequences of the sum rules. The  $s=0$  sum rule (equation (11)), gives, on Taylor-expanding  $n(z_1)$  and  $n(z_2)$  about  $\bar{z}$ ,

$$\log \frac{n_l}{n_v} = \frac{p}{T} \left( \frac{1}{n_v} - \frac{1}{n_l} \right) - \pi(n_l - n_v) \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} d\bar{z} \sum_{n=0}^{\infty} \frac{(z/2)^{2n+1}}{(2n+1)!} \\ \times \theta^{(2n+1)}(\bar{z}) z \int_{|z|}^{\infty} dr g(r, \bar{z}) \phi'(r) \quad (18)$$

( $\theta^{(m)}$  stands for the  $m$ th derivative of  $\theta$ ). The integral over  $z (= z_{12})$  may be evaluated:

$$\log \frac{n_l}{n_v} = \frac{p}{T} \left( \frac{1}{n_v} - \frac{1}{n_l} \right) - \pi(n_l - n_v) \sum_{n=0}^{\infty} \frac{2^{-2n}}{(2n+3)(2n+1)!} \\ \times \int_0^{\infty} dr r^{2n+3} \phi'(r) \int_{-\infty}^{\infty} d\bar{z} \theta^{(2n+1)}(\bar{z}) g(r, \bar{z}). \quad (19)$$

If in the last integral we use the simplest approximation for  $g(r, \bar{z})$ , equation (14), and the identities

$$\int_{-\infty}^{\infty} d\bar{z} \theta^{(2n+1)}(\bar{z}) = 2\delta_{n0} \quad \text{and} \quad \int_{-\infty}^{\infty} d\bar{z} \theta^{(2n+1)}(\bar{z})\theta(\bar{z}) = 0, \quad (20)$$

we obtain

$$\log \frac{n_l}{n_v} = \frac{p}{T} \left( \frac{1}{n_v} - \frac{1}{n_l} \right) - \frac{\pi}{3} (n_l - n_v) \int_0^{\infty} dr r^3 \phi'(r) [g_l(r) + g_v(r)] \quad (21)$$

or

$$\frac{p}{T} = \frac{n_l n_v}{(n_l - n_v)^2} \left\{ n_l + n_v - \frac{2n_l n_v}{n_l - n_v} \log \frac{n_l}{n_v} \right\}. \quad (22)$$

When  $n_l \gg n_v$  (i.e. near the triple point end of the coexistence curve) equation (22) correctly tends to the ideal gas law  $p = n_v T$ . At the critical point equation (22) gives

$$\frac{p_c}{n_c T_c} = \frac{1}{3}.$$

All the sum rules give this value for the critical ratio when  $g$  is approximated by (14): In terms of the variables

$$x = \frac{n_l - n_v}{n_l + n_v}, \quad \bar{n} = \frac{1}{2}(n_l + n_v)$$

the interface term in (12) is reducible to

$$(1-s)x\bar{n}^{s+1} \frac{2\pi}{3} \int_0^\infty dr r^3 \phi' \int_{-1}^1 d\theta [\frac{1}{2}(g_l + g_v) - \frac{1}{2}(g_l - g_v)\theta] \\ \times \left\{ 1 - sx\theta + \frac{s(s-1)}{2} x^2 \theta^2 \right\} + O(x^4) + O(x^{3+2\nu/\beta}), \quad (23)$$

where the critical exponents  $\nu$  and  $\beta$  are defined by, [9],

$$\text{interface thickness} \sim (T_c - T)^{-\nu}, \quad n_l - n_v \sim (T_c - T)^\beta.$$

The  $\theta$  integral in (23) is easily performed, and the  $r$  integral may be evaluated using (8) as before. Expansion of the remaining terms in (12) up to the third power of  $x$  then shows that  $p_c/n_c T_c = \frac{1}{3}$  for all  $s$ , in the approximation (14). This value is higher than the experimental ratios for monatomic fluids (Ar, Kr and Xe have values near 0.29, as do fluids with nearly spherical molecules [10]), but lies closer than the van der Waals value ( $\frac{2}{3}$ ) or modern versions of the van der Waals theory (see for example § 10.3 of [13]).

For non-zero  $F$ , (17) and (18) give (on neglecting all but first-order density gradient terms when evaluating integrals involving  $F$ )

$$\frac{p}{T} = \frac{n_l n_v \left[ n_l + n_v - \frac{2n_l n_v}{n_l - n_v} \log \frac{n_l}{n_v} - 2F_0(n_l - n_v) \right]}{(n_l - n_v)^2 - 2F_0(n_l^2 - n_v^2)}, \quad (24)$$

where

$$F_0 = \frac{1}{2} \int_{-1}^1 d\theta F(\theta). \quad (25)$$

In terms of  $x$  and  $\bar{n}$ , (24) reads

$$\frac{p}{\bar{n}T} = \frac{(1-x^2) \left[ 1 - \frac{1-x^2}{2x} \log \frac{1+x}{1-x} - 2F_0 x \right]}{2x^2 - 4F_0 x} \\ \xrightarrow{x \rightarrow 0} \frac{1}{3} \frac{1 - 3F_0/x}{1 - 2F_0/x}. \quad (26)$$

If the leading term in the  $x$  expansion of  $F_0$  is  $bx$ ,

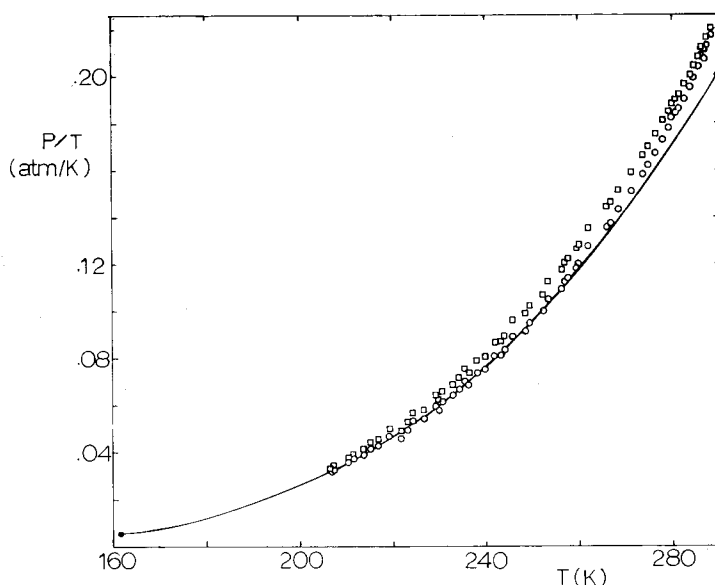
$$\frac{p_c}{n_c T_c} = \frac{1}{3} \frac{1 - 3b}{1 - 2b}. \quad (27)$$

It is straightforward to show that all the sum rules give the result (27) when  $g$  is approximated by (17) with  $F_0 = bx$ . The proof proceeds by expanding (12) in powers of  $n_l - n_v$ , as described above for the case  $F \equiv 0$ . The value  $b \simeq 0.1$  gives the experimental ratio  $p_c/n_c T_c \simeq 0.29$ .

Coexistence curve equations similar to (22) and (24) may be derived from the other sum rules, provided all but first-order density gradient terms are neglected. For example, from the  $s = 2$  sum rule and (14) we find

$$\frac{\bar{p}}{T} = \frac{n_l n_v (n_l + n_v)}{n_l^2 + 4n_l n_v + n_v^2}. \quad (28)$$

This again gives  $\bar{p}_c/n_c T_c = \frac{1}{3}$ , and the ideal gas law when  $n_l \gg n_v$ .



Comparison of experimental  $\bar{p}$ ,  $T$  data for Xe (solid curve, drawn through points from table 6 of Streett *et al.* [11] and the best fit critical point of Levelt Sengers *et al.* [10]) with  $\bar{p}/T$  values calculated from (22) (circles) and (28) (squares), using the liquid and vapour density data of Cornfeld and Carr [12].

In the figure, equations (22) and (28) are compared with xenon experimental pressure and temperature data [10, 11] using liquid and vapour density data [12]. Agreement with experiment is good, the largest deviation occurring in the critical region. It is clear from (27) that there the agreement can be improved with suitable  $F$ . Corrections to the equations derived here (based on improved approximations to  $g(r, z_1, z_2)$ ) can be simply added on, since the sum rules are linear in the pair correlation function.

Finally, we should note an earlier attempt by Berry and Reznick [14] at using the first Yvon equation to obtain a relation between coexistent densities and  $\bar{p}/T$ . These authors used  $g = g_1(r)$  at the outset, and obtained  $\bar{p}_c/n_c T_c = \frac{1}{2}$ .

We are grateful to Anneke Levelt Sengers for her help in locating experimental data, and to Professor Carr for supplying the Xe density data.

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