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The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids

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ABSTRACT

Recent theoretical work on the microscopic structure and surface tension of the liquid–vapour interface of simple (argon-like) fluids is critically reviewed. In particular, the form of pairwise intermolecular correlations in the liquid surface and the capillary wave treatment of the interface are examined in some detail. It is argued that conventional capillary wave theory, which leads to divergences in the width of the density profile, is unsatisfactory for describing all the equilibrium aspects of the interface. The density functional formalism which has been developed to study the liquid–vapour interface can also be profitably applied to other problems in the statistical mechanics of non-uniform fluids; here a new generalization of the 'linear' theory of spinodal decomposition is formulated and by considering a 'nearly uniform' fluid, some useful results for the long-wavelength behaviour of the liquid structure factor of various monatomic liquids are obtained. Some other topics of current interest in this area are briefly discussed.

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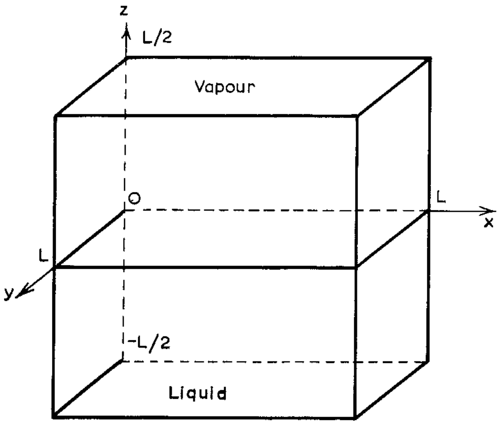
§1. INTRODUCTION

Whilst considerable progress has been made over the last decade in understanding the equilibrium properties of uniform liquids, the microscopic structure and thermodynamical properties of non-uniform fluids, i.e. fluids for which the average number density exhibits spatial variation, are relatively less well understood. On the other hand many important physical phenomena are associated with strongly non-uniform situations. For example, at the surface of a liquid in equilibrium with its vapour in a gravitational field (fig. 1), the density will vary extremely rapidly (see fig. 2) for temperatures close to the triple point. Consequently any proper treatment of the structure of the liquid–vapour interface and the corresponding surface tension requires a detailed theory for the statistical mechanics of non-uniform fluids. Similarly any theory of contact angle, wetting and other interfacial phenomena must concern itself with the highly non-uniform density distributions which arise as a result of the interactions between the liquid molecules and those of the solid surface. Phase separation is another subject which is concerned with non-uniform fluids: the theories of nucleation and of spinodal decomposition involve both the equilibrium and non-equilibrium behaviour of density fluctuations in inhomogeneous situations.

Fig. 1



Geometry for the liquid–vapour system. The Gibbs dividing surface is located at $z=0$.

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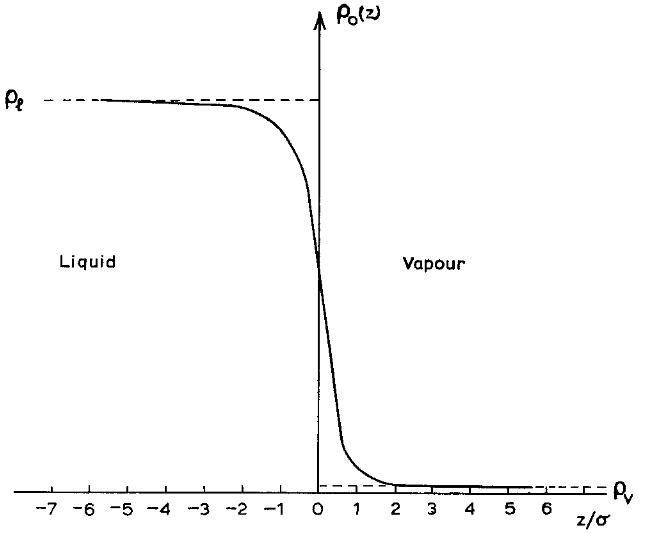
Fig. 2



The equilibrium density profile for a simple, monatomic fluid in the neighbourhood of its triple point (schematic). σ is the molecular diameter. ρ_l and ρ_v are the co-existent liquid and vapour densities.

During the last few years there have been significant developments in the formal theory of the statistical mechanics of non-uniform classical fluids. Most applications of this work have been aimed at the problem of the liquid–vapour interface. It is the main purpose of the present article to assess critically our present understanding of the structure and surface tension of simple (argon-like) liquids near their triple points. We will show that rather good progress has been achieved. The second purpose of this paper is to show how the general formalism can be used to derive useful results for other problems. In particular, we develop a new and rather general theory of the early stages of spinodal decomposition and, by considering a 'nearly uniform' fluid, we derive some tractable theories for the long-wavelength behaviour of the Ornstein–Zernike direct correlation function of a uniform liquid, or, equivalently, the liquid structure factor. The latter is the quantity which is measured in diffraction experiments on liquids. Other possible applications of the formalism to surface and interface problems are also discussed.

Since it is our impression that the general formalism is not widely known, the first part of this paper gives a self-contained account of the statistical theory. The remainder and bulk of the article is concerned with the topics mentioned above. The statistical mechanics of non-uniform classical fluids was originally developed by Morita and Hiroike [1] and independently by De Dominicis [2] using the techniques of functional differentiation and cluster expansion. A similar approach was later developed by Stillinger and Buff [3] and Lebowitz and Percus [4] who derived explicit results for the various thermodynamic potentials of a non-uniform fluid in an external potential in terms of integrals with respect to density of the Ornstein–Zernike direct correlation function. Whilst the general formalism proved extremely fruitful for the development of approximate integral equations for the pair distribution function of a uniform fluid [5, 6], it application to the statistical mechanics and thermodynamics of intrinsically non-uniform systems was not forthcoming until quite recently when several authors [7, 8, 9, 10, 11, 12] employed the formalism to develop theories of the liquid–vapour interface.

Our presentation of the theory differs from that of Morita and Hiroike and De Dominicis. Whereas these authors use cluster expansion techniques to derive the fundamental variational principle for the grand potential, we obtain the same principle more directly using an argument borrowed from the theory of the interacting electron gas [13, 14]. This approach also has the merit that it readily yields useful approximation schemes. In particular the van der Waals expansion of the Helmholtz free energy of a fluid as a series of density gradients can be derived and the coefficients properly identified, for the case where the density is slowly varying throughout the fluid. A presentation of the theory which is *similar* to the present can be found in an appendix to a recent paper by Yang *et al.* [15].

Our article is arranged as follows. In § 2 we derive the variational principle for the grand potential and this introduces two key quantities $\mathscr{F}[\rho]$ and $\Omega_V[\rho]$ which are functionals of the one-particle density $\rho(\mathbf{r})$. For a given interaction potential and a fixed external potential, $\Omega_V[\rho]$ has a minimum value when $\rho(\mathbf{r})=\rho_0(\mathbf{r})$, the equilibrium density of the system and this minimum value $\Omega_V[\rho_0]$ is the grand potential; $\mathscr{F}[\rho]$ is a unique functional, independent of the external potential; $\mathscr{F}[\rho_0]$ is the 'intrinsic' Helmholtz free energy of the fluid. In § 3 we show that both $\mathscr{F}$ and Ω_V act as generating functionals for hierarchies of correlation functions. The functional derivatives of $\mathscr{F}$ with respect to $\rho(\mathbf{r})$ give rise to the direct correlation functions while the functional derivatives of Ω_V with respect to the external potential yield the n particle distribution functions. Some formal results for the various thermodynamic potentials of a non-uniform fluid as integrals with respect to density of the direct correlation functions are given in § 4. Although these results are identical to those of Stillinger and Buff [3] and Lebowitz and Percus [4] our analysis dispels earlier uncertainty concerning their uniqueness. We also discuss the functional dependence of $\mathscr{F}$ on the interaction potential. For systems in which the latter can be represented as a sum of pairwise intermolecular potentials ϕ, $\mathscr{F}[\rho_0]$ can be usefully written in terms of the free energy of a reference system in which the molecules interact via a potential ϕ_r, plus a 'perturbation' contribution from the remainder of the intermolecular potential i.e. $\phi-\phi_r$. This result forms the starting point for the various thermodynamic perturbation theories of non-uniform fluids. In § 5 exact integro-differential equations for the equilibrium density are presented. These were originally derived by Lovett *et al.* [9] and Wertheim [10] and they form the basis for much of the recent work on liquid surfaces. We discuss the case of slowly varying density in some detail in § 6. The gradient expansion is derived and a procedure for calculating the coefficients is given. This procedure is only strictly valid when the density is both slowly varying *and* exhibits only small departures from its mean value. It is possible to effect a partial summation of the gradient expansion and recently Ebner *et al.* [14] have used this to develop a practicable scheme for calculating the free energy of non-uniform systems. Their work is also described in this section. In § 7 we describe a recent application of the formalism to the theory of uniform liquids; we show that the results of §§ 3 and 4 can be employed to construct useful approximate theories for the long wavelength behaviour of the Ornstein–Zernike direct correlation function of a dense liquid in which the molecules interact via pairwise potentials [16, 17].

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Section 8 constitutes an extensive summary of recent work on the statistical mechanics of liquid surfaces. In § 8.1 we describe the van der Waals theory of the surface tension and density profile of a planar interface and compare this approach with the more sophisticated thermodynamic perturbation theories [18, 19]. We show that these various treatments all give roughly the same monotonic density profile and qualitatively similar surface tensions for a Lennard–Jones fluid near its triple point. The Kirkwood–Buff [20] theory of surface tension and the use of closure approximations for solving the associated integro-differential equation for the density profile are briefly discussed in § 8.2. We derive a result for the surface tension in terms of the Ornstein–Zernike direct correlation function of the non-uniform fluid [7, 8] in § 8.3. The import of this result is discussed. By analysing two of the integro-differential equations for the equilibrium density, we show that the density profile should decay exponentially into each bulk phase but that the decay length is much larger for the liquid side of the interface [11]. In § 8.4 we discuss the form of pairwise correlations in the interface and review the interesting and important work of Wertheim [10] which predicts the occurrence of long-ranged correlations parallel to the surface. We show that such correlations are consistent with a description of the surface in terms of capillary waves [11, 12]. The possibility of building up the equilibrium density profile by 'unfreezing' capillary wave-like fluctuations in some hypothetical 'bare' interface is examined in § 8.5. Conventional capillary wave theory is found to lead to unrealistic (divergent) results for the width of the density profile. We also comment on recent applications [8, 12, 21] of capillary wave models. In § 8.6 we compare the results of recent molecular dynamics simulations of the density profile and surface tension with those obtained from the van de Waals and related approximate theories. For a Lennard-Jones fluid near its triple point the results for the density profile are found to be in good agreement; the '10–90' width of the profile is about two molecular diameters. For parameters appropriate to liquid argon the calculated surface tensions lie in the range 12–18 dyn cm^{-1}.

§ 9 we show that the theory of spinodal decomposition can be placed on a proper microscopic basis using the methods of this paper. Finally, in § 10 we briefly discuss some other topics of current interest and present some conclusions and perspectives.

§ 2. THE VARIATIONAL PRINCIPLE FOR THE GRAND POTENTIAL AND THE EQUILIBRIUM DENSITY

We consider a grand canonical ensemble of particles and define the equilibrium probability density f_0 for N particles at temperature T:

$$f_0 = \Xi^{-1} \exp(-\beta(H_N - \mu N)), \tag{1}$$

where H_N is the hamiltonian when there are N particles present, μ is the chemical potential and $\beta = 1/K_B T$. The grand partition function Ξ is given by

$$\Xi = \mathrm{Tr}_{\mathrm{cl}} \exp(-\beta(H_N - \mu N)), \tag{2}$$

where $\mathrm{Tr}_{\mathrm{cl}}$ denotes the usual 'classical' trace, i.e.

$$\mathrm{Tr}_{\mathrm{cl}} \equiv \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \int d\mathbf{p}_1 \ldots d\mathbf{p}_N,$$

where $\mathbf{r}_1$, etc. denote position variables and $\mathbf{p}_1$, etc. momentum variables. Following Mermin [13] we consider the functional

$$\Omega[f] = \mathrm{Tr}_{\mathrm{cl}} f(H_N - \mu N + \beta^{-1} \ln f). \tag{3}$$

For the equilibrium probability density we clearly have

$$\Omega[f_0] = -\beta^{-1} \ln \Xi \equiv \Omega. \tag{4}$$

Ω is the grand potential. The functional $\Omega[f]$ also satisfies the inequality

$$\Omega[f] > \Omega[f_0], \quad f \neq f_0 \tag{5}$$

for all probability densities with $\mathrm{Tr}_{\mathrm{cl}} f = 1$. This result is easily proved since from (1, 3 and 4) it follows that

$$\Omega[f] = \Omega[f_0] + \beta^{-1}(\mathrm{Tr}_{\mathrm{cl}} f \ln f - \mathrm{Tr}_{\mathrm{cl}} f \ln f_0)$$

and the term in brackets is positive if $f \neq f$ The latter follows from a Gibbs inequality (see e.g. [22]).

We now restrict consideration to hamiltonians of the form

$$H_N = T + U + V, \tag{6}$$

where

$$T = \sum_{i=1}^{N} p_i^2/2m,$$

$$U \equiv U(\mathbf{r}_1, \ldots, \mathbf{r}_N),$$

and

$$V = \sum_{i=1}^{N} V_{\mathrm{ext}}(\mathbf{r}_i).$$

U is the potential energy of interaction of the particles. Pairwise additivity of this function is not, in general, assumed. $V_{\mathrm{ext}}(\mathbf{r})$ is an arbitrary external potential and m is the mass of each particle. The system is assumed to be enclosed in a volume $\mathscr{V}$. The equilibrium density $\rho_0(\mathbf{r})$ for such a system is given by

$$\rho_0(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle \tag{7}$$

where $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$ is the density operator and the configuration average of any operator $\hat{O}$ is defined by

$$\langle \hat{O} \rangle \equiv \mathrm{Tr}_{\mathrm{cl}} f_0 \hat{O}.$$

Since f_0 is a function of V_{ext} it follows that $\rho_0(\mathbf{r})$ is also a functional of V_{ext}. We can also prove the more useful result that f_0 is a functional of $\rho_0(\mathbf{r})$. The proof (see Appendix 1) proceeds by showing that, for a given interaction potential U, $V_{\mathrm{ext}}(\mathbf{r})$ is uniquely determined by $\rho_0(\mathbf{r})$, i.e. only one $V_{\mathrm{ext}}(\mathbf{r})$ can determine a given $\rho_0(\mathbf{r})$. The resultant V_{ext} then determines f_0. Thus, it follows that f_0 is a functional of $\rho_0(\mathbf{r})$.

This result implies that, for a given U,

$$\mathscr{F}[\rho] = \mathrm{Tr}_{\mathrm{cl}} f_0 (T + U + \beta^{-1} \ln f_0) \tag{8}$$

is a unique functional of the density $\rho(\mathbf{r})$. The same form is valid for all external potentials. $\mathscr{F}[\rho]$ plays a key role in the development of the theory. The other key quantity is the functional

$$\Omega_V[\rho] = \int d\mathbf{r}\, \rho(\mathbf{r}) V_{\mathrm{ext}}(\mathbf{r}) + \mathscr{F}[\rho] - \mu \int d\mathbf{r}\, \rho(\mathbf{r}). \tag{9}$$

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When $\rho(\mathbf{r})=\rho_0(\mathbf{r})$, the equilibrium density, $\Omega_V[\rho]$ reduces to the grand potential Ω. Furthermore, this is the minimum value of the functional. In order to prove this we suppose $\rho'(\mathbf{r})$ is the equilibrium density associated with another probability density f' of unit trace,† then

$$\begin{aligned}\Omega[f'] &= \mathrm{Tr}_{\mathrm{cl}} f' \,(H_N-\mu N+\beta^{-1}\ln f') \\ &= \int d\mathbf{r}\,\rho'(\mathbf{r})\,V_{\mathrm{ext}}(\mathbf{r})+\mathscr{F}[\rho']-\mu\int d\mathbf{r}\,\rho'(\mathbf{r}) \\ &= \Omega_V[\rho'], \end{aligned} \tag{10}$$

where

$$\mathscr{F}[\rho']=\mathrm{Tr}_{\mathrm{cl}} f'(T+U+\beta^{-1}\ln f').$$

From (5) we have $\Omega[f_0]<\Omega[f']$ so it follows that

$$\Omega_V[\rho_0]<\Omega_V[\rho']. \tag{11}$$

Thus, the correct equilibrium density $\rho_0(\mathbf{r})$ minimizes the functional $\Omega_V[\rho]$ over all density functions that can be associated with the potential $V_{\mathrm{ext}}(\mathbf{r})$.

We can express these important results as follows:

$$\left.\frac{\delta\Omega_V[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho_0}=0 \tag{12a}$$

and

$$\Omega_V[\rho_0]=\Omega. \tag{12b}$$

From (9) and (12 b) it is clear that $\mathscr{F}[\rho_0]$ is the 'intrinsic' Helmholtz free energy of the system. The total Helmholtz free energy F is

$$F=\int d\mathbf{r}\rho_0(\mathbf{r})\,V_{\mathrm{ext}}(\mathbf{r})+\mathscr{F}[\rho_0], \tag{13}$$

which includes the contribution from the external potential. From (12 a) we have

$$V_{\mathrm{ext}}(\mathbf{r})+\mu_{\mathrm{in}}[\rho_0;\mathbf{r}]=\mu, \tag{14}$$

where we have defined an intrinsic chemical potential

$$\mu_{\mathrm{in}}[\rho;\mathbf{r}]\equiv\frac{\delta\mathscr{F}[\rho]}{\delta\rho(\mathbf{r})}. \tag{15}$$

Equation (14) is the fundamental equation in the theory of non-uniform fluids. Given some means of determing $\mathscr{F}[\rho]$, this is an explicit equation for the equilibrium density. For example, in an non-interacting system ($U=0$), $\mathscr{F}[\rho]$ reduces to

$$\mathscr{F}_{\mathrm{ideal}}[\rho]=\beta^{-1}\int d\mathbf{r}\,\rho(\mathbf{r})(\ln(\lambda^3\rho(\mathbf{r}))-1) \tag{16}$$

where $\lambda=(h^2\beta/2m\pi)^{1/2}$ and the intrinsic chemical potential is $\beta^{-1}\ln(\lambda^3\rho(\mathbf{r}))$. In this case (14) yields the familiar result

$$\rho_0(\mathbf{r})=z\exp(-\beta V_{\mathrm{ext}}(\mathbf{r})), \tag{17}$$

where $z=\lambda^{-3}\exp(\beta\mu)$ is the fugacity. When the effects of interactions between the particles are included, μ_{in}, and hence μ, are *not* simple functions of the local particle

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†This proof assumes the existence of a potential $V'_{\mathrm{ext}}(\mathbf{r})$ which gives rise to the density $\rho'(\mathbf{r})$ so that the appropriate f' exists. The existence of $\mathscr{F}[\rho']$, as given above, is then guaranteed.

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density and, in general, μ_{in} cannot be identified with the chemical potential of a uniform fluid with density equal to the local density. In § 6 we will see that only in the limit of very slowly varying densities will such an identification become valid.

§ 3. Direct correlation functions and molecular distribution functions

The effects of interactions between particles are most readily incorporated by introducing a hierarchy of direct correlation functions. We define a functional $\Phi[\rho]$ as the interaction part of $\mathscr{F}[\rho]$:

$$\mathscr{F}[\rho] \equiv \mathscr{F}_{\text{ideal}}[\rho] - \Phi[\rho]. \tag{18}$$

For a given interaction potential U, Φ is a unique functional of $\rho(\mathbf{r})$. The intrinsic chemical potential can then be written as:

$$\beta\mu_{\text{in}}[\rho; \mathbf{r}] = \ln(\lambda^3\rho(\mathbf{r})) - c[\rho; \mathbf{r}] \tag{19}$$

where

$$c[\rho; \mathbf{r}] \equiv \beta\frac{\delta\Phi[\rho]}{\delta\rho(\mathbf{r})} \tag{20}$$

is the contribution due to interactions. From (14) we find that the equilibrium density is given by

$$\rho_0(\mathbf{r}) = z\exp(-\beta V_{\text{ext}}(\mathbf{r}) + c[\rho_0; \mathbf{r}]). \tag{21}$$

The quantity $-\beta^{-1}c[\rho_0; \mathbf{r}]$ is the additional, effective one-body potential which determines, in a self-consistent fashion, the equilibrium density. It is completely analogous to the effective potential which appears in the one-electron Schrödinger equation in the Kohn–Sham [23] theory of the inhomogeneous electron gas.

$c[\rho; \mathbf{r}]$ is only the first member of the hierarchy of correlation functions generated by $\Phi[\rho]$. The higher order functions are obtained by further differentiation:

$$\left.\begin{aligned} c[\rho; \mathbf{r}_1, \mathbf{r}_2] &= \frac{\delta c[\rho; \mathbf{r}_1]}{\delta\rho(\mathbf{r}_2)} = \frac{\beta\delta^2\Phi[\rho]}{\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_1)} = \frac{\beta\delta^2\Phi[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} = c[\rho; \mathbf{r}_2, \mathbf{r}_1] \\ c[\rho; \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3] &= \frac{\delta^2 c[\rho; \mathbf{r}_1]}{\delta\rho(\mathbf{r}_3)\delta\rho(\mathbf{r}_2)} = c[\rho; \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3] \text{ etc.} \end{aligned}\right\} \tag{22}$$

The second derivative, evaluated at the equilibrium density, is usually referred to as the Ornstein–Zernike direct correlation function of the non-uniform fluid. The reason for this will become clear but first we note that $\Omega_V[\rho]$ is also a generating functional. If we set

$$u(\mathbf{r}) \equiv \mu - V_{\text{ext}}(\mathbf{r}) \tag{23}$$

then (9) becomes

$$\Omega_V[\rho] = -\int d\mathbf{r}\, \rho(\mathbf{r})u(\mathbf{r}) + \mathscr{F}[\rho] \tag{24}$$

Differentiating w. r. t. $u(\mathbf{r})$ and recalling that $\rho(\mathbf{r})$ is a functional of $u(\mathbf{r})$ we find

$$\frac{\delta\Omega_V[\rho]}{\delta u(\mathbf{r})} = -\rho(\mathbf{r}) + \int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}')}{\delta u(\mathbf{r})}\left(\frac{\delta\mathscr{F}[\rho]}{\delta\rho(\mathbf{r}')} - u(\mathbf{r}')\right)$$

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From (14) it follows that when $\rho(\mathbf{r})=\rho_0(\mathbf{r})$, the term in brackets vanishes and

$$\frac{\delta\Omega_V[\rho_0]}{\delta u(\mathbf{r})}=-\rho_0(\mathbf{r}). \tag{25}$$

Thus Ω_V is a generating functional, w.r.t. the variable $u(\mathbf{r})$, for the equilibrium density $\rho_0(\mathbf{r})$. Since $\Omega_V[\rho_0]=\Omega$, (25) could, of course, have been derived directly from the grand partition function (see Appendix 2). Differentiating Ω a second time we can show (Appendix 2) that

$$\mathscr{G}(\mathbf{r}_1,\mathbf{r}_2)\equiv\beta^{-1}\frac{\delta\rho_0(\mathbf{r}_1)}{\delta u(\mathbf{r}_2)}=\langle(\hat\rho(\mathbf{r}_1)-\rho_0(\mathbf{r}_1))\,(\hat\rho(\mathbf{r}_2)-\rho_0(\mathbf{r}_2))\rangle. \tag{26}$$

$\mathscr{G}(\mathbf{r}_1,\mathbf{r}_2)$ is often referred to as the density fluctuation function or the density–density correlation function and is proportional to the static linear density response function (see Appendix 3). It is a positive definite quantity which is closely related to the usual pairwise distribution function $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$:

$$\mathscr{G}(\mathbf{r}_1,\mathbf{r}_2)=\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)+\rho_0(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2)-\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2). \tag{27}$$

(This result and the definitions of the molecular distribution functions are given in Appendix 2). The higher order distribution functions can be obtained by further differentiation [4].

The *inverse* of $\mathscr{G}$ is related to the Ornstein–Zernike direct correlation function as defined above. In order to demonstrate this we re-write (21) as

$$c[\rho_0;\mathbf{r}_1]=\ln(\lambda^3\rho_0(\mathbf{r}_1))-\beta u(\mathbf{r}_1) \tag{28}$$

and differentiate w. r. t. $\rho_0(\mathbf{r}_2)$:

$$c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\equiv c[\rho_0;\mathbf{r}_1,\mathbf{r}_2]=\frac{\delta(\mathbf{r}_1-\mathbf{r}_2)}{\rho_0(\mathbf{r}_1)}-\frac{\beta\delta u(\mathbf{r}_1)}{\delta\rho_0(\mathbf{r}_2)}. \tag{29}$$

The second term on the r. h. s. of (29) is $-\mathscr{G}^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ where the inverse is defined in the conventional way by

$$\int d\mathbf{r}_3\,\mathscr{G}^{-1}(\mathbf{r}_1,\mathbf{r}_3)\mathscr{G}(\mathbf{r}_3,\mathbf{r}_2)=\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{30}$$

Substituting from (27) and (29) into (30) we find that $c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ and $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ satisfy the integral equation:

$$\begin{aligned}\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)-\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)= {} & \rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\\ & +\rho_0(\mathbf{r}_2)\int d\mathbf{r}_3\,(\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_3)-\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_3))c^{(2)}(\mathbf{r}_3,\mathbf{r}_2)\end{aligned} \tag{31}$$

For a uniform fluid of density ρ_0, $c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\equiv c^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)$ and $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\equiv\rho_0^2\,g(|\mathbf{r}_1-\mathbf{r}_2|)$, where $g(r)$ is the radial distribution function, and (31) reduces to the usual Ornstein–Zernike equation:

$$g(r)-1=c^{(2)}(r)+\rho_0\int d\mathbf{r}'\,(g(r')-1)c^{(2)}(|\mathbf{r}-\mathbf{r}'|). \tag{32}$$

Consequently, $c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ can be legitimately described as the generalized Ornstein–Zernike correlation function.

§4. THERMODYNAMIC POTENTIALS FOR ARBITRARY EXTERNAL POTENTIALS

In this section we derive some formal expressions for the various thermodynamic potentials by functional integration w. r. t. (1) the particle density, (2) the external potential and (3) the interaction potential.

4.1. *Integration w. r. t. particle density*

We suppose that for a given β, U and V_{ext} we have some prescription for solving (14) for the equilibrium density of the system. If we suppose further that we can evaluate the Ornstein–Zernike correlation function for a range of non-uniform densities then we can evaluate the thermodynamic potentials of our system by functional integration w. r. t. density. We concentrate on the functional $\Phi[\rho]$ and consider a path in the space of density functions which is characterized by a single parameter α:

$$\begin{aligned}\rho_\alpha \equiv \rho(\mathbf{r};\alpha) &= \rho_i(\mathbf{r}) \text{ at } \alpha=0\\ &= \rho(\mathbf{r}) \text{ at } \alpha=1\end{aligned} \tag{33}$$

where $\rho_i(\mathbf{r})$ is some initial (reference) density and α varies between 0 and 1.

Integrating (20) we have

$$\begin{aligned}\Phi[\rho] &= \Phi[\rho_i] + \int_0^1 d\alpha \int d\mathbf{r} \frac{\partial \rho(\mathbf{r};\alpha)}{\partial \alpha} \frac{\delta \Phi[\rho_\alpha]}{\delta \rho(\mathbf{r};\alpha)}\\ &= \Phi[\rho_i] + \beta^{-1} \int_0^1 d\alpha \int d\mathbf{r} \frac{\partial \rho(\mathbf{r};\alpha)}{\partial \alpha} c[\rho_\alpha;\mathbf{r}]\end{aligned} \tag{34}$$

and if we choose

$$\rho(\mathbf{r};\alpha) = \rho_i(\mathbf{r}) + \alpha(\rho(\mathbf{r}) - \rho_i(\mathbf{r})) \tag{35}$$

(34) simplifies to

$$\Phi[\rho] = \Phi[\rho_i] + \beta^{-1} \int_0^1 d\alpha \int d\mathbf{r}\, (\rho(\mathbf{r}) - \rho_i(\mathbf{r})) c[\rho_\alpha;\mathbf{r}]. \tag{36}$$

A further simplification is possible if the initial density $\rho_i(\mathbf{r}) = 0$. In this case $\Phi[\rho_i] = 0$ since the effect of interactions become negligible at sufficiently low densities (we assume finite range intermolecular potentials) and (36) reduces to

$$\Phi[\rho] = \beta^{-1} \int_0^1 d\alpha \int d\mathbf{r}\, \rho(\mathbf{r}) c[\alpha\rho;\mathbf{r}]. \tag{37}$$

Using (22) this can be integrated again along the same path (35):

$$\Phi[\rho] = \beta^{-1} \int_0^1 d\alpha\, \alpha \int_0^1 d\alpha' \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) c[\alpha\alpha'\rho;\mathbf{r}_1,\mathbf{r}_2]. \tag{38}$$

Since $\Phi[\rho]$ is a unique functional of $\rho(\mathbf{r})$ this result is independent of the choice of integration path i.e. paths other than (35) lead to the same value for Φ.

The Helmholtz free energy of the equilibrium system of density $\rho_0(\mathbf{r})$ is given by (13) and (18):

$$F = \int d\mathbf{r}\, \rho_0(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) + \mathcal{F}_{\text{ideal}}[\rho_0] - \Phi[\rho_0]. \tag{39}$$

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This result is useful provided we can evaluate $c[\alpha\rho_0;\mathbf{r}_1,\mathbf{r}_2]$ for all density distributions $\alpha\rho_0(\mathbf{r}_1)$ with $0\leqslant\alpha\leqslant1$. The Gibbs free energy G is simply

$$G=\mu\int d\mathbf{r}\,\rho_0(\mathbf{r})$$

with a free energy density

$$\mu\rho_0(\mathbf{r})=\beta^{-1}\rho_0(\mathbf{r})(\beta V_{\text{ext}}(\mathbf{r})+\ln(\lambda^3\rho_0(\mathbf{r}))-c[\rho_0;\mathbf{r}]),\tag{40}$$

where we have used (28). The grand potential then follows from (39, 40 and 16) by formally eliminating the chemical potential:

$$\begin{aligned}\Omega&=F-G\\&=\beta^{-1}\int d\mathbf{r}\,\rho_0(\mathbf{r})(c[\rho_0;\mathbf{r}]-1)-\Phi[\rho_0].\end{aligned}\tag{41}$$

As stressed recently by Saam and Ebner [24], these results for the thermodynamic potentials are unique and do not depend on the particular choice of integration path. The expressions for Ω and F can be simplified by integrating by parts in (38)

$$\Omega=\beta^{-1}\int d\mathbf{r}_1\,\rho_0(\mathbf{r}_1)\left[\int_0^1 d\alpha\,\alpha\int d\mathbf{r}_2\,\rho_0(\mathbf{r}_2)c[\alpha\rho_0;\mathbf{r}_1,\mathbf{r}_2]-1\right]\tag{42}$$

and

$$\begin{aligned}F=\beta^{-1}\int d\mathbf{r}_1\,\rho_0(\mathbf{r}_1)\Big[&\beta V_{\text{ext}}(\mathbf{r}_1)+\ln(\lambda^3\rho_0(\mathbf{r}_1))-1\\&+\int_0^1 d\alpha\,(\alpha-1)\int d\mathbf{r}_2\,\rho_0(\mathbf{r}_2)c[\alpha\rho_0;\mathbf{r}_1,\mathbf{r}_2]\Big].\end{aligned}\tag{43}$$

For a uniform fluid ($V_{\text{ext}}\equiv0$; $\rho_0(\mathbf{r})\equiv\rho_0$) these formulae for the thermodynamic potentials reduce to well-known results. In this limit the zeroth Fourier coefficient of the direct correlation function satisfies the Ornstein–Zernike compressibility equation:

$$1-\rho_0\int d\mathbf{r}\,c^{(2)}(r)=\beta(\rho_0\chi_T)^{-1}\tag{44}$$

where χ_T is the isothermal compressibility at the appropriate density and temperature. The chemical potential and pressure p are obtained by integration since

$$(\rho_0\chi_T)^{-1}=\rho_0\left(\frac{\partial\mu}{\partial\rho_0}\right)_T=\left(\frac{\partial p}{\partial\rho_0}\right)_T\tag{45}$$

and $\Omega=-p\mathscr{V}$ for a uniform fluid. The Helmholtz free energy is just $\Omega+G$.

As (40), (42) and (43) were originally derived by Stillinger and Buff [3] using cluster expansion techniques, the validity of these formulae for dense liquids was queried. Later Lebowitz and Percus [4] derived identical formulae using functional integration methods equivalent to the present and thus showed the results were also valid for liquids. These authors, however, had doubts concerning the uniqueness and hence, usefulness, of the results for the Helmholtz free energy and the grand potential. They noted that of the three free energy densities only the Gibbs density is a 'local functional' of the equilibrium density, (this follows since μ depends solely on the effective one-body potential at the equilibrium density) and argued that it was not possible to find path independent expressions for the other energy densities. For these reasons Lebowitz and Percus discussed only approximations for the Gibbs free energy. Our present derivation should dispel such doubts [24]. The existence of the

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unique functional $\mathscr{F}[\rho]$ (or equivalently $\Phi[\rho]$) implies that all three potentials should be generated from the same scheme. This point will be illustrated in § 6 where we derive approximations for the thermodynamic potentials of systems in which the density varies slowly.

As noted at the beginning of this section, any application of the general formalism described above requires the determination of $\rho_0(\mathbf{r}_1)$ plus some prescription for $c[\rho; \mathbf{r}_1, \mathbf{r}_2]$ in a non-uniform fluid. Finding an exact solution of eqn. (21) for the equilibrium density is, of course, difficult. This equation can be transformed to an integro-differential equation (see § 5) involving the Ornstein–Zernike correlation function but this remains a daunting task. For practical purposes it is better to write

$$\Omega_V[\rho]=\beta^{-1}\int d\mathbf{r}\,\rho(\mathbf{r})(\beta V_{\text{ext}}(\mathbf{r})-\beta\mu+\ln(\lambda^3\rho(\mathbf{r}))-1)-\Phi[\rho], \tag{46}$$

with $\Phi[\rho]$ given by (38) and parametrize the final density $\rho(\mathbf{r})$. By minimizing the r. h. s. of (46) w. r. t. the parameters an approximate equilibrium density and grand potential can be found directly. Saam and Ebner [24] have suggested that it should be practicable to solve the Percus–Yevick equations for a non-uniform fluid over a wide range of densities and hence evaluate $c[\rho; \mathbf{r}_1, \mathbf{r}_2]$. This would make a calculation of Ω along these lines quite feasible.

4.2. *Integration w.r.t. an external potential*

Ω_V is itself a generating functional for the equilibrium density so we can formally integrate (25) using the potential function

$$u_\alpha \equiv u(\mathbf{r};\alpha)=u_i(\mathbf{r})+\alpha(u(\mathbf{r})-u_i(\mathbf{r})) \tag{47}$$

where $u_i(\mathbf{r})$ is some initial (reference) value of the quantity $\mu - V_{\text{ext}}(\mathbf{r})$. This yields

$$\Omega=\Omega_i-\int_0^1 d\alpha \int d\mathbf{r}\,\rho(u_\alpha;\mathbf{r})(u(\mathbf{r})-u_i(\mathbf{r})), \tag{48}$$

where Ω_i is the grand potential of the initial state. This procedure requires $\rho(u_\alpha; \mathbf{r})$, the equilibrium density for an 'intermediate' value of the potential function. While this could be expressed as an integral over $\mathscr{G}(\mathbf{r}_1, \mathbf{r}_2)$ (see (26)) such a scheme does not appear to be useful for the purpose of calculation.

4.3. *Integration w.r.t. a pairwise interaction potential*

The grand potential is, of course, a functional of the interaction potential U. If the latter can be written as a sum of pairwise potentials:

$$U(\mathbf{r}_1\ldots\mathbf{r}_N)=\tfrac{1}{2}\sum_{i\neq j}\phi(\mathbf{r}_i,\mathbf{r}_j), \tag{49}$$

it is easy to prove (see Appendix 2) that

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=2\frac{\delta\Omega}{\delta\phi(\mathbf{r}_1,\mathbf{r}_2)}=2\frac{\delta\Omega_V[\rho_0]}{\delta\phi(\mathbf{r}_1,\mathbf{r}_2)} \tag{50}$$

for a fixed potential $u(\mathbf{r})$. Thus, for pairwise intermolecular potentials, the grand potential is a convenient generating functional for the equilibrium pairwise distribution function. From (9), (18) and (50) it follows that

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=2\frac{\delta\mathscr{F}[\rho_0]}{\delta\phi(\mathbf{r}_1,\mathbf{r}_2)}=-2\frac{\delta\Phi[\rho_0]}{\delta\phi(\mathbf{r}_1,\mathbf{r}_2)}. \tag{51}$$

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These equations can be functionally integrated. For example,

$$\mathscr{F}[\rho_0]=\mathscr{F}_r[\rho_0]+\tfrac{1}{2}\int_0^1 d\alpha\int d\mathbf{r}_1\int d\mathbf{r}_2\,\rho^{(2)}(\phi_\alpha;\mathbf{r}_1,\mathbf{r}_2)(\phi(\mathbf{r}_1,\mathbf{r}_2)-\phi_r(\mathbf{r}_1,\mathbf{r}_2)),\tag{52}$$

where we have chosen a one-parameter integration path:

$$\phi_\alpha\equiv\phi(\mathbf{r}_1,\mathbf{r}_2;\alpha)=\phi_r(\mathbf{r}_1,\mathbf{r}_2)+\alpha(\phi(\mathbf{r}_1,\mathbf{r}_2)-\phi_r(\mathbf{r}_1,\mathbf{r}_2)).\tag{53}$$

$\mathscr{F}_r[\rho_0]$ corresponds to an initial (non-equilibrium) reference system in which the pairwise potential is $\phi_r(\mathbf{r}_1,\mathbf{r}_2)$ and the density is $\rho_0(\mathbf{r})$. $\rho^{(2)}(\phi_\alpha;\mathbf{r}_1,\mathbf{r}_2)$ is the pairwise distribution function for a system of density $\rho_0(\mathbf{r})$ in which the particles interact via a pairwise potential ϕ_α. If $\phi_r(\mathbf{r}_1,\mathbf{r}_2)=0$ then $\mathscr{F}_r=\mathscr{F}_{\text{ideal}}$ and (52) reduces to

$$\mathscr{F}[\rho_0]=\mathscr{F}_{\text{ideal}}[\rho_0]+\tfrac{1}{2}\int_0^1 d\alpha\int d\mathbf{r}_1\int d\mathbf{r}_2\,\rho^{(2)}(\phi_\alpha;\mathbf{r}_1,\mathbf{r}_2)\phi(\mathbf{r}_1,\mathbf{r}_2).\tag{54}$$

The grand potential can be derived in a similar fashion. This scheme avoids the need to calculate correlation functions at different densities (once the equilibrium density has been determined) and thus it might find useful applications.† For uniform fluids (52) reduces to the familiar coupling constant algorithm for the Helmholtz free energy of a system in terms of that of a reference system at the same density and temperature. This algorithm forms the basis of the various thermodynamic perturbation theories of bulk liquids [22]. Equation (52) has been employed as the starting point for perturbation theories of the surface tension and density profile of the liquid–vapour interface (see §8.1) and in §7 we will use (52) to formulate a perturbation theory for the long-wavelength behaviour of the Ornstein–Zernike direct correlation function of a dense *uniform* fluid.

§5. INTEGRO-DIFFERENTIAL EQUATIONS FOR THE EQUILIBRIUM DENSITY

Here we present several exact equations for the equilibrium density $\rho_0(\mathbf{r})$ of the fluid in an external potential. We begin with eqn. (28) which is equivalent to the fundamental result (14). Taking the gradient on each side we have

$$\begin{aligned}\beta^{-1}\nabla_1\ln\rho_0(\mathbf{r}_1)+\nabla_1 V_{\text{ext}}(\mathbf{r}_1)&=\beta^{-1}\nabla_1 c[\rho_0;\mathbf{r}_1]\\&=\beta^{-1}\int d\mathbf{r}_2\,c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\nabla_2\rho_0(\mathbf{r}_2),\end{aligned}\tag{55}$$

where we used (22) and (29). Equation (55) has a simple physical interpretation. It states that the effective force on a particle due to interactions with the other particles $\beta^{-1}\nabla_1 c[\rho_0;\mathbf{r}_1]$ is exactly balanced by the sum of the external force $-\nabla_1 V_{\text{ext}}(\mathbf{r}_1)$ and the kinetic term. Given some (approximate) means of evaluating the Ornstein–Zernike correlation function, (55) could, in principle, be solved for $\rho_0(\mathbf{r}_1)$.

The manipulation involved in going from the first to the second line of (55) is not immediately transparent and warrants clarification. Since the potential $u(\mathbf{r})$ is a unique functional of the equilibrium density $\rho_0(\mathbf{r})$ (see Appendix 1) it follows that if $\rho_0(\mathbf{r})$ is displaced by a spatial distance $\mathbf{s}$, then $u(\mathbf{r})$ must be similarly displaced, i.e. if $u(\mathbf{r}_1;[\rho_0(\mathbf{r})])=u(\mathbf{r}_1)$, where we have explicitly indicated the functional dependence on

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† For the interacting electron gas, the analogous procedure can be used to calculate the correlation energy.

$\rho_0(\mathbf{r})$, then $u(\mathbf{r}_1; [\rho_0(\mathbf{r}+\mathbf{s})]) = u(\mathbf{r}_1+\mathbf{s})$. We now make a functional Taylor expansion in $\rho_0(\mathbf{r})$:

$$u(\mathbf{r}_1; [\rho_0(\mathbf{r}+\mathbf{s})]) = u(\mathbf{r}_1; [\rho_0(\mathbf{r})]) + \int d\mathbf{r}_2 \left.\frac{\delta u(\mathbf{r}_1; [\rho_0])}{\delta \rho_0(\mathbf{r}_2)}\right|_{\mathbf{s}=0} (\rho_0(\mathbf{r}_2+\mathbf{s}) - \rho_0(\mathbf{r}_2)) + \dots$$

where the derivative is taken at the undisplaced density. It then follows that

$$u(\mathbf{r}_1+\mathbf{s}) - u(\mathbf{r}_1) = \int d\mathbf{r}_2 \left.\frac{\delta u(\mathbf{r}_1; [\rho_0])}{\delta \rho_0(\mathbf{r}_2)}\right|_{\mathbf{s}=0} (\rho_0(\mathbf{r}_2+\mathbf{s}) - \rho_0(\mathbf{r}_2)) + \dots,$$

so that in the limit $\mathbf{s}\to 0$ we have

$$\nabla_1 u(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\delta u(\mathbf{r}_1)}{\delta \rho_0(\mathbf{r}_2)} \nabla_2 \rho_0(\mathbf{r}_2)$$

and (55) then follows directly using (28) and (29).

Similarly, we can use the fact that since $u(\mathbf{r})$ is the only field which locates $\rho_0(\mathbf{r})$ in space, shifting $u(\mathbf{r})$ by a distance $\mathbf{s}$ must cause a similar shift in $\rho_0(\mathbf{r})$. Such an argument simply leads to the inverse of the last equation:

$$\nabla_1 \rho_0(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\delta \rho_0(\mathbf{r}_1)}{\delta u(\mathbf{r}_2)} \nabla_2 u(\mathbf{r}_2),$$

which, from (26) and (27), can be written as

$$\nabla_1 \rho_0(\mathbf{r}_1) = -\beta \int d\mathbf{r}_2 (\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \rho_0(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2) - \rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)) \nabla_2 V_{\text{ext}}(\mathbf{r}_2). \quad (56)$$

Equations (55) and (56) were derived, independently, by Lovett *et al.* [9] and Wertheim [10]. Neither equation depends explicitly on the form of interaction potential; they are completely general. For a fluid in which the particles interact via pairwise potentials (55) is equivalent to the first member of the Yvon–Born–Green hierarchy. In this case the effective force acting on a particle at position $\mathbf{r}_1$ due to interactions can be calculated explicitly from the pairwise potential $\phi(\mathbf{r}_1, \mathbf{r}_2)$ and we have

$$\beta^{-1} \nabla_1 c[\rho_0; \mathbf{r}_1] = -\frac{1}{\rho_0(\mathbf{r}_1)} \int d\mathbf{r}_2 \, \nabla_1 \phi(\mathbf{r}_1, \mathbf{r}_2) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \quad (57)$$

Using (55) we find

$$\nabla_1 \rho_0(\mathbf{r}_1) + \beta \rho_0(\mathbf{r}_1) \nabla_1 V_{\text{ext}}(\mathbf{r}_1) = -\beta \int d\mathbf{r}_2 \, \nabla_1 \phi(\mathbf{r}_1, \mathbf{r}_2) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2), \quad (58)$$

which is the first YBG equation. This result is usually derived directly from the definitions of the distribution functions. Equations (55), (56) and (58) are important in the theory of liquid surfaces and we will make use of them in § 8. For practical calculations on insulating fluids, (55) is probably the most useful since it involves only the direct correlation function. The latter is still short ranged in a non-uniform insulating fluid, i.e. $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \to 0$ when $|\mathbf{r}_1 - \mathbf{r}_2| > l$, the range of intermolecular forces in the fluid. Thus it may be easier to construct approximations for $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ than for the long range function $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ [9]. Furthermore, if $\rho_0(\mathbf{r})$ is slowly varying over the range of intermolecular forces so that $l|\nabla \rho_0(\mathbf{r})| \ll \rho_0(\mathbf{r})$ eqn. (55) reduces to the equation of hydrostatics. Under this condition

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$\int d\mathbf{r}_2 c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\nabla_2\rho_0(\mathbf{r}_2)\rightarrow\nabla_1\rho_0(\mathbf{r}_1)\int d\mathbf{r}_2\, c^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)$ where $c^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)$ refers to a uniform fluid of density $\rho_0(\mathbf{r}_1)$. Equation (55) can then be written as

$$\beta^{-1}\nabla_1\rho_0(\mathbf{r}_1)(1-\rho_0(\mathbf{r}_1)\int d\mathbf{r}\, c^{(2)}(r))=-\rho_0(\mathbf{r}_1)\nabla_1 V_{\text{ext}}(\mathbf{r}_1). \tag{59}$$

The term in brackets is $\beta(\rho_0\chi_T)^{-1}$ where χ_T is the isothermal compressibility of the uniform fluid of density $\rho_0(\mathbf{r}_1)$. From (45) it then follows

$$\nabla_1 p(\mathbf{r}_1)=\left(\frac{\partial p}{\partial\rho_0}\right)\nabla_1\rho_0(\mathbf{r}_1)=-\rho_0(\mathbf{r}_1)\nabla_1 V_{\text{ext}}(\mathbf{r}_1) \tag{60}$$

where $p(\mathbf{r}_1)$ is the local pressure. A more systematic treatment of the case of slowly varying densities is presented in the next section.

§6. SLOWLY VARYING DENSITIES

In many problems of interest we are concerned with density distributions which vary slowly over the range of molecular correlations. Such distributions occur, for example, for fluids in gravitational or centrifugal fields. In such circumstances the various thermodynamic potentials possess energy densities which are equal to those of a hypothetical uniform fluid whose density is everywhere $\rho_0(\mathbf{r})$, the equilibrium density at position $\mathbf{r}$ in the real non-uniform system. When the density varies more rapidly it is natural to expand the energy densities about their local density values in a series of density gradients.

6.1. *The gradient expansion*

The formal development of gradient expansions is most easily accomplished by extending the arguments originally presented by Hohenberg and Kohn [25] for the interacting electron gas. We suppose that a density distribution $\rho(\mathbf{r})$ can be usefully written in the form $\rho(\mathbf{r})=\Psi(\mathbf{r}/r_0)$ where the scale parameter $r_0\rightarrow\infty$. The function Ψ can exhibit considerable, but long-wavelength variation. We choose to expand the functional $\mathscr{F}[\rho]$ but we could equally well work with $\Phi[\rho]$. For large r_0 we assume that the energy density $f[\rho]$ can be expanded as a series of density gradients:

$$\mathscr{F}[\rho]=\int d\mathbf{r}\, f[\rho]$$

with

$$f|\rho|=f_0(\rho(\mathbf{r}))+\sum_{i=1}^{3} f_i(\rho(\mathbf{r}))\nabla_i\rho(\mathbf{r})+\sum_{i,j=1}^{3}[f_{i,j}^{(1)}(\rho(\mathbf{r}))\nabla_i\rho(\mathbf{r})\nabla_j\rho(\mathbf{r})$$
$$+f_{i,j}^{(2)}(\rho(\mathbf{r}))\nabla_i\nabla_j\rho(\mathbf{r})]+\ldots. \tag{61}$$

The coefficients $f_0(\rho(\mathbf{r}))$, $f_i(\rho(\mathbf{r}))$ etc., are functions of $\rho(\mathbf{r})$ not functionals, and the subscripts i,j denote cartesian components. Successive terms in (61) correspond to successive powers of the inverse scale parameter r_0^{-1}. For a finite r_0, this series does not strictly converge but, provided r_0 is large enough, it may be useful in an asymptotic sense. Since $f[\rho]$ is a unique functional of ρ independent of $V_{\text{ext}}(\mathbf{r})$, it must be invariant under rotations about $\mathbf{r}$. The coefficients f_0, f_i etc., are functions of scalar $\rho(\mathbf{r})$ so these are invariant under rotations. It is straightforward to show that $f[\rho]$ must have the form

$$f[\rho]=f_0(\rho)+f_2^{(a)}(\rho)\,\nabla^2\rho+f_2^{(b)}(\rho)\nabla\rho\,.\,\nabla\rho+O(\nabla_i^4)$$

where the subscript 2 now refers to the number of gradient operations. The term in ∇^2

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ρ can be written as

$$\nabla\,.\,(f_2^{(a)}(\rho)\nabla\rho)-\frac{df_2^{(a)}(\rho)}{d\rho}(\rho)\nabla\rho\,.\,\nabla\rho$$

and it is clear that the divergence term will vanish on integrating $f[\rho]$ over the volume of the system. Thus the energy density simplifies by symmetry arguments to

$$f[\rho]=f_0(\rho)+f_2(\rho)\nabla\rho\,.\,\nabla\rho+\mathrm{O}\,(\nabla_i^4)$$

and the appropriate expansion of $\mathscr{F}[\rho]$ must be of the form

$$\mathscr{F}[\rho]=\int d\mathbf{r}\,(f_0(\rho(\mathbf{r}))+f_2(\rho(\mathbf{r}))|\nabla\rho(\mathbf{r})|^2+\mathrm{O}\,(\nabla_i^4)) \tag{62}$$

Clearly $f_0(\rho)$ is the Helmholtz free energy density of a uniform fluid of density ρ but the other coefficients $f_2(\rho)$ etc., are as yet, undetermined.

The intrinsic chemical potential is readily evaluated

$$\mu_{\mathrm{in}}[\rho;\mathbf{r}]\equiv\frac{\delta\mathscr{F}[\rho]}{\delta\rho(\mathbf{r})}=f_0'(\rho)-f_2'(\rho)|\nabla\rho|^2-2f_2(\rho)\nabla^2\rho+\ldots \tag{63}$$

where the prime denotes differentiation w.r.t. ρ. From (14) it follows that the equilibrium density $\rho_0(\mathbf{r})$ satisfies the differential equation

$$\mu=V_{\mathrm{ext}}(\mathbf{r})+\mu(\rho_0(\mathbf{r}))-f_2'(\rho_0(\mathbf{r}))|\nabla\rho_0(\mathbf{r})|^2-2f_2(\rho_0(\mathbf{r}))\nabla^2\rho_0(\mathbf{r})+\ldots, \tag{64}$$

where $\mu(\rho)=f_0'(\rho)$ is the chemical potential of the uniform fluid of density ρ. Given some procedure for evaluating $f_2(\rho)$ etc., (64) can be solved for $\rho_0(\mathbf{r})$ and the various thermodynamic potentials calculated.

6.2. *Evaluation of the coefficients in the gradient expansion*

Provided we restrict consideration to density distributions which vary slowly *and* exhibit only small departures from some mean value ρ_{u}, the coefficients f_2 etc., can be expressed in terms of the density response functions of a uniform fluid of density ρ_{u}. If $|\tilde{\rho}(\mathbf{r})|\equiv|\rho(\mathbf{r})-\rho_{\mathrm{u}}|\ll\rho_{\mathrm{u}}$ the functional $\mathscr{F}[\rho]$ can be expanded in powers of $\tilde{\rho}(\mathbf{r})$. The existence of such a series then guarantees the existence of the gradient expansion. Here we derive the result for $f_2(\rho)$. This involves only linear response theory. The higher-order coefficients can also be evaluated but they require, in general, higher-order, non-linear response functions [25] and are consequently more difficult to calculate.

The functional Taylor expansion of $\mathscr{F}$ is

$$\mathscr{F}[\rho]=\mathscr{F}[\rho_{\mathrm{u}}]+\int d\mathbf{r}\left.\frac{\delta\mathscr{F}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho_{\mathrm{u}}}\tilde{\rho}(\mathbf{r})+\tfrac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\left.\frac{\delta^2\mathscr{F}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_{\mathrm{u}}}\tilde{\rho}(\mathbf{r})\tilde{\rho}(\mathbf{r}')+\ldots, \tag{65}$$

where $|_{\rho_{\mathrm{u}}}$ means the densities are to be set equal to ρ_{u}, a constant, after performing the functional differentiation. The second derivative of $\mathscr{F}$ is related to the Ornstein–Zernike correlation function (see (18), (19) and (22)):

$$\beta\frac{\delta^2\mathscr{F}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}=\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r})}-c[\rho;\mathbf{r},\mathbf{r}'] \tag{66}$$

and for a uniform system this can only depend on $|\mathbf{r}-\mathbf{r}'|$. Equation (65) can then be rewritten:

$$\begin{aligned}\mathscr{F}[\rho]=\mathscr{F}[\rho_u]&+\int d\mathbf{r}\,\mu(\rho_u)\tilde{\rho}(\mathbf{r})\\&+\frac{1}{2\beta}\int\int d\mathbf{r}\,d\mathbf{r}'\left(\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho_u}-c[\rho_u;|\mathbf{r}-\mathbf{r}'|]\right)\tilde{\rho}(\mathbf{r})\tilde{\rho}(\mathbf{r}')\\&+\mathrm{O}(\tilde{\rho}^3)\end{aligned}$$

On Fourier transforming the term in $\tilde{\rho}^2$ we have

$$\mathscr{F}[\rho]=\mathscr{F}[\rho_u]+\int d\mathbf{r}\,\mu(\rho_u)\tilde{\rho}(\mathbf{r})-\frac{1}{2\beta\mathscr{V}}\sum_{\mathbf{q}}\left(c[\rho_u;q]-\frac{1}{\rho_u}\right)\tilde{\rho}(\mathbf{q})\tilde{\rho}(-\mathbf{q})+\mathrm{O}(\tilde{\rho}^3) \quad (67)$$

$c[\rho_u;q]$ is the Fourier transform of the Ornstein–Zernike direct correlation function of a uniform fluid and for a fluid in equilibrium is related (see Appendix 3) to the (static) linear density response function $\chi(q)$:

$$c[\rho_u;q]-\frac{1}{\rho_u}=\beta/\chi(q) \quad (68)$$

Equation (67) is valid for any density distribution provided $|\tilde{\rho}(\mathbf{r})/\rho_u|$ is small. If, in addition, $\rho(\mathbf{r})$ is slowly varying only the low q Fourier components will be important in the expansion of the term in $\tilde{\rho}^2$ and we can expand the direct correlation function in powers of q^2:

$$c[\rho_u;q]=a(\rho_u)+b(\rho_u)q^2+d(\rho_u)q^4+\dots \quad (69)$$

Substituting into (67) and Fourier transforming we find

$$\begin{aligned}\mathscr{F}[\rho]=\mathscr{F}[\rho_u]+\int d\mathbf{r}\,\mu(\rho_u)\tilde{\rho}(\mathbf{r})-\frac{1}{2\beta}\Bigg[\left(a(\rho_u)-\frac{1}{\rho_u}\right)\int d\mathbf{r}\tilde{\rho}(\mathbf{r})^2\\+b(\rho_u)\int d\mathbf{r}\,|\nabla\tilde{\rho}(\mathbf{r})|^2+\dots\Bigg]+\mathrm{O}(\tilde{\rho}^3)\end{aligned} \quad (70)$$

In order to compare this result with the original gradient expansion we expand $f_0(\rho)$ and $f_2(\rho)$ in (62) in Taylor series about ρ_u:

$$\begin{aligned}\mathscr{F}[\rho]=\int d\mathbf{r}\Bigg[&f_0(\rho_u)+f'_0(\rho_u)\tilde{\rho}(\mathbf{r})+\frac{f''_0(\rho_u)}{2}(\rho_u)\tilde{\rho}(\mathbf{r})^2+\dots\\&+|\nabla\tilde{\rho}(\mathbf{r})|^2(f_2(\rho_u)+f'_2(\rho_u)\tilde{\rho}(\mathbf{r})+\dots)+\mathrm{O}(\nabla_i^4)\Bigg].\end{aligned} \quad (71)$$

Comparing coefficients between (70) and (71) we find

$$f'_0(\rho_u)=\mu(\rho_u) \quad (72a)$$

$$f''_0(\rho_u)=-\beta^{-1}(a(\rho_u)-1/\rho_u) \quad (72b)$$

$$f_2(\rho_u)=\frac{-b(\rho_u)}{2\beta} \quad (72c)$$

Equation (72*a*) is the standard thermodynamic identity and (72*b*) is merely a statement of the compressibility sum rule (see (44) and (45)). The non-trivial result is (72*c*) which shows that f_2 is proportional to the coefficient of q^2 in the expansion of the direct correlation function, i.e.

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$$f_2(\rho)=\frac{1}{12\beta}\int d\mathbf{r}\, r^2 c[\rho;r]. \tag{73}$$

This result appears to have been derived first by Yang *et al.* [15] who used a somewhat different approach.

6.3. *Energy densities in the slowly varying limit*

Having made the above identification of $f_2(\rho)$ we return to (64), the differential equation for the equilibrium density. An equation of the same form as (64) appears in the paper of Lebowitz and Percus [4]. Whilst they correctly identify the coefficient of $\nabla^2\rho_0$, i.e. they showed this coefficient was $-2f_2(\rho_0)$ with f_2 given by (73), it is not obvious that their expression for the coefficient of $|\nabla\rho_0|^2$ is simply $-f'_2(\rho_0)$ [15]. As mentioned in § 4.1, Lebowitz and Percus did not extend their analysis to the other free energy densities. These follow directly from our present analysis.

The Helmholtz free energy density is

$$\begin{aligned}\psi[\rho_0]&=\rho_0(\mathbf{r})V_{\text{ext}}(\mathbf{r})+f[\rho_0]\\&=\rho_0 V_{\text{ext}}+f_0(\rho_0)+f_2(\rho_0)\,|\nabla\rho_0|^2+\mathrm{O}\,(\nabla_i^4)\end{aligned} \tag{74}$$

while the grand potential has an energy density

$$\begin{aligned}\omega[\rho_0]&=\psi[\rho_0]-\mu\rho_0(\mathbf{r})\\&=f_0(\rho_0)+f_2(\rho_0)|\nabla\rho_0|^2-\rho_0(f'_0(\rho_0)-f'_2(\rho_0)|\nabla\rho_0|^2-2f_2(\rho_0)\nabla^2\rho_0)+\mathrm{O}\,(\nabla_i^4),\end{aligned} \tag{75}$$

where we have used (64) to eliminate $\mu-V_{\text{ext}}(\mathbf{r})$.

When f_2 and all higher-order coefficients are set equal to zero it is easy to show that

$$\begin{aligned}\nabla\omega[\rho_0]&=-\rho_0\, f''_0(\rho_0)\nabla\rho_0\\&=\rho_0(\mathbf{r})\nabla V_{\text{ext}}(\mathbf{r})\end{aligned} \tag{76}$$

and it is reasonable to identify a local hydrostatic pressure $p(\mathbf{r})$ with $-\omega[\rho_0]$ (see (60)). In other words, the conventional thermodynamic identification applies locally throughout the non-uniform fluid. If, however, we include the first gradient correction f_2 such an identification is no longer valid since in this case, $\nabla\omega[\rho_0]\neq\rho_0(\mathbf{r})\nabla V_{\text{ext}}(\mathbf{r})$. An expression for the pressure *tensor* $\boldsymbol{\sigma}$ can be found [15]

$$\boldsymbol{\sigma}=-\omega[\rho_0]\mathbf{1}+2f_2(\rho_0)\nabla\rho_0\nabla\rho_0 \tag{77}$$

which satisfies the equation of hydrostatics:

$$\nabla\,.\,\boldsymbol{\sigma}=-\rho_0(\mathbf{r})\nabla V_{\text{ext}}(\mathbf{r}) \tag{78}$$

This result forms the basis of the van der Waals theory of surface tension and we will return to it in § 8.1.

6.4. *A partial summation of the gradient expansion*

In their work on the inhomogeneous electron gas Hohenberg and Kohn [25] and later Kohn and Sham [23] introduced an approximation scheme for the analogue of the functional $\mathscr{F}[\rho]$ which should be valid when either the density has nearly the

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same value everywhere *or* is slowly varying. This approximation now permits short wavelength variation in $\rho(\mathbf{r})$, provided the departure from the mean is small, and can therefore be used to treat certain oscillatory density distributions. Formally, the approximation corresponds to summing terms of the form $f_m(\rho)\nabla\rho^n \cdot \nabla\rho^{m-n}$, where m and n are integers, in the gradient expansion but it can easily be derived from the following argument.

Suppose $\mathscr{F}[\rho]$ can be expressed in terms of a local energy density plus an expansion in powers of the difference between densities at different points in the fluid. To second order in this difference $\mathscr{F}[\rho]$ must have the form

$$\mathscr{F}[\rho]=\int d\mathbf{r} f_0(\rho(\mathbf{r}))-\frac{1}{2\beta}\int\int d\mathbf{r}d\mathbf{r}'\, K(\mathbf{r},\mathbf{r}')(\rho(\mathbf{r})-\rho(\mathbf{r}'))^2 \tag{79}$$

(Any term linear in $\rho(\mathbf{r})-\rho(\mathbf{r}')$ will vanish by symmetry). We further suppose that the kernel K can be written as

$$K(\mathbf{r},\mathbf{r}')=K[\bar{\rho};|\mathbf{r}-\mathbf{r}'|]$$

where $\bar{\rho}$ is some average of the local densities, e.g. $\bar{\rho}=(\rho(\mathbf{r})+\rho(\mathbf{r}'))/2$. In order to specify K further we insist that (79) reduces to (67) in the limit $|\tilde{\rho}(\mathbf{r})|\equiv|\rho(\mathbf{r})-\rho_u|\ll\rho_u$ i.e. we ask that $\mathscr{F}[\rho]$ reproduce the linear response result. It is straightforward to show that, to order $\tilde{\rho}^2$, (67) and (79) are identical provided

$$\begin{aligned}K[\rho_u;|\mathbf{r}-\mathbf{r}'|]&=\frac{\beta}{2}\frac{\delta^2\mathscr{F}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\bigg|_{\rho_u}\\&=\tfrac{1}{2}\left(\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho_u}-c[\rho_u;|\mathbf{r}-\mathbf{r}'|]\right)\end{aligned} \tag{80}$$

With this identification (79) clearly contains short wavelength (large q) contributions but it also reduces to the aforementioned series of gradient terms, with the coefficients given in § 6.2, for slowly varying densities. Combining (79) and (80) we have

$$\mathscr{F}[\rho]=\int d\mathbf{r} f_0(\rho(\mathbf{r}))+\frac{1}{4\beta}\int\int d\mathbf{r}d\mathbf{r}'\, c[\bar{\rho};|\mathbf{r}-\mathbf{r}'|](\rho(\mathbf{r})-\rho(\mathbf{r}'))^2. \tag{81}$$

All that is required to use this approximation is some prescription for the direct correlation function of a uniform fluid at arbitrary densities.

Recently Ebner *et al.* [14] have carried out extensive calculations of the surface tension and equilibrium density profile of a Lennard-Jones fluid over a wide range of temperatures using this approximation. These authors also used the theory to calculate the oscillatory density profile for a fluid in the neighbourhood of a model container wall. All their calculations were based on the Percus–Yevick solution for the direct correlation function and suitably parametrized functions were chosen to represent $\rho(\mathbf{r})$. It appears that (81) is a useful and tractable approximation. Saam and Ebner [24] have compared (81) with the exact expression for $\mathscr{F}[\rho]$ as obtained

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by integrating the direct correlation function of the non-uniform system w.r.t. density. The latter can be written as

$$\begin{aligned}\mathscr{F}[\rho]&=\mathscr{F}_{\mathrm{ideal}}[\rho]-\Phi[\rho]\\&=\beta^{-1}\int d\mathbf{r}\left(\rho(\mathbf{r})(\ln(\lambda^3\rho(\mathbf{r}))-1)-\frac{\rho(\mathbf{r})^2}{2}s(\mathbf{r})\right)\\&\quad+\frac{1}{4\beta}\int\int d\mathbf{r}d\mathbf{r}'\,\tilde{c}(\mathbf{r},\mathbf{r}')(\rho(\mathbf{r})-\rho(\mathbf{r}'))^2\end{aligned}\tag{82}$$

where

$$\tilde{c}(\mathbf{r},\mathbf{r}')\equiv 2\int_0^1 d\alpha\,\alpha\int_0^1 d\alpha'\,c[\alpha\alpha'\rho;\mathbf{r},\mathbf{r}']$$

and

$$s(\mathbf{r})\equiv\int d\mathbf{r}'\,\tilde{c}(\mathbf{r},\mathbf{r}')$$

and we have used (38) and the symmetry property (22). The nature of the two approximations made in (81) are now apparent. Firstly, $c[\alpha\alpha'\rho;\mathbf{r},\mathbf{r}']$ is replaced by $c[\bar{\rho};|\mathbf{r}-\mathbf{r}'|]$, the direct correlation function of a uniform fluid whose density is arbitrarily fixed at $\bar{\rho}$. The second approximation replaces the quantity

$$\frac{-\rho(\mathbf{r})^2s(\mathbf{r})}{2\beta}$$

by the interaction part of the local free energy density. This replacement would be exact for a uniform fluid so the second approximation simply assumes that the equivalence applies locally.

§ 7. THE LONG-WAVELENGTH BEHAVIOUR OF THE DIRECT CORRELATION FUNCTION OF A UNIFORM FLUID

Recently Evans and Schirmacher [17] have used the formalism described in the earlier sections of this paper to derive some useful approximations for the long-wavelength behaviour of the Ornstein–Zernike direct correlation function of a uniform fluid. Their analysis is appropriate to a fluid in which the particles interact via a central pairwise potential $\phi(r)$. This potential is divided into a suitable 'reference' part ϕ_{r} and a 'perturbation' part ϕ_{p}:

$$\phi(r)=\phi_{\mathrm{r}}(r)+\phi_{\mathrm{p}}(r).$$

The free energy of the system with pair potential ϕ can then be related to that of a system with pair potential ϕ_{r} using (52). From (66) it follows that

$$c^{(2)}(r_{12})-c_{\mathrm{r}}^{(2)}(r_{12})=-\frac{\beta\delta^2}{2\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}\int_0^1 d\alpha\int\int d\mathbf{r}_1d\mathbf{r}_2\,\rho^{(2)}(\alpha;\mathbf{r}_1,\mathbf{r}_2)\phi_{\mathrm{p}}(r_{12})\Big|_{\rho(\mathbf{r})=\rho}\tag{83}$$

where $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$, $c^{(2)}(r)$ is the direct correlation function for the uniform fluid of equilibrium density ρ (corresponding to pair potential ϕ) and $c_{\mathrm{r}}^{(2)}(r)$ is the corresponding function for the reference fluid at the same density (pair potential ϕ_{r}). $\rho^{(2)}(\alpha;\mathbf{r}_1,\mathbf{r}_2)$ is the pairwise distribution function of a non-uniform fluid in which the particles interact via a pairwise potential $\phi_r + \alpha\phi_p$. While (83) is formally exact its usefulness is restricted by the necessity of having to evaluate $\rho^{(2)}(\alpha; \mathbf{r}_1, \mathbf{r}_2)$.

The crudest approximation simply ignores all correlations between the particles and sets

$$\rho^{(2)}(\alpha; \mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2). \tag{84}$$

The functional differentiation in (83) is then trivial and leads to

$$c^{(2)}(r) - c_r^{(2)}(r) = -\beta\phi_p(r) \tag{85}$$

which is the well-known random phase approximation (RPA) [22]. In order to progress beyond the RPA we first expand $\rho^{(2)}(\alpha; \mathbf{r}_1, \mathbf{r}_2)$ in powers of $\phi_p(r_{12})$. To the lowest order the integral in (83) is

$$\int\int d\mathbf{r}_1 d\mathbf{r}_2\, \rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\phi_p(r_{12}),$$

where $\rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho^{(2)}(\alpha = 0; \mathbf{r}_1, \mathbf{r}_2)$ is the pairwise distribution function of the non-uniform reference fluid. The problem is now reduced to finding a suitable prescription for this quantity. There is, however, no general theory for the pairwise distribution function in strongly inhomogeneous systems and so we are forced into approximation schemes which apply only to *weakly* non-uniform fluids. We expand $\rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ about its uniform density value $\rho_r^{(2)}(r_{12})$:

$$\rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_r^{(2)}(r_{12}) + \tfrac{1}{2}(\rho(\mathbf{r}_1) - \rho + \rho(\mathbf{r}_2) - \rho)\frac{\partial \rho_r^{(2)}(r_{12})}{\partial \rho}$$
$$+ \tfrac{1}{2}(\rho(\mathbf{r}_1) - \rho)(\rho(\mathbf{r}_2) - \rho)\frac{\partial^2 \rho_r^{(2)}(r_{12})}{\partial \rho^2} + \dots, \tag{86}$$

with $\rho_r^{(2)}(r) \equiv \rho^2 g_r(r)$, where $g_r(r)$ is the radial distribution function of the uniform reference system of density ρ. The derivatives in (86) are to be evaluated at density ρ. Using this expansion we find

$$c^{(2)}(r) - c_r^{(2)}(r) = -\frac{\beta}{2}\phi_p(r)\frac{\partial^2 \rho_r^{(2)}(r)}{\partial \rho^2}. \tag{87}$$

This result was first obtained by Henderson and Ashcroft [16] from a rather different derivation. These authors named it the mean density approximation (MDA) and used it to study phase separation in binary metallic alloys.

On Fourier transforming, we have

$$c^{(2)}(q) - c_r^{(2)}(q) = -\frac{\beta}{2(2\pi)^3}\int d\mathbf{k}\, \phi_p(k)\frac{\partial^2}{\partial \rho^2}\rho_r^{(2)}(|\mathbf{q} - \mathbf{k}|), \tag{88}$$

which can be re-written in terms of the liquid structure factor $S_r(q)$ of the reference fluid:

$$c^{(2)}(q) - c_r^{(2)}(q) = -\beta\phi_p(q) - \frac{\beta}{(2\pi)^3}\int d\mathbf{k}\phi_p(k)\left(\frac{\partial S_r(|\mathbf{q}-\mathbf{k}|)}{\partial \rho} + \frac{\rho\partial^2 S_r(|\mathbf{q}-\mathbf{k}|)}{2\partial \rho^2}\right). \tag{89}$$

since the structure factor and radial distribution function are related by the usual equation:

$$S_r(q) - 1 = \rho\int d\mathbf{r}\exp(i\mathbf{q}\,.\,\mathbf{r})(g_r(r) - 1). \tag{90}$$

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We can only expect (89) to be a realistic approximation at small wave vectors because the expansion in (86) is only appropriate when $\rho(\mathbf{r})$ varies slowly and exhibits small departures from the mean value. At $q=0$ (89) is exact, to first order in ϕ_{p}. In this limit the result can be derived [17], without recourse to the theory of non-uniform fluids, using the compressibility sum rule (72 *b*) and the coupling constant algorithm for uniform fluids mentioned in § 4.2.

Given some procedure for calculating $S_{\mathrm{r}}(q)$ at different densities (89) can be used to obtain explicit corrections to the RPA results. Evans and Schirmacher [17] have suggested a further simplifying approximation which is to neglect the density dependence of $g_{\mathrm{r}}(r)$. Equation (87) then reduces to

$$c^{(2)}(r)-c_{\mathrm{r}}^{(2)}(r)=-\beta\phi_{\mathrm{p}}(r)g_{\mathrm{r}}(r) \tag{91}$$

and (89) becomes

$$c^{(2)}(q)-c_{\mathrm{r}}^{(2)}(q)=-\beta\phi_{\mathrm{p}}(q)-\frac{\beta}{\rho(2\pi)^3}\int d\mathbf{k}\,\phi_{\mathrm{p}}(k)(S_{\mathrm{r}}(|\mathbf{q}-\mathbf{k}|)-1) \tag{92}$$

The second term in (92) should yield an estimate of the importance of correlations at small q. Equations (91) and (92) are referred to as the extended random phase approximation (ERPA).

The ERPA and the RPA have been used to calculate the $q=0$ limit of the direct correlation function and, hence the isothermal compressibility of several simple fluids and a wide variety of liquid metals at temperatures close to their triple points [17]. In these calculations the pairwise potential was divided into a reference part ϕ_{r} and a perturbation part ϕ_{p} according to the Weeks, Chandler, Andersen (WCA) [26] prescription, i.e. ϕ_{r} refers to the short-range repulsive force part while ϕ_{p} represents the remainder of the intermolecular pair potential. $S_{\mathrm{r}}(q)$ can then be calculated using the WCA perturbation theory based on the hard-sphere structure factor. The compressibilities calculated from the ERPA differ by only a few per cent from those obtained from the RPA and are in good agreement with the results of computer simulations based on the same potential—where these are available. Thus it appears that with the WCA division of the potential, correlation effects are rather small at $q=0$. It would be interesting to examine the accuracy of all three approximation schemes for small but finite values of q.

§ 8. APPLICATIONS TO LIQUID SURFACES

In this section we apply the formalism developed earlier in the paper to the statistical thermodynamics of liquid surfaces. For simplicity we first consider a monatomic fluid in zero external potential. We assume this fluid possesses a planar surface of area $A=L^2$ parallel to the x–y plane (see figure 1). The volume of the fluid is $\mathscr{V}=L^3$ and L is macroscopic. We assume further that the equilibrium density profile $\rho_0(\mathbf{r})\equiv\rho_0(z)$ and at temperatures close to the triple point has the form sketched in fig. 2. $\rho_0(z)$ is expected to vary rapidly (typically over two or three molecular diameters) between the co-existent densities ρ_{l} and ρ_{v}. As the temperature is increased ρ_{l} will decrease, ρ_{v} will increase and the density profile will become less 'sharp', i.e. the interfacial width will increase. At the critical temperature the interfacial width will diverge with the same exponent as the bulk correlation length

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in either of the bulk phases [27]. In general, the equilibrium profile should satisfy the following boundary conditions:

$$\rho_0(L/2)=\rho_v,\quad \rho_0(-L/2)=\rho_1,$$
$$\left.\frac{d\rho_0}{dz}\right|_{L/2}=0,\quad \left.\frac{d\rho_0}{dz}\right|_{-L/2}=0, \tag{93}$$

provided L is macroscopic.

Of course, planar interfaces of this kind do not exist in the absence of an external field (e.g. gravity). If the gravitational acceleration g is zero one fluid phase would form in one or more spherical regions embedded in the second phase. It is the external field which determines the location of the interface in space. Thus, if we set $g=0$ initially we should strictly work with spherical interfaces. We may suppose, however, that one phase forms a sphere of essentially infinite radius so that its surface is effectively planar. The gravitational field plays another more subtle role in surface problems [28, 27, 10, 12, 21] by surpressing capillary wave-like fluctuations in the position of the Gibbs dividing surface. We will return to this later in § 8.4, where we consider such fluctuations in some detail.

In the absence of an external field, the thermodynamics of liquid surfaces is straightforward [29]. By considering the Helmholtz free energy as a function $F(T, \mathscr{V}, A, N)$ it is easy to show that the liquid–vapour surface tension is given by

$$\gamma=\left(\frac{\partial F}{\partial A}\right)_{T,\mathscr{V},N}, \tag{94}$$

where N is the total number of molecules. Often it is more convenient to work with the grand potential $\Omega(T,\mathscr{V},A,\mu)$ from which it follows that

$$\gamma=\left(\frac{\partial \Omega}{\partial A}\right)_{T,\mathscr{V},\mu}. \tag{95}$$

The grand potential can also be explicitly decomposed into bulk and surface contributions:

$$\Omega=-p\mathscr{V}+\gamma A, \tag{96}$$

where p is the pressure of the co-existing bulk phases. Another useful formula for the surface tension relates this quantity to the integral through the interface of the difference between the normal and the tangential components of the stress tensor:

$$\gamma=\int_{-L/2}^{L/2} dz\,(\sigma_{\mathrm{N}}(z)-\sigma_{\mathrm{T}}(z)). \tag{97}$$

The component normal to the interface $\sigma_{\mathrm{N}}(z)=p$ is constant for a fluid in hydrostatic equilibrium in zero external field. The tangential component $\sigma_{\mathrm{T}}(z)$ reduces to p for z in either bulk phase but varies for z in the interface region. Consequently it is possible to replace $L/2$ by ∞ and $-L/2$ by $-\infty$ in the limits of (97). This equation is often referred to as the 'mechanical' definition of surface tension.

8.1. *The van der Waals and related approximate theories*

The approximation schemes developed in § 6 are readily applied to the strictly planar model of an interface. If the expansion of the Helmholtz free energy is

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terminated after the second term, i.e.

$$\mathscr{F}[\rho]=\int d\mathbf{r}\,(f_0(\rho(\mathbf{r}))+f_2(\rho(\mathbf{r}))|\nabla\rho(\mathbf{r})|^2), \tag{98}$$

then it follows from (64) that the equilibrium density profile should satisfy

$$\mu=\mu(\rho_0(z))-f'_2(\rho_0(z))\left|\frac{d\rho_0(z)}{dz}\right|^2-2f_2(\rho_0(z))\frac{d^2\rho_0(z)}{dz^2}. \tag{99}$$

This equation has been analysed in some detail by Yang *et al.* [15] who have concluded that a solution $\rho_0(z)$ does exist and has the form indicated in fig. 1†. These authors have also shown that this solution is identical to the one which would be obtained by solving (64) in zero external field for spherical geometry in the limit of a sphere of infinite radius.

The surface tension can be obtained using the prescription of either (96) or (97). From (77) the tangential and normal components of the stress tensor are given by

$$\sigma_T(z)=-\omega[\rho_0] \tag{100}$$

and

$$\sigma_N(z)=-\omega[\rho_0]+2f_2(\rho_0(z))\left|\frac{d\rho_0(z)}{dz}\right|^2.$$

So from (97) it follows

$$\gamma=2\int_{-\infty}^{\infty}dz f_2(\rho_0(z))\left|\frac{d\rho_0(z)}{dz}\right|^2. \tag{101}$$

Since the pressure of the co-existing bulk phases is $p=\sigma_N$, the same result follows immediately from (96).

The results embodied by (99) and (101) represent what is probably the simplest microscopic treatment of the liquid–vapour interface. This type of approach was introduced by van der Waals in 1894 [30] who suggested a free energy of the form given in (98) but treated f_2 as a constant positive parameter. (Incidentally a formula similar to (101) was derived in 1892 by Lord Rayleigh [31] using a different approach.) For an excellent account of the van der Waals theory of interfaces and its application to critical phenomena see the article by Widom [27]. In order to make the theory quantitative some prescription for $f_2(\rho)$ is required. The obvious choice is that given by (73). One then has a well-defined procedure for calculating both the density profile and surface tension from a given intermolecular potential. Clearly such a theory should not be accurate near the triple point since here the density is varying too rapidly to meet the conditions required in § 6. Thus, for low temperatures a van der Waals type of approach can be expected to be useful only in an asymptotic sense. At high temperatures approaching the critical point the density profile varies slowly over the range of intermolecular forces and the departures from the mean value are everywhere small, so a gradient expansion of the kind described in § 6 should be valid. There is, however, no reason to expect a theory based on truncating the expansion after the second term to be especially accurate even at high temperatures [27].

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† The same authors [74] later demonstrated that a solution also exists when the gravitational field is included and that this solution approaches the solution of (99) as the gravitational acceleration approaches zero.

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It is necessary to mention another caveat concerning the van der Waals theory. In applying (98) to the surface problem we are forced to consider the free energy density $f_0(\rho)$ and the function $f_2(\rho)$ for densities ρ in the range $\rho_v < \rho < \rho_l$, i.e. for densities corresponding to a two-phase system. The theory implicitly assumes that $f_0(\rho)$ and $f_2(\rho)$ are given by analytic continuation of these functions from the bulk equilibrium phases into the two-phase region [27]. Similar assumptions are inherent in all the approximate theories of liquid surfaces and we will return to this important point in § 8.4.

One obvious extension of the van der Waals theory is to perform a partial summation of the gradient expansion and use (81) for $\mathscr{F}[\rho]$ rather than (98). This is the scheme employed by Ebner *et al.* [14] which was described in § 6.4. A different modification of the van der Waals theory has been proposed by Bongiorno and Davis [32].

Thermodynamic perturbation theories have been developed for the study of the planar interface [18, 33, 34, 35]. These methods can also be considered as generalizations of the van der Waals theory. They are, however, primarily intended for triple point studies since they are based on the successful perturbation theories of dense liquids. All these theories start from (52) which expresses the free energy $\mathscr{F}[\rho]$ of the actual non-uniform fluid, in which the intermolecular pair potential is ϕ, in terms of the free energy $\mathscr{F}_r[\rho]$ of a suitable reference system in which the particles interact via a reference potential ϕ_r. If $\phi_p = \phi - \phi_r$ is the perturbation potential, then (52) can be expanded as:

$$\mathscr{F}[\rho] = \mathscr{F}_r[\rho] + \tfrac{1}{2}\int\int d\mathbf{r}_1 d\mathbf{r}_2\, \rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\phi_p(r_{12}) + O(\phi_p^2), \tag{102}$$

where $\rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is the pairwise distribution function of the reference system (see also § 7). It is then assumed that $\mathscr{F}_r[\rho]$ and $\rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ can be approximated as follows:

$$\mathscr{F}_r[\rho] \approx \int d\mathbf{r} f_{r0}(\rho(\mathbf{r})) \tag{103a}$$

$$\rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \approx \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) g_r(\bar{\rho}; r_{12}), \tag{103b}$$

where $f_{r0}(\rho)$ is the free energy density of the uniform reference fluid and $g_r(\bar{\rho}; r_{12})$ is the radial distribution function of the uniform reference fluid evaluated at some mean density, e.g. $\bar{\rho} = (\rho(\mathbf{r}_1) + \rho(\mathbf{r}_2))/2$. Equations (103 *a*, *b*) constitute the simplest 'local density' ansatz. Two prescriptions for the division of the pairwise potential into reference and perturbation parts have been used. These are the Barker–Henderson (BH) [36] and Weeks–Chandler–Andersen (WCA) [26] schemes. In the former the reference system is chosen to be that of hard spheres while in the latter ϕ_r is the 'repulsive force' part of the pairwise potential. Since the free energy and radial distribution function of the uniform hard-sphere system are readily available it is then straightforward to calculate $\mathscr{F}[\rho]$ for a suitably parametrized (exponential or tanh) density profile $\rho(z)$. The chemical potential μ and the co-existing bulk densities ρ_l and ρ_v are obtained by solving the simultaneous equations

$$\mu = \mu(\rho_l) = \mu(\rho_v) \tag{104a}$$

$$p = p(\rho_l) = p(\rho_v). \tag{104b}$$

The grand potential $\Omega[\rho] = \mathscr{F}[\rho] - \int d\mathbf{r}\, \mu\rho(z)$ can then be minimized with respect to the parameters which specify $\rho(z)$ to obtain both the equilibrium profile and the surface tension.

Table 1. Interfacial '10–90' widths (w) and surface tensions (γ) calculated from van der Waals and related theories for a Lennard–Jones 12–6 fluid near its triple point.†

Theory	Reference	T(K)	w/σ	γ(dyn cm^{-1})
BH perturbation theory	[18]	90	2·3	14
BH perturbation theory	[38]	84	2·2	16
BH perturbation theory	[33]	90	1·5	17
WCA perturbation theory	[33]	90	1·8	17
WCA perturbation theory (simplified)	[37]	85	2·8	14
WCA perturbation theory (extended)	[19]	84	1·4	18
Partial summation of gradient expansion	[14]	84	1·7	18
van der Waals (eqn. 98)	[39]	84	2·7	25

† In order to compare with 'real' argon, the parameters of the Lennard–Jones potential are taken as $\sigma = 3{\cdot}405$ Å and $\varepsilon/k_B = 119{\cdot}8$ K. The experimental results are $\gamma = 13{\cdot}1$ dyn cm^{-1} at 85 K and $\gamma = 11{\cdot}9$ dyn cm^{-1} at 90 K [40].

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For a Lennard-Jones 12–6 fluid at temperatures close to the triple point the density profiles calculated from the perturbation theories have the form indicated in fig. 2. The calculated interfacial '10–90' widths w (defined as the distance over which the density changes from $0{\cdot}9\rho_l$ to $0{\cdot}1\rho_l$) are listed in table 1. w results from a balance between the attractive forces (the term in ϕ_p) which favour a sharp transition and the repulsive forces ($\mathscr{F}_r$) which favour a broad transition region [37]. The corresponding results for the surface tension are also given in table 1. The perturbation theories predict an increase of w with an accompanying linear decrease in γ as the temperature is increased [18, 37, 38].

Recently Singh and Abraham [19] have attempted to improve upon the approximations (103 *a*, *b*) by adding what are essentially gradient corrections or partial summations of gradient expansions. The results of calculations incorporating these modifications are not substantially different from those based on the local density ansatz. These authors find w is slightly smaller and γ is reduced by about 2 dyn cm^{-1}. In table 1 we include the results of Ebner *et al.* [14] which are based on the more direct extension of the van der Waals theory (see § 6.4). We also present results calculated using (98) and the Percus–Yevick solutions for f_0 and f_2 [39].

It is clear that all versions of the van der Waals theory predict an interfacial width of about two atomic diameters at the triple point, and a surface tension which is in rough agreement with experiment.

8.2. *The Kirkwood–Buff theory*

Another theory which is frequently employed in the study of the liquid–vapour surface is that due originally to Kirkwood and Buff [20]. In this approach, it is assumed from the outset that the potential energy of the fluid can be expressed as a sum of pairwise intermolecular potentials and the stress tensor is evaluated in terms of the intermolecular virial. For the planar surface the tangential and normal components can be written as:

$$\sigma_T(z_1) = \beta^{-1}\rho_0(z_1) - \tfrac{1}{2}\int d\mathbf{r}_{12}\frac{x_{12}^2}{r_{12}}\frac{d\phi(r_{12})}{dr_{12}}\int_0^1 d\alpha\,\rho^{(2)}(\mathbf{r}_1 - \alpha\mathbf{r}_{12}, \mathbf{r}_1 + (1-\alpha)\mathbf{r}_{12}) \qquad (105\,a)$$

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and

$$\sigma_N(z_1)=\beta^{-1}\rho_0(z_1)-\tfrac{1}{2}\int d\mathbf{r}_{12}\frac{z_{12}^2}{r_{12}}\frac{d\phi(r_{12})}{dr_{12}}\int_0^1 d\alpha\,\rho^{(2)}(\mathbf{r}_1-\alpha\mathbf{r}_{12},\mathbf{r}_1+(1-\alpha)\mathbf{r}_{12}). \tag{105b}$$

The condition of hydrostatic equilibrium ($\sigma_N=$ a constant) then implies

$$\frac{d\rho_0(z_1)}{dz_1}=\beta\int d\mathbf{r}_{12}\frac{z_{12}}{r_{12}}\frac{d\phi(r_{12})}{dr_{12}}\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2), \tag{106}$$

which is identical to the first YBG equation (58) for planar geometry and zero external field. This means that the stress tensor in (105) is consistent with the requirements of thermodynamic equilibrium. The surface tension follows from the mechanical definition (97):

$$\gamma=\tfrac{1}{2}\int_{-\infty}^{\infty}dz_1\int d\mathbf{r}_{12}\frac{x_{12}^2-z_{12}^2)}{r_{12}}\frac{d\phi(r_{12})}{dr_{12}}\rho^{(2)}(\mathbf{r}_2{}^1,\mathbf{r}_2), \tag{107}$$

where use is made of the fact that $\rho^{(2)}$ is invariant under a renumbering of the particles. The formula for the surface tension can also be derived from the grand partition function using (95) [41] or from the canonical partition function using (94). These methods are equivalent to the following argument which makes use of the fact that the grand potential is a functional of the pairwise potential ϕ. From (50) we have that the infinitesimal change in grand potential due to an infinitesmal change in the pairwise potential is

$$\Delta\Omega=\tfrac{1}{2}\int\int d\mathbf{r}_1 d\mathbf{r}_2\,\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\Delta\phi(\mathbf{r}_1,\mathbf{r}_2), \tag{108}$$

for a fixed chemical potential. Suppose $\Delta\phi$ corresponds to the following transformation which increases the surface area by $\Delta A=\xi L^2$ but keeps the volume fixed

$$\phi(x_1,y_1,z_1,x_2,y_2,z_2,)\to\phi(x_1(1+\xi),y_1,z_1(1+\xi)^{-1},x_2(1+\xi),y_2,z_2(1+\xi)^{-1})$$

where ξ is an infinitesimal, then $\Delta\phi$ is of the form

$$\Delta\phi=\xi\left(x_1\frac{\partial\phi}{\partial x_1}+x_2\frac{\partial\phi}{\partial x_2}-z_1\frac{\partial\phi}{\partial z_1}-z_2\frac{\partial\phi}{\partial z_2}\right)+\mathrm{O}(\xi^2).$$

If $\phi(\mathbf{r}_1,\mathbf{r}_2)\equiv\phi(r_{12})$ then this reduces to

$$\Delta\phi=\xi\frac{(x_{12}^2-z_{12}^2)}{r_{12}}\frac{d\phi(r_{12})}{dr_{12}}+\mathrm{O}(\xi^2). \tag{109}$$

Combining (108) and (109) and using $\gamma=\Delta\Omega/\Delta A$ we rederive (107). Although (106) and (107) are formally exact results for a planar interface, they are not useful unless some prescription can be found for the equilibrium distribution functions $\rho_0(z)$ and $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$. Several attempts have been made to produce approximate solutions of the first YBG equation (see the review by Toxvaerd [42]). These usually assume that $\rho^{(2)}$ can be approximated by some suitable weighted mean of the bulk radial distribution functions and solve (106) by iteration. It now seems to be well established (see, however, [43]) that these methods give rise to monatomic density profiles whose interfacial widths are similar to those calculated from the van der Waals types of theory and surface tensions which are somewhat smaller than those

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reported in § 8.1. Recently Toxvaerd [44] has extended his analysis by approximating $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\approx\rho_0(z_1)\rho_0(z_2)g(\bar{\rho};r_{12})$ with $\bar{\rho}=\rho_0((z_1+z_2)/2)$ and used a thermodynamic perturbation theory to calculate the radial distribution function at the required densities $\bar{\rho}$. The profiles which he obtained by iterating (106) are again similar to those obtained from the calculations described in § 8.1.

Local density approximations to $\rho^{(2)}$ will be accurate in the 'wings' of the density profile where $\rho_0(z)$ is close to ρ_l or ρ_v and in these regions we can use the first YBG equation to evaluate the functional form of $\rho_0(z)$ [11]. We set $\rho^{(2)}$ $(\mathbf{r}_1,\mathbf{r}_2)=\rho_0(z_2)g(\rho_b;r_{12})$, where ρ_b refers to either ρ_l or ρ_v, and integrate (106) from the bulk into the interface:

$$\beta^{-1}\ln\left(\frac{\rho_0(z)}{\rho_b}\right)=\int^z dz_1\int d\mathbf{r}_{12}\frac{z_{12}}{r_{12}}\frac{d\phi(r_{12})}{dr_{12}}\rho_0(z_1+z_{12})g(\rho_b;r_{12}) \tag{110}$$

If $\rho_0(z)$ is slowly varying over the range of the intermolecular force $d\phi/dr$ then $\rho_0(z_1+z_{12})$ may be usefully expanded in a Taylor series about z_1. The integration over $d\mathbf{r}_{12}$ can be performed using cylindrical coordinates

$$\int d\mathbf{r}_{12}\rightarrow 2\pi\int_0^\infty dr_{12}\,r_{12}\int_{-r_{12}}^{r_{12}}dz_{12}$$

and after some straightforward algebra we find

$$\ln\left(\frac{\rho_0(z)}{\rho_b}\right)=\alpha_0(\rho_0(z)-\rho_b)+\alpha_2\frac{d^2\rho_0(z)}{dz^2}+\text{higher derivatives}, \tag{111}$$

where

$$\alpha_0=\frac{4\pi\beta}{3}\int_0^\infty dr\,r^3\frac{d\phi(r)}{dr}g(\rho_b:r),$$

$$\alpha_2=\frac{2\pi\beta}{15}\int_0^\infty dr\,r^5\frac{d\phi(r)}{dr}g(\rho_b;r)$$

and we have assumed that all derivatives of $\rho_0(z)$ vanish when $\rho_0=\rho_b$. Multiplying each side of (111) by $d\rho_0(z)/dz$ and integrating we obtain

$$2\rho_0(z)\ln\left(\frac{\rho_0(z)}{\rho_b}\right)+2(\rho_b-\rho_0(z))=\alpha_0(\rho_0(z)-\rho_b)^2+\alpha_2\left(\frac{d\rho_0(z)}{dz}\right)^2,$$

which can be further simplified by expanding in $\tilde{\rho}(z)=\rho_0(z)-\rho_b$ to give

$$\alpha_2\left(\frac{d\tilde{\rho}(z)}{dz}\right)^2=\left(\frac{1}{\rho_b}-\alpha_0\right)\tilde{\rho}(z)^2. \tag{112}$$

This predicts that $\tilde{\rho}(z)$ has exponential behaviour as the bulk liquid or vapour is approached from the interface region. The decay length λ associated with this behaviour is given by

$$\lambda=\left|\left(\frac{1}{\rho_b}-\alpha_0\right)\Big/\alpha_2\right|^{-1/2} \tag{113}$$

and it follows that near the triple point λ is much larger for the liquid side of the interface than for the vapour, i.e. there is a more rapid decrease in $\rho_0(z)$ for z approaching the bulk vapour region.

8.3. *Theory based on the direct correlation function*

Rather than focusing attention on the pairwise distribution function in the interface, it may be more convenient to work with the direct correlation function and seek realistic approximations for this quantity. For a planar surface in the limit of zero external field we have from (55)

$$\frac{d\ln\rho_0(z_1)}{dz_1}=\int d\mathbf{r}_2\, c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\frac{d\rho_0(z_2)}{dz_2}, \tag{114}$$

which is an exact equation for the equilibrium density profile and, as stressed in § 5, is equivalent to the first YBG equation, i.e. (106).

The surface tension can be evaluated with this approach by either calculating the change in grand potential due to the increase in surface area caused by a fluctuation in density [7] or calculating the pressure difference across a spherical surface with a large radius of curvature [8]. These yield identical results so here we present a derivation using the former method only. We consider the zero-field functional (see (9))

$$\Omega_{V=0}[\rho]\equiv\mathscr{F}[\rho]-\mu\int d\mathbf{r}\,\rho(\mathbf{r}) \tag{115}$$

and calculate the change in grand potential due to a change in density $\tilde{\rho}(\mathbf{r})$ at *fixed* chemical potential μ. Using (14) we find

$$\Delta\Omega=\Omega_{V=0}[\rho_0+\tilde{\rho}]-\Omega_{V=0}[\rho_0]=\tfrac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\left.\frac{\delta^2\mathscr{F}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_0}\tilde{\rho}(\mathbf{r})\tilde{\rho}(\mathbf{r}')+\ldots, \tag{116}$$

where $\rho_0(\mathbf{r})$ is the equilibrium density distribution. Thus to lowest order the change in grand potential is quadratic in the density fluctuations and depends on

$$C^{(2)}(\mathbf{r},\mathbf{r}')\equiv\beta\left.\frac{\delta^2\mathscr{F}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_0}=\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho_0(\mathbf{r})}-c^{(2)}(\mathbf{r},\mathbf{r}') \tag{117}$$

For the planar interface it is convenient to introduce the variable $\mathbf{R}$ which refers to the x–y plane, i.e. $\mathbf{r}\equiv(\mathbf{R},z)\equiv(x,y,z)$ so that two-point functions such as $c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ and $\rho(\mathbf{r}_1,\mathbf{r}_2)$ depend only on the variables z_1,z_2 and $R_{12}=((x_2-x_1)^2+(y_2-y_1)^2)^{1/2}$. It is also useful to introduce the two dimensional Fourier transforms

$$\tilde{\rho}(\mathbf{Q},z)=\int d\mathbf{R}\exp(i\mathbf{Q}\,.\,\mathbf{R})\tilde{\rho}(\mathbf{R},z) \tag{118a}$$

and

$$C^{(2)}(Q,z_1,z_2)=\int d\mathbf{R}_{12}\exp(i\mathbf{Q}\,.\,\mathbf{R}_{12})C^{(2)}(R_{12},z_1,z_2), \tag{118b}$$

so that (116) can be expressed as

$$\Delta\Omega=\frac{1}{2A\beta}\int\int dz_1dz_2\sum_{\mathbf{Q}}C^{(2)}(Q,z_1,z)\tilde{\rho}(\mathbf{Q},z_1)\tilde{\rho}(-\mathbf{Q},z_2)+\mathrm{O}(\tilde{\rho}^3), \tag{119}$$

where A is the area of the planar (unperturbed) surface. In order to proceed, we consider a fluctuation which changes the location of the Gibbs dividing surface from $z=0$ at equilibrium to $z=z_G(\mathbf{R})$. The latter is given by

$$\int_{-\infty}^{z_G}dz\,(\rho(\mathbf{R},z)-\rho_l)+\int_{z_G}^{\infty}(\rho(\mathbf{R},z)-\rho_v)=0 \tag{120}$$

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where ρ_l and ρ_v are, as usual, the co-existing bulk densities. After a straightforward manipulation it follows that

$$z_G(\mathbf{R}) = (\rho_l - \rho_v)^{-1} \int_{-\infty}^{\infty} dz\, \tilde{\rho}(\mathbf{R}, z) \tag{121}$$

This new dividing surface will have an area

$$A' = \int d\mathbf{R}\, (1 + |\nabla_{\mathbf{R}} z_G(\mathbf{R})|^2)^{1/2}, \tag{122}$$

where the integral is over the original surface. Thus for a given $\tilde{\rho}(\mathbf{R}, z)$ we can calculate both $\Delta\Omega$ and $\Delta A = A' - A$. Equation (119) is only useful, however, if the amplitude of $\tilde{\rho}$ is small and if the summation over wave vectors can be restricted. With this aim in mind, we consider a long wavelength small amplitude fluctuation in the position of the dividing surface. The surface then deviates only slightly from planarity and the perturbed density should correspond to a rigid shift of the equilibrium profile, i.e.

$$\rho(\mathbf{R}, z) = \rho_0(z - z_G(\mathbf{R}))$$

or

$$\tilde{\rho}(\mathbf{R}, z) = \rho(\mathbf{R}, z) - \rho_0(z) \approx -z_G(\mathbf{R}) \frac{d\rho_0(z)}{dz}, \tag{123}$$

which certainly satisfies (121). The corresponding change in area is then

$$\Delta A = \tfrac{1}{2} \int d\mathbf{R}\, |\nabla_R z_G(\mathbf{R})|^2. \tag{124}$$

Parallel to the surface $\tilde{\rho}$ has only long wavelength components so we need only consider the small Q expansion of $C^{(2)}$:

$$C^{(2)}(Q, z_1, z_2) = C_0(z_1, z_2) + Q^2 C_2(z_1, z_2) + \dots, \tag{125}$$

Substituting into (119) and Fourier transforming back to real space we find

$$\Delta\Omega = \frac{1}{2\beta} \int\int dz_1 dz_2\, \Big(C_0(z_1, z_2) \int d\mathbf{R}\, \tilde{\rho}(\mathbf{R}, z_1) \tilde{\rho}(\mathbf{R}, z_2)$$
$$+ C_2(z_1, z_2) \int d\mathbf{R}\, \nabla_R \tilde{\rho}(\mathbf{R}, z_1) . \nabla_R \tilde{\rho}(\mathbf{R}, z_2) + \dots \Big)$$

which simplifies on using (123) for the fluctuation to

$$\Delta\Omega = \frac{1}{2\beta} \int\int dz_1 dz_2 \frac{d\rho_0(z_1)}{dz_1} \frac{d\rho_0(z_2)}{dz_2} \Big(C_0(z_1, z_2) \int d\mathbf{R} |z_G(\mathbf{R})|^2$$
$$+ C_2(z_1, z_2) \int d\mathbf{R}\, |\nabla_R z_G(\mathbf{R})|^2 + \dots \Big) \tag{126}$$

The first term on the r. h. s. of (126) is zero. This follows from (114) for the equilibrium profile which can be re-written as

$$\int d\mathbf{r}_2 \frac{d\rho_0(z_2)}{dz_2} C^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \int dz_2 \frac{d\rho_0(z_2)}{dz_2} C_0(z_1, z_2) = 0 \tag{127}$$

This result implies that shifting the Gibbs dividing surface vertically by a *constant* requires zero energy provided the external field is zero—an eminently reasonable conclusion. The second term of (126) yields the surface tension since it is proportional to ΔA, i.e.

$$\gamma = \beta^{-1} \int\int dz_1 dz_2 \frac{d\rho_0(z_1)}{dz_1} \frac{d\rho_0(z_2)}{dz_2} C_2(z_1, z_2), \tag{128}$$

where, from (125) and (117),

$$\begin{aligned} C_2(z_1, z_2) &= -\tfrac{1}{4} \int d\mathbf{R}_{12} R_{12}^2 C^{(2)}(R_{12}, z_1, z_2) \\ &= \tfrac{1}{4} \int\int dx_{12} dy_{12} (x_{12}^2 + y_{12}^2) c^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \tag{129}$$

To complete the derivation we must check that the chemical potential μ' does not change from its equilibrium value μ as a result of the fluctuation described by (123). Clearly

$$\begin{aligned} \mu' &= \mu + \int d\mathbf{r}_2 \left. \frac{\delta u(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)} \right|_{\rho_0} \tilde{\rho}(\mathbf{r}_2) + \mathrm{O}(\tilde{\rho}^2) \\ &= \mu - \beta^{-1} \int d\mathbf{r}_2 \, z_{\mathrm{G}}(\mathbf{R}_2) \frac{d\rho_0(z_2)}{dz_2} C^{(2)}(R_{12}, z_1, z_2) + \mathrm{O}(\tilde{\rho}^2), \end{aligned} \tag{130}$$

where we have used (29) and (117). The integral vanishes and μ remains constant to the appropriate order.

We believe (128) to be an exact result for the surface tension of the planar interface. The validity of this assertion has been queried (see Leng *et al.* [45] for a recent discussion) since it has not yet proved possible to show that (128) reduces to the Kirkwood–Buff result (107) when only pairwise interactions are considered (see § 10, however). The difficulty lies in finding a suitable representation for the stress tensor in terms of the direct correlation function, i.e. performing an *integration* of equation (57) which expresses the equivalence of the two representations for the force acting on a particle. Leng *et al.* [45] have demonstrated the equivalence of the Kirkwood–Buff and direct correlation function approach for a 'penetrable sphere model' but only within a mean-field approximation. Lekner and Henderson [46] have shown the two approaches lead to identical results in the low density limit, i.e. with $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_0(z_1)\rho_0(z_2) \exp(-\beta\phi(r_{12}))$ and $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \exp(-\beta\phi(r_{12})) - 1$. It is also possible to show that for a van der Waals free energy density (see (98)) the surface tension as obtained from (128) is identical to that of (101), i.e. that calculated from the stress tensor or via (96). In this case $C^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ can be evaluated explicitly by functional differentiation and we find

$$\begin{aligned} C^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \beta(& f_0''(\rho_0) - f_2''(\rho_0)|\nabla\rho_0|^2 - 2f_2'(\rho_0)\nabla^2\rho_0 \\ & - 2f_2(\rho_0)\nabla\rho_0 . \nabla - 2f_2(\rho_0)\nabla^2)\delta(\mathbf{r}_1 - \mathbf{r}_2). \end{aligned} \tag{131}$$

Only the last term of this expression makes a finite contribution to $C_2(z_1, z_2)$ and this is an amount $2f^2(\rho_0(z_1))\delta(z_1 - z_2)$ as required. Furthermore, on substituting (131) into (127) we regain (99) for the equilibrium density profile. This exercise shows that the formula for γ in terms of the direct correlation function is *not* a linear response approximation as one might (erroneously) suspect from the derivation.

As in § 8.2 we can determine the functional form of $\rho_0(z)$ in the 'wings' of the distribution by integrating (114) using a local density approximation for the direct correlation function [11]. Setting $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = c^{(2)}(\rho_b; r_{12})$, where ρ_b again refers to bulk liquid or bulk vapour, we have

$$\ln\left(\frac{\rho_0(z)}{\rho_b}\right) = \int^z dz_1 \int d\mathbf{r}_{12} \frac{d\rho_0(z_1 + z_{12})}{dz_{12}} c^{(2)}(\rho_b; r_{12}). \tag{132}$$

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If $\rho_0(z_1+z_{12})$ is Taylor expanded about z_1 we find

$$\ln\left(\frac{\rho_0(z)}{\rho_\mathrm{b}}\right)=\alpha'(\rho_0(z)-\rho_\mathrm{b})+\alpha''\frac{d^2\rho_0(z)}{dz^2}+\text{higher derivatives,} \tag{133}$$

where

$$\alpha'=4\pi\int_0^\infty dr\, r^2 c^{(2)}(\rho_\mathrm{b};r)$$

and

$$\alpha''=\frac{2\pi}{3}\int_0^\infty dr\, r^4 c^{(2)}(\rho_\mathrm{b};r),$$

which has exactly the same form as (111) from the first YBG equation. Consequently, this theory also predicts an exponential decay of $\rho_0(z)$ as the bulk phases are approached. The decay length is given by

$$\lambda'=\left|\left(\frac{1}{\rho_\mathrm{b}}-\alpha'\right)\Big/\alpha''\right|^{-1/2}, \tag{134}$$

which differs from λ of (113). This is to be expected since the local density approximations for $\rho^{(2)}$ and $c^{(2)}$, which were employed in these analyses, are not strictly equivalent. (The Ornstein–Zernike relation of (31) is not satisfied to the appropriate order.) Exponential decay characterized by the length λ' *is* predicted by the van der Waals theory. Equation (133) follows from (99) provided $f_0(\rho)$ and $f_2(\rho)$ are identified as in § 6.2 and the direct correlation function of the uniform fluid is assumed density independent.

8.4. *Correlations in the interface*

At this stage the reader might be under the impression that the statistical mechanics of the liquid surface is reasonably well understood. The modern theories appear to have merely put the classical van der Waals theory on a sounder microscopic basis. They seem to confirm the physical picture of a rather uninteresting, monotonic transition from the liquid to the vapour and give, at least, a good qualitative account of the surface tension. Recent computer simulations of the liquid–vapour interface [47, 48, 49] yield similar density profiles and surface tensions and would appear to reinforce the above viewpoint.

In fact the modern formalism is much richer and makes important predictions concerning the form of intermolecular correlations in the interface. To be more specific, the formalism shows that while a local density approximation to $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ may be reasonably accurate when one considers vertical correlations (i.e. correlations along the z axis, perpendicular to the interface) it cannot give a proper description of horizontal correlations (i.e. correlation parallel to the interface) since the latter are of macroscopic range when z_1 and z_2 lie in the interface region.

The existence of long-ranged correlations was first pointed out in an elegant and important paper by Wertheim [10]. He noticed that (56) for the equilibrium density in an external field exhibits an interesting feature in the limit of the field going to zero. If we specialize, as usual, to planar geometry but retain the gravitational potential so that $V_{\text{ext}}(\mathbf{r}) \equiv mgz$, (56) reduces to

$$\begin{aligned}\frac{d\rho_0(z_1)}{dz_1} &= -\beta mg \int d\mathbf{r}_2\, (\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \rho_0(z_1)\delta(\mathbf{r}_1 - \mathbf{r}_2) - \rho_0(z_1)\rho_0(z_2)) \\ &= -\beta mg \int d\mathbf{r}_2\, \mathscr{G}(\mathbf{r}_1, \mathbf{r}_2),\end{aligned} \tag{135}$$

where we have re-introduced the density fluctuation function $\mathscr{G}(\mathbf{r}_1, \mathbf{r}_2) \equiv \mathscr{G}(R_{12}, z_1, z_2)$ defined in (27). Above the critical temperature in the single phase region we expect $d\rho_0(z)/dz$ to go to zero as g tends to zero. This implies the integral in (135) is finite. At an arbitrary temperature below the critical temperature we suppose that as g tends to zero $\rho_0(z)$ approaches a limit representing two co-existing phases so that $d\rho_0(z)/dz$ is finite. (We have assumed such behaviour throughout the present article.) We are led to conclude that the integral in (135) diverges as g^{-1} in this range of temperature. This, in turn, indicates the growth of long-ranged correlations.

Wertheim [10] has analysed the correlations in some detail using matrix techniques (see Appendix 4 for a resumé of his analysis) and shown that the long-ranged behaviour occurs only in the x and y directions and is restricted to the interface region. The divergence of the integral in (135) reflects a pointwise divergence of $\mathscr{G}_0(z_1, z_2) = \int d\mathbf{R}_{12}\, \mathscr{G}(R_{12}, z_1, z_2)$ and this function can be approximated by

$$\mathscr{G}_0(z_1, z_2) = \frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}((\rho_l - \rho_v)\beta mg)^{-1} + \text{less singular terms.} \tag{136}$$

This result indicates that the long-ranged correlations are rapidly damped as either z_1 or z_2 moves out of the interface. $\mathscr{G}_0(z_1, z_2)$ is the $Q = 0$ limit of the Fourier transform with respect to horizontal coordinates of the density fluctuation function. For an arbitrary wave vector Q we define

$$\mathscr{G}(Q, z_1, z_2) = \int d\mathbf{R}_{12} \exp(i\mathbf{Q}\,.\,\mathbf{R}_{12})\mathscr{G}(R_{12}, z_1, z_2) \tag{137}$$

and in Appendix 4 we show that for small finite Q

$$\mathscr{G}(Q, z_1, z_2) \approx \beta^{-1}\frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}((\rho_l - \rho_v)mg + \gamma Q^2)^{-1} + \text{less singular terms,} \tag{138}$$

where γ is the surface tension as given by (128). This approximation is valid to O (Q^2). Equation (138) represents Ornstein–Zernike-like behaviour of the horizontal density–density correlation function. The correlation length is

$$\xi = (\gamma/(\rho_l - \rho_v)mg)^{1/2} \tag{139}$$

which for liquid argon near its triple point in the earth's gravity is ~ 1 mm. Since $\mathscr{G}(\mathbf{r}, \mathbf{r}')$ is also a measure of the density response of a system to the change in an applied external field (see Appendix 3) it is clear that ξ is a horizontal decay length for the interface. In other words, if the interface is disturbed by an external force there will be a displacement of the interface which decays horizontally with decay length ξ. The derivation leading to (138) is rather general but still approximate. The form of the result suggests that the horizontal correlations correspond to surface modes (capillary waves) thermally excited against surface tension and gravity. This

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interpretation can be made explicit using a slight extension of an argument due to Kalos *et al.* [11].

We consider a fluid in a gravitational field with, initially, a planar Gibbs dividing surface of area A located at $z=0$. The corresponding density profile is $\rho_0(z)$ and the surface tension is γ. Suppose an external potential $\Delta V_{\text{ext}}(\mathbf{r})$ is applied and this produces a distortion of the Gibbs dividing surface of amplitude $z_G(\mathbf{R})$. Provided the amplitude of the distortion is small and the wavelength is long (see § 8.3) the perturbed density profile will be $\rho(\mathbf{R},z)=\rho_0(z-z_G(\mathbf{R}))$. The change in energy associated with such a perturbation is

$$\Delta E=\gamma\int d\mathbf{R}\,(1+|\nabla_{\mathbf{R}}z_G(\mathbf{R})|^2)^{1/2}-\gamma A+\int d\mathbf{r}\,\rho_0(z-z_G(\mathbf{R}))mgz$$

$$-\int d\mathbf{r}\,\rho_0(z)mgz+\int d\mathbf{r}\,\rho_0(z-z_G(\mathbf{R}))\Delta V_{\text{ext}}(\mathbf{r}),$$

where we have assumed the surface contribution can be obtained macroscopically as $\gamma\Delta A$. Expanding in z_G we find that the gravitational contribution which is linear in z_G vanishes because of our choice of the initial dividing surface, and

$$\Delta E=\frac{\gamma}{2}\int d\mathbf{R}\,|\nabla_{\mathbf{R}}z_G(\mathbf{R})|^2+\tfrac{1}{2}(\rho_l-\rho_v)mg\int d\mathbf{R}\,|z_G(\mathbf{R})|^2+\int d\mathbf{r}\rho_0(z)\Delta V_{\text{ext}}(\mathbf{r})$$

$$-\int d\mathbf{r}\frac{d\rho_0(z)}{dz}z_G(\mathbf{R})\Delta V_{\text{ext}}(\mathbf{r})+\text{higher order terms} \tag{140}$$

We Fourier expand:

$$z_G(\mathbf{R})=A^{-1}\sum_{\mathbf{Q}}a(\mathbf{Q})\exp(-i\mathbf{Q}\,.\,\mathbf{R}) \tag{141}$$

so that

$$\Delta E=\frac{1}{2A}\sum_{\mathbf{Q}}a(\mathbf{Q})a(-\mathbf{Q})((\rho_l-\rho_v)mg+\gamma Q^2)+\int d\mathbf{r}\,\rho_0(z)\Delta V_{\text{ext}}(\mathbf{r})$$

$$-A^{-1}\sum_{\mathbf{Q}}a(\mathbf{Q})\int d\mathbf{r}\frac{d\rho_0(z)}{dz}\exp(-i\mathbf{Q}\,.\,\mathbf{R})\Delta V_{\text{ext}}(\mathbf{r})+\dots$$

Completing the square we have

$$\Delta E=\frac{1}{2A}\sum_{\mathbf{Q}}\Bigg[a'(\mathbf{Q})a'(-\mathbf{Q})((\rho_l-\rho_v)mg+\gamma Q^2)-\frac{\left|\int d\mathbf{r}\frac{d\rho_0(z)}{dz}\exp(-i\mathbf{Q}\,.\,\mathbf{R})\Delta V_{\text{ext}}(\mathbf{r})\right|^2}{(\rho_l-\rho_v)mg+\gamma Q^2}\Bigg]$$

$$+\int d\mathbf{r}\,\rho_0(z)\Delta V_{\text{ext}}(\mathbf{r})+\dots, \tag{142}$$

where

$$a'(\mathbf{Q})=a(\mathbf{Q})-\int d\mathbf{r}\frac{d\rho_0(z)}{dz}\exp(-i\mathbf{Q}\,.\,\mathbf{R})\Delta V_{\text{ext}}(\mathbf{r})((\rho_l-\rho_v)mg+\gamma Q^2)^{-1}.$$

ΔE refers to a particular amplitude $z_G(\mathbf{R})$. In order to calculate the free energy due to thermal fluctuations we must perform the appropriate statistical average over all

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values of $z_G(\mathbf{r})$. This type of averaging is described in Appendix 5. If we ignore all the higher order contributions in (142) we find

$$\langle a'(\mathbf{Q})a'(-\mathbf{Q})\rangle = A[\beta((\rho_{\mathrm{l}}-\rho_{\mathrm{v}})mg+\gamma Q^2)]^{-1} \tag{143}$$

and the free energy

$$\Delta F = \sum_{\mathbf{Q}}\left[\frac{1}{2\beta}\ln\left(\frac{\beta((\rho_{\mathrm{l}}-\rho_{\mathrm{v}})mg+\gamma Q^2)}{2A\pi\mathscr{N}}\right)\right.$$
$$\left. -\frac{1}{2A}\frac{\left|\displaystyle\int d\mathbf{r}\,\frac{d\rho_0(z)}{dz}\exp(-i\mathbf{Q}\,.\,\mathbf{R})\Delta V_{\mathrm{ext}}(\mathbf{r})\right|^2}{(\rho_{\mathrm{l}}-\rho_{\mathrm{v}})mg+\gamma Q^2}\right]$$
$$+\int d\mathbf{r}\,\rho_0(z)\Delta V_{\mathrm{ext}}(\mathbf{r}). \tag{144}$$

$\mathscr{N}$ is a normalization factor. If the chemical potential remains unchanged by the perturbation (see § 8.3) the change in grand potential $\Delta\Omega = \Delta F$ and can be expressed in terms of $\Delta u(\mathbf{r}) \equiv \Delta\mu - \Delta V_{\mathrm{ext}} = -\Delta V_{\mathrm{ext}}$:

$$\Delta\Omega = \sum_{\mathbf{Q}}\left[\frac{1}{2\beta}\ln\left(\frac{\beta((\rho_{\mathrm{l}}-\rho_{\mathrm{v}})mg+\gamma Q^2)}{2A\pi\mathscr{N}}\right)\right] - \int d\mathbf{r}\,\rho_0(z)\Delta u(\mathbf{r})$$
$$-\frac{1}{2A}\sum_{\mathbf{Q}}((\rho_{\mathrm{l}}-\rho_{\mathrm{v}})mg+\gamma Q^2)^{-1}\iint d\mathbf{r}d\mathbf{r}'\,\frac{d\rho_0(z)}{dz}\frac{d\rho_0(z')}{dz'}$$
$$\times\exp(-i\mathbf{Q}\,.\,(\mathbf{R}-\mathbf{R}'))\Delta u(\mathbf{r})\Delta u(\mathbf{r}'). \tag{145}$$

Since

$$\mathscr{G}(\mathbf{r},\mathbf{r}') = -\frac{1}{\beta}\frac{\delta^2\Omega}{\delta u(\mathbf{r})\delta u(\mathbf{r}')}$$

(see (25) and (26)), the coefficient of $(\Delta u)^2$ yields the density fluctuation function for the unperturbed planar surface

$$\mathscr{G}(\mathbf{r},\mathbf{r}') = \frac{1}{\beta A}\frac{d\rho_0(z)}{dz}\frac{d\rho_0(z')}{dz'}\sum_{\mathbf{Q}}((\rho_{\mathrm{l}}-\rho_{\mathrm{v}})mg+\gamma Q^2)^{-1}\exp(-i\mathbf{Q}\,.\,(\mathbf{R}-\mathbf{R}')). \tag{146}$$

On Fourier transforming with respect to horizontal variables we regain precisely (138). The present derivation is only valid for long wavelength fluctuations so we can only expect the result to be accurate for wave vectors $Q \ll 2\pi/\sigma$ where σ is a typical molecular diameter.

Kalos *et al.* [11] have performed a detailed molecular dynamics simulation of the liquid–vapour interface of a Lennard-Jones fluid in zero external field ($g=0$). They calculated the correlation function $\mathscr{G}(Q, z_1, z_1)$ at various values of z_1. For z_1 in the interface region they found $\mathscr{G}(Q, z_1, z_1) \propto Q^{-2}$ for $Q \lesssim 1{\cdot}4/\sigma$. (The finite size of their periodic box restricts the calculation to $Q > 0{\cdot}5/\sigma$.) For z_1 in the bulk liquid or bulk vapour, where $d\rho_0(z)/dz \approx 0$, they find no such behaviour in $\mathscr{G}(Q, z_1, z_1)$. These results provide direct evidence for the validity of (138).

It is clear that local density approximations for the pairwise distribution function, $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ as introduced in (103 *b*) or in § 8.2, cannot generate singular low Q behaviour since there is no reason to expect $g(\bar{\rho}; r)$, as obtained by extrapolation from physical (one-phase) densities, to exhibit special features. This failing of the local

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density approximation has important consequences. It casts doubt on the validity of those theories of the interface which are based on this assumption, i.e. thermodynamic perturbation theories as described in § 8.1 and theories which attempt closure of the first YBG equation as outlined in § 8.2. However, these theories are primarily concerned with the density profile and the surface tension which involve averages over both horizontal and vertical correlations of all wavelengths, so the shortcomings at low Q may not be too important. Indeed, there are some preliminary indications [11] that the local density approximation may be reasonably accurate for vertical correlations. The more fundamental question concerns the implications for the detailed microscopic structure of the interface.

The occurrence of long-ranged horizontal correlations is a consequence of spontaneous symmetry breaking of a two-phase system [10]. Since the local density approximation to $\rho^{(2)}$ fails to account for such behaviour, we are forced to re-examine the two-phase aspect of the interface problem. Whilst it may be reasonable to suppose that the analytic continuation of the free energy density $f_0(\rho)$ into the two-phase region can be realized in the interface, as in the van der Waals theory, it is not obvious that *any* extrapolation procedure will be valid for the pairwise or, indeed, the higher order distribution functions. A promising start in the search for a realistic model of correlations in the interface has been made by Kalos *et al.* [11]. These authors base their model on experience with a *bulk* two-phase system. In discussing the statistical mechanics of the latter [50] it is usually implied that liquid and vapour are predominantly present only in very large clusters so that at any given time all points $\mathbf{r}_1 \ldots \mathbf{r}_n$ (relevant to a n-body distribution function) can be regarded as internal to the same single phase cluster. Kalos *et al.* then assume the two-phase interface system "can be viewed as a temporal sequence, or phase space ensemble of configurations sharply divided into gas and liquid regions. The geometic form of the dividing surface is, however, open.".

At the crudest level they take the dividing surface to be planar and assume that for a given plane located at height Z there is pure vapour for $z>Z$ and pure liquid uncorrelated with vapour for $z<Z$. The conditional distribution functions for this particular dividing surface are then

$$\begin{aligned} \rho(Z;z) = \rho_1, &\quad z<Z \\ \rho_v, &\quad z>Z \end{aligned} \tag{147}$$

and

$$\begin{aligned} \rho^{(2)}(Z;\mathbf{r}_1,\mathbf{r}_2) = \rho_1^2 g_1(|\mathbf{r}_1-\mathbf{r}_2|), &\quad z_1<Z; z_2<Z \\ \rho_1\rho_v' &\quad z_1>Z; z_2<Z \\ \text{or} &\quad z_1<Z; z_2>Z \\ \rho_v^2 g_v(|\mathbf{r}_1-\mathbf{r}_2|) &\quad z_1>Z; z_2>Z. \end{aligned} \tag{148}$$

If Z is distributed with a probability density $P(Z)$ the equilibrium distribution functions are given by

$$\begin{aligned} \rho_0(z) &= \int dZ\, \rho(Z;z)P(Z) \\ \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) &= \int dZ\, \rho^{(2)}(Z;\mathbf{r}_1,\mathbf{r}_2)P(Z) \end{aligned} \tag{149}$$

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These equations can be integrated and $P(Z)$ eliminated to give a relationship between $\rho^{(2)}$ and ρ_0 [11]. Here, for simplicity, we set the density of the vapour to zero and it is easy to prove that

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_l \rho_0(\mathrm{Max}\,(z_1, z_2)) g_l(|\mathbf{r}_1 - \mathbf{r}_2|) \tag{150}$$

This approximation should be compared with the local density approximation which, we recall, sets $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_0(z_1)\rho_0(z_2) g(\bar{\rho}; |\mathbf{r}_1 - \mathbf{r}_2|)$.

For vertical correlations, $\mathbf{R}_{12} = 0$, both approximations yield a good qualitative account of the computer generated $\rho^{(2)}$ [11]. For horizontal correlations with $z_1 = z_2$ the approximations are significantly different. Equation (150) gives

$$\mathscr{G}(R_{12}; z_1, z_1) = \left(\frac{\rho_0(z_1)}{\rho_l}\right)\rho_l^2\,(g_l(R_{12}) - 1) + \rho_0(z_1)(\rho_l - \rho_0(z_1)) + \rho_0(z_1)\delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{151}$$

while the local density approximation yields

$$\mathscr{G}(R_{12}, z_1, z_1) = \rho_0^2(z_1)(g(\rho_0(z_1); R_{12}) - 1) + \rho_0(z_1)\delta(\mathbf{r}_1 - \mathbf{r}_2). \tag{152}$$

On Fourier transforming w.r.t. R_{12} we expect (151) and (152) to give qualitatively similar behaviour at finite wave vectors Q. At $Q = 0$ however, the local density approximation will lead to regular behaviour as mentioned above while (151) gives rise to a δ-function singularity. This argument of Kalos *et al.* shows how it is possible to construct a simple microscopic model of the interface which generates a $Q = 0$ divergence in the horizontal correlations. The approximation of (150) cannot be accurate since as $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$, $\rho^{(2)}$ must satisfy the asymptotic relation

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \to \rho_0(z_1)\rho_0(z_2).$$

The latter is, of course, consistent with the local density approximation. Furthermore, the true $\mathscr{G}(Q, z_1, z_1)$ does not have a δ-function singularity but exhibits a weaker small Q divergence (see (138)). The restriction to strictly planar interfaces is responsible for the δ-function singularity. If this is lifted and the location of the dividing surface is permitted to show long wavelength variation with $\mathbf{R}$ as considered in earlier sections, presumably the divergence will be weakened appropriately. Recently, Weeks [12] has developed a model along these lines. His model can be solved explicitly in certain limiting cases and he finds that for $z_1 = z_2 = 0$ the zeroth Fourier component of $\mathscr{G}(Q, z_1, z_2)$ agrees, to within a trivial numerical factor, with the general result of (136).

Further support for a very sharp liquid–vapour interface but which fluctuates in position and time is provided by the computer simulation of Kalos *et al.* [11]. These calculations also show a tendency for atoms to cluster in the surface-forming regions of high and low density.

Before concluding this section it is instructive to examine the general implications of (138) for the density fluctuation function $\mathscr{G}(Q, z_1, z_2)$ when the gravitational field is zero. Provided the temperature is below the critical point T_c so that $d\rho_0(z)/dz$ is finite, this function diverges as Q^{-2}. Above T_c $d\rho_0(z)/dz$ is zero and there is no divergence. Such behaviour in a static correlation function is usually associated with spontaneous symmetry breaking. For example, in a ferromagnet below the Curie temperature all the spins lie parallel to a preferred direction, say the z axis, and the average magnetization $\langle M_z \rangle$ is finite. Above the Curie temperature in the

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paramagnetic state the spins are randomly oriented, $\langle M_z \rangle = 0$ and there is no long-range order. Thus there is a breakdown of rotational symmetry associated with the preferred direction of the ferromagnetic state. The corresponding long-range order is characterized by the non-vanishing order parameter $\langle M_z \rangle$ and by a static transverse susceptibility (i.e. the correlation function corresponding to variables M_x or M_y) which diverges as q^{-2}. In the interface problem it is natural to treat $d\rho_0(z)/dz$ as the order parameter. Below T_c we have a non-uniform, two-phase system and the order parameter is finite due to the breakdown of *translational* symmetry. Thus, by analogy we would *expect* to find a long-wavelength divergence in the static correlation function of some associated dynamical variable.

Very recently Jhon *et al.* [75] have shown that the appropriate variable is $z_G(\mathbf{R}, t)$, the time-dependent normal displacement of the Gibbs dividing surface, and have demonstrated, using arguments based on sum rules and dynamical correlation functions, that the static correlation function $\langle z_G(\mathbf{R}_1, 0) z_G(\mathbf{R}_2, 0) \rangle$ exhibits long-range order below T_c. To be more specific, they have shown that the Fourier transform of this correlation function w.r.t. Q behaves as $(\beta \gamma Q^2)^{-1}$ as Q tends to zero. Their result is equivalent to (138). In order to show this, we recall that for long wavelength, small amplitude distortions of the Gibbs surface $\rho(\mathbf{R}, z) - \rho_0(z) = -z_G(\mathbf{R})\, d\rho_0(z)/dz$ so that the (time-dependent) density–density correlation function in this limit is simply

$$\frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}\langle z_G(\mathbf{R}_1, t_1) z_G(\mathbf{R}_2, t_2) \rangle.$$

Thus, setting $t_1 = t_2 = 0$ and Fourier transforming, we find

$$\mathscr{G}(Q, z_1, z_2) = \frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}(\beta\gamma Q^2)^{-1}$$

for small Q, which is identical to (138) with $g = 0$.

Jhon *et al.* have also developed a detailed memory function approach for interfacial dynamics. They find that associated with the symmetry breaking variable $z_G(\mathbf{R}, t)$ are propagating modes whose long-wavelength dispersion relation is identical to the classical hydrodynamic result for capillary waves, i.e.

$$\omega(Q) = \left(\frac{\gamma}{m(\rho_l - \rho_v)}\right)^{1/2} Q^{3/2}.$$

It then follows that capillary waves arise from the spatial symmetry breaking which occurs at an interface, i.e. from having a non-uniform density distribution. Propagating modes of this kind are well known in *uniform* systems where they are called zero-mass bosons or Goldstone bosons. Spontaneous symmetry breaking in uniform condensed systems is accompanied by the appearance of Bose-type excitations whose energy tends to zero as the wave vector tends to zero. For example, the transition from the paramagnetic state to the ferromagnetic state leads to spin waves. Since these are associated with local deviations of the atomic spins from perfect alignment, it requires no energy to excite them in the long-wavelength limit. The propagating modes in the interface problem are associated with local distortions of the Gibbs dividing surface. Shifting this surface vertically by a constant then corresponds to taking the long-wavelength limit. This process must require zero energy in the absence of an external field (see also 127)). In the light of these considerations it would seem reasonable to describe capillary waves as Goldstone bosons for non-uniform fluids [75].

Clearly the study of correlations in the interface is an important area of current and future research. One obvious question which has been discussed at some length in several papers [28, 27, 8, 11, 12, 21] concerns the role of the capillary wave-like fluctuations of the dividing surface in determining the width of the density profile. We discuss this in the next section.

8.5. *The width of the density profile*

It is tempting to use the capillary wave model to investigate the form of the equilibrium density profile. We suppose there exists some 'bare' density profile $\rho_{\text{bare}}(z)$ referred to a planar Gibbs dividing surface located at $z=0$. This profile may not necessarily have infinite gradient as in (147) but will, in general, be very sharp. Let the corresponding surface tension be γ_{bare} and the area of the interface be $A=L^2$ with $L\to\infty$. We consider fluctuations in the location of the dividing surface of amplitude $z_G(\mathbf{R})$. If their wavelength is sufficiently long and their amplitude sufficiently small we can use the analysis leading to (144) (see Appendix 5) and calculate the mean square fluctuation in the average location of the dividing surface. The latter is defined as

$$\sigma_G^2=\langle\overline{z_G^2}-\langle\overline{z_G}\rangle^2\rangle, \tag{153}$$

where

$$\overline{z_G^2}=A^{-1}\int d\mathbf{R}\, z_G^2(\mathbf{R})=A^{-2}\sum_{\mathbf{Q}} a(\mathbf{Q})a(-\mathbf{Q})$$

and

$$\overline{z_G}=A^{-1}\int d\mathbf{R}\, z_G(\mathbf{R})=A^{-1}a(0).$$

Since z_G is linear in a, its expectation value is zero and from (143) it follows that

$$\sigma_G^2=\frac{1}{\beta A}\sum_{\mathbf{Q}}((\rho_l-\rho_v)mg+\gamma_{\text{bare}}Q^2)^{-1}. \tag{154}$$

Transforming the summation to an integral we have

$$\begin{aligned}\sigma_G^2&=\frac{1}{2\pi\beta}\int_{Q\min}^{Q\max} dQ\, Q((\rho_l-\rho_v)mg+\gamma_{\text{bare}}Q^2)^{-1}\\ &=\frac{1}{4\pi\beta\gamma_{\text{bare}}}\ln\left(\frac{\xi_{\text{bare}}^{-2}+Q_{\max}^2}{\xi_{\text{bare}}^{-2}+Q_{\min}^2}\right),\end{aligned} \tag{155}$$

where $\xi_{\text{bare}}=(\gamma_{\text{bare}}/mg(\rho_l-\rho_v))^{1/2}$ is the 'bare' correlation length. It remains to specify the upper and lower limits of integration, i.e. $Q_{\max}$ and $Q_{\min}$. We can take $Q_{\min}=2\pi/L$ since this is the smallest wave vector which can sensibly be defined. The choice of $Q_{\max}$ is, however, somewhat arbitrary and the present continuum treatment cannot make a rigorous identification of this quantity. In their original capillary wave treatment of the liquid–vapour interface Buff *et al* [28] assumed a $Q_{\max}$ inversely proportional to the width of the equilibrium density profile which depends of course, on σ_G. This procedure leads to a transcendental equation for σ_G. For simplicity we take $Q_{\max}=2\pi/\sigma$, where σ is a molecular diameter.

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It is clear from (154) that the major contribution to σ_G^2 comes from fluctuations with small values of Q. This implies that the bare density profile is broadened by long wavelength capillary waves. For the idealized bare profile $\rho_{\text{bare}}(z)=\rho_l\Theta(-z)$, where $\Theta(z)$ is the Heaviside function, an explicit formula for the equilibrium density can be obtained [11, 12]. In this case

$$\rho_0(z)=\langle\rho_{\text{bare}}(z-z_G(\mathbf{R}))\rangle=\rho_l\;\langle\Theta(z_G(\mathbf{R})-z)\rangle \tag{156}$$

which gives, on differentiating,

$$\begin{aligned}\frac{d\rho_0(z)}{dz}&=-\rho_l\langle\delta(z_G(\mathbf{R})-z)\rangle\\&=-\frac{\rho_l}{2\pi}\left\langle\int_{-\infty}^{\infty}ds\exp\left(is(z_G(\mathbf{R})-z)\right)\right\rangle\end{aligned} \tag{157}$$

The relevant expectation value is

$$\begin{aligned}\langle\exp\left(isz_G(\mathbf{R})\right)\rangle&=\left\langle\exp\left(\frac{is}{A}\sum_{\mathbf{Q}}a(\mathbf{Q})\exp\left(-i\mathbf{Q}\,.\,\mathbf{R}\right)\right)\right\rangle\\&=\exp\left[\frac{-s^2}{2\beta A}\sum_{\mathbf{Q}}\left((\rho_l-\rho_v)mg+\gamma_{\text{bare}}Q^2\right)^{-1}\right],\end{aligned}$$

where we have used the methods of Appendix 5. From (157) and (154) it then follows that

$$\frac{d\rho_0(z)}{dz}=-\frac{\rho_l}{(2\pi)^{1/2}\sigma_G}\exp\left(\frac{-z^2}{2\sigma_G^2}\right) \tag{158}$$

and hence

$$\rho_0(z)=\frac{\rho_l}{2}\operatorname{erfc}\left(z/\surd 2\sigma_G\right). \tag{159}$$

The '10–90' width of this density profile is $2{\cdot}56\sigma_G$ and thus depends explicitly on both the area of the interface and the strength of the gravitational field.

In the absence of gravity $\xi_{\text{bare}}^{-1}=0$ and $\sigma_G^2=(2\pi\beta\gamma_{\text{bare}})^{-1}\ln(L/\sigma)$. As the area of the interface becomes infinite σ_G^2 diverges logarithmically. Long-wavelength divergences of this kind are common in the study of strictly two-dimensional systems† (e.g. [51]). We note that this divergence is extremely slow; choosing parameters appropriate to liquid argon near its triple point, i.e. $\gamma_{\text{bare}}=14$ dyn cm^{-1}, $T=85$ K and $\sigma=3{\cdot}4$ Å, we find for $L=1$ mm, $\sigma_G=1{\cdot}32\sigma$. The corresponding result for $L=1$ m is $1{\cdot}59\sigma$.

For statistical mechanical application it is natural to take the limit $L\to\infty$ first and then examine the system as $g\to 0$. In this case $Q_{\min}=0$ and $\sigma_G^2=(4\pi\beta\gamma_{\text{bare}})^{-1}\ln(1+\xi_{\text{bare}}^2\,Q_{\max}^2)$ and for argon in the earth's gravitional field $\sigma_G\approx 1{\cdot}39\sigma$. As $g\to 0$, however, σ_G diverges as $(-\ln g)^{1/2}$.

Although these divergences are extremely weak they have important repercussions. The last result, when inserted into (158), implies $d\rho_0(z)/dz\to 0$ as $(-\ln g)^{-1/2}$ in

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† In two dimensions long-wavelength fluctuations (Goldstone modes) have sufficient density to destroy the ordered state; in the present case the capillary waves force $d\rho_0(z)/dz$ to zero.

the limit $g \to 0$ and indicates that, in general, the equilibrium density should not have a finite width in zero gravitational field [28]. Since this result is contrary to what we have supposed throughout this paper we examine both it status and its implications.

Earlier we demonstrated that the van der Waals and related approximate theories yield equilibrium profiles of finite width in the limit of infinite interfacial area and zero gravity. We also indicated in § 8.2 and § 8.3 how the exact integro-differential equations imply exponential-like profiles of finite decay length in the same limit. The corresponding interfacial widths are clearly intrinsic to the phase equilibrium itself. Equations (155) and (159), on the other hand, predict a density profile which depends on A or g or both and hence its width cannot be an intrinsic property of the fluid. To quote Wertheim [10]†: "Such behaviour is completely at odds with what is usually held.". We are of the opinion that the true equilibrium profile cannot be *rigorously* constructed by simply 'unfreezing' capillary waves in the hypothetical bare interface. The difficulty lies ultimately in the fact that the liquid–vapour interface is a three-dimensional system. In applying capillary wave theory we are forced to (a) select a particular bare profile with a corresponding surface tension and (b) make some statement about the number of 'surface' atoms, i.e. we must specify $Q_{\max}$ and $Q_{\min}$. Although there is no unique procedure for doing either of these, this may not be the major problem. We suspect the capillary wave model, as described in Appendix 5, is inapplicable to the real surface problem when the amplitude $z_G(\mathbf{R})$ becomes finite or develops short-wavelength Fourier components or has a large gradient. Under these circumstances (A 29) is not a valid free-energy functional for a proper three-dimensional interface and something more realistic is required. We note that merely including a term $|z_G(\mathbf{R})|^4$ in the functional does not appear to remove the logarithmic divergence in σ_G[76]. (We should stress that this objection to the use of capillary wave ideas does not apply to the analysis leading to (146) for the density fluctuation function of the equilibrium system. The latter is a linear response function and is, therefore, solely concerned with infinitesimal changes in the amplitude z_G. Furthermore that analysis was specifically aimed at the long-wavelength limit.)

It is now appropriate to comment on some recent papers on this topic. Lovett *et al.* [8] imply that the width of the equilibrium profile can be calculated using a model based on capillary wave theory (with $L = \infty$ and finite g) and that the result can be legitimately compared with the width obtained from a van der Waals type of approach. It is clear from the argument of the previous paragraph that such a procedure cannot be strictly correct. The widths which Lovett *et al.* obtained from the capillary wave route appear to be quite reasonable but this is probably fortuitous; we recall that $\sigma_G \sim 1{\cdot}39\sigma$ for parameters appropriate to liquid argon which would yield a '10–90' width of $\lesssim 4\sigma$. Davis [21], on the other hand, has argued that the density profile should be determined by unfreezing capillary waves on a bare planar interface whose underlying form is that given by a van der Waals type of theory. He then compares the resultant total width, which is now dependent on L and g and hence not an intrinsic property, with the results of computer simulations. This would seem to be inconsistent. It would make more sense to compare the van der Waals widths directly with those obtained from computer simulation—provided

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† Wertheim also shows that $d\rho_0(z)/dz$ having a finite limit as $g \to 0$ is consistent with the invariance properties of a system in a gravitational field provided $\rho_0(z)$ can be associated with the usual Gibbs dividing surface.

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the latter are suitably modified to take into account the finite size of the interface (see below).

Another model of the interface has been proposed by Weeks [12]. He divides the fluid into an array of vertical columns whose horizontal width is of the order of a bulk correlation length and then considers fluctuations in the number of particles in each column. These fluctuations can be related to changes in the location of the local Gibbs dividing surface. The free energy associated with such distortions is then calculated using macroscopic arguments which are essentially equivalent to those of capillary wave theory. Weeks suggests that the local interface width, i.e. the width relevant to a single column, should be identified with the width as calculated from a van der Waals type of approach. Not surprisingly he finds that, as a result of the capillary wave-like fluctuations, the total interface width diverges in the same fashion as we described above. In particular he finds that, for infinite interfacial area, the derivative of the equilibrium density $d\rho_0(z)/dz$ should go to zero as $(-\ln g)^{1/2}$ in the limit $g\rightarrow 0$ and shows that within his model, this divergence is due to "the same fluctuations which lead to the long-ranged horizontal correlations"†. Whilst we accept that Weeks' model is probably the best microscopic model which is presently available for describing density correlations in the interface, we are not convinced that it gives a good description of the equilibrium density profile. As we argued earlier, it is important to distinguish between theories for the density response of the equilibrium system (this being characterized by the long-ranged horizontal correlations) and theories for the equilibrium density itself. For the sake of clarity we summarize our arguments.

In zero gravity the density–density correlation function $\mathcal{G}(Q,z_1,z_2)$ of the equilibrium fluid exhibits a Q^{-2} divergence as $Q\rightarrow 0$ for z_1 and z_2 in the interface region. This result (see Appendix 4) was derived using rather general arguments by Wertheim [10], Kalos *et al.* [11] and indeed Weeks [12]. In § 8.4, we showed that, since $\mathcal{G}$ is directly proportional to the density response of the equilibrium system to an infinitesimal change in the external potential, the long-wavelength behaviour of $\mathcal{G}(Q, z_1, z_2)$ can be calculated by generating capillary wave-like fluctuations of the Gibbs dividing surface. The Q^{-2} divergence, which is the indicator of long-ranged horizontal correlations, then has a natural and rigorous interpretation in terms of these fluctuations. The equilibrium density profile itself has nothing to do with these fluctuations; it forms the underlying structure and determines the surface tension of the interface whose long-wavelength density response has capillary wave-like behaviour. In a diffraction experiment one measures a 'structure factor' corresponding to (138) and γ is the usual 'equilibrium' surface tension. This point of view would appear to be the same as that of Widom [27].

On the other hand, we have shown that attempts to build up the equilibrium profile by unfreezing capillary waves on some 'bare' non-equilibrium interface are unsatisfactory. They produce profiles which depend on the area of the interface and on g and thus cannot be intrinsic to the phase equilibrium. (The surface tension has a bounded anomaly and can be considered as intrinsic—see Appendix 5.)

We do not wish to imply that capillary wave theory is not useful. Indeed, the basic idea that the density profile is broadened by capillary wave-like fluctuations in

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† We should recall that the argument of § 8.4 which predicted long-ranged horizontal correlations assumed that $d\rho_0(z)/dz$ was finite for $g=0$. The same argument goes through, however, provided $d\rho_0(z)/dz\rightarrow 0$ more slowly than g.

some 'bare' interface must be qualitatively correct. However, a proper theory must be able to treat both finite amplitude and short-wavelength fluctuations. We are not aware of such a theory but work along these lines is in progress [21]. Clearly a theory of this kind would be useful for extrapolating the results of computer simulations on systems of finite interfacial area to infinite area. The shortest horizontal wave vector which can be allowed in a computer simulation is $2\pi/L = Q_{\min}$ where L is typically 5–20σ. Consequently, fluctuations with wave vectors $< Q_{\min}$ are not permitted and we can expect the density profile calculated for a small finite system to be rather sharper than for the case of infinite interfacial area. The results of Chapela *et al.* [49] for a Lennard–Jones model of argon illustrate this quite nicely. As the number of atoms in their molecular dynamics simulation was increased from 255 to 1020, the width of the interface increased by about 19%, while their 4080-atom simulation gave a width 4% greater than the 1020-atom simulation. The values of L corresponding to these three simulations are 5σ, 10σ and 20σ respectively. The increase in the width of the density profile clearly saturates for L in the region of 20σ.

We conclude this section by presenting in table 2 results for the '10–90' width of the density profile and the surface tension as obtained by recent molecular dynamics simulations of the interface of a Lennard-Jones fluid. Several Monte-Carlo simulations have been performed (see Abraham *et al.* [52] for references to earlier work) some of which produced non-monotonic density profiles, i.e. oscillations in the liquid side of the interface. The present consensus [49] is that these oscillations are an artefact of over constraining the system or not averaging over enough configurations.

Table 2. Interfacial '10–90' widths w and surface tensions γ obtained from molecular dynamics simulations of a Lennard-Jones 12–6 fluid at various temperatures T†. The experimental results γ_{exp} are for argon [40].

Reference	T(K)	w/σ	γ(dyn cm^{-1})	γ_{exp}(dyn cm^{-1})
a	84	~2·0	~12	12·9
b	84	2·0	15·7	12·9
b	94	2·2	11·8	10·4
b	100	2·7	10·6	9.4

(a) Rao and Levesque [48], (b) Chapela *et al.* [49] using 1020 atoms.

† In order to compare with 'real' argon the parameters of the Lennard–Jones potential are taken as $\sigma = 3{\cdot}405$ Å and $\varepsilon/K_B = 119{\cdot}8$ K.

It can be seen that the two independent simulations at 84 K agree on the width of the profile $w \approx 2\sigma$. This result is essentially the median of the widths obtained from the van der Waals and related theories (see table 1). The surface tensions calculated in these two simulations differ. This may be due to different treatments of truncation of the Lennard–Jones potential [19]. Experience with thermodynamic perturbation theories for the surface tension [38, 47] indicates that replacing the Lennard–Jones potential by a more accurate argon potential function (including triplet interactions) reduces γ by ~3 dyn cm^{-1} in the temperature range of table 2. This suggests that the results of Chapela *et al.* [49] give a rather good description of the surface tension of argon near its triple point and therefore, by inference, so do the approximate theories described in § 8.1.

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§ 9. SPINODAL DECOMPOSITION

The liquid–vapour interface is not the only problem of interest in the statistical physics of non-uniform fluids. One closely related topic, where the general formalism can make a useful contribution, is the theory of spinodal decomposition. This is the name given to the process of phase separation which occurs in the 'unstable' region of the phase diagram (see fig. 3). (For a recent discussion and references to earlier work see Abraham [53].) The equilibrium and kinetic aspects of this problem have traditionally been treated in terms of the empirical van der Waals square-gradient approximation to the Helmholtz free energy of a non-uniform fluid [54]. A general treatment of the equilibrium aspects can now be given.

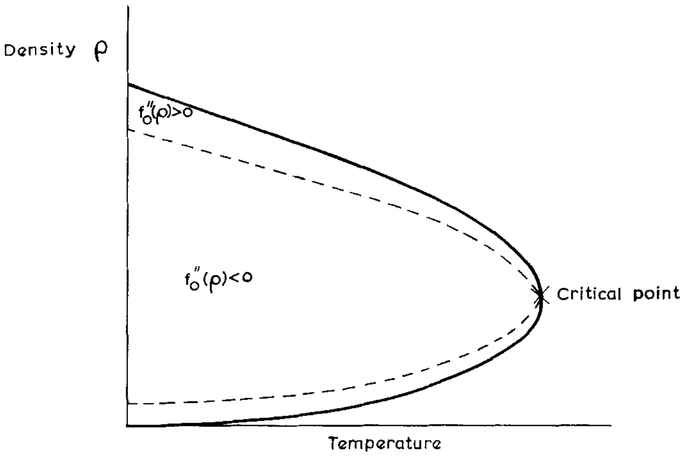
We consider an initially uniform fluid of density ρ_u and examine the stability of this fluid to infinitesimal density fluctuations $\tilde{\rho}(\mathbf{r})=\rho(\mathbf{r})-\rho_u$. Expanding the free energy as in (65) we have

$$\begin{aligned}\mathcal{F}[\rho]=&\mathcal{F}[\rho_u]+\mu(\rho_u)\int d\mathbf{r}\,\tilde{\rho}(\mathbf{r})\\&+\frac{1}{2\beta}\int\int d\mathbf{r}d\mathbf{r}'\left(\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho_u}-c[\rho_u;|\mathbf{r}-\mathbf{r}'|]\right)\tilde{\rho}(\mathbf{r})\tilde{\rho}(\mathbf{r}')+\dots\end{aligned}\tag{160}$$

where $\mu(\rho_u)$ is the chemical potential of the uniform fluid and $c[\rho_u;|\mathbf{r}-\mathbf{r}'|]$ is the corresponding Ornstein–Zernike direct correlation function. We assume that the number of molecules is unchanged by the fluctuation so that the second term in the expansion vanishes. It then follows that

$$\begin{aligned}\Delta\mathcal{F}=\mathcal{F}[\rho]-\mathcal{F}[\rho_u]&=\frac{1}{2\beta}\int\int d\mathbf{r}d\mathbf{r}'\left(\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho_u}-c[\rho_u;|\mathbf{r}-\mathbf{r}'|]\right)\tilde{\rho}(\mathbf{r})\tilde{\rho}(\mathbf{r}')\\&=\frac{1}{2\beta\mathcal{V}}\sum_{\mathbf{q}}\left(\frac{1}{\rho_u}-c[\rho_u;q]\right)\tilde{\rho}(\mathbf{q})\tilde{\rho}(-\mathbf{q}).\end{aligned}\tag{161}$$

Fig.3



Phase diagram for a simple monatomic fluid (schematic). The solid curve denotes the liquid–vapour coexistence curve and the dashed curve the spinodal $f''_0(\rho)=0$. In the unstable region $f''_0(\rho)<0$ phase separation occurs by spinodal decomposition. In the metastable region $f''_0(\rho)>0$ phase separation occurs by nucleation and growth.

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If $\Delta\mathscr{F}>0$ the fluid is stable with respect to infinitesimal density fluctuations. For an arbitrary fluctuation $\Delta\mathscr{F}$ may be rather complicated but if we restrict consideration to long wavelength fluctuations we can profitably expand $c[\rho_u;q]$ as in (69)and we find

$$\Delta\mathscr{F}=\frac{1}{\mathscr{V}}\sum_{\mathbf{q}}\left(\frac{f_0''(\rho_u)}{2}+q^2f_2(\rho_u)+\dots\right)\tilde{\rho}(\mathbf{q})\tilde{\rho}(-\mathbf{q}), \tag{162}$$

where we have used (72) to re-introduce the free energy density $f_0(\rho_u)$ and the coefficient of the square-gradient term $f_2(\rho_u)$. If we consider a fluctuation of amplitude α with a single Fourier component, i.e. $\rho(\mathbf{r})=\alpha\exp(-i\mathbf{q}\,.\,\mathbf{r})$ then to O (q^2)

$$\frac{\Delta\mathscr{F}}{\mathscr{V}}=\alpha^2\left(\frac{f_0''(\rho_u)}{2}+q^2f_2(\rho_u)\right). \tag{163}$$

Henceforward, we assume $f_2(\rho_u)>0$ for any density ρ_u of interest. (This should be valid for any potential with a reasonable attractive tail—see (73).) If $f_0''(\rho_u)>0$ (positive isothermal compressibility) then $\Delta\mathscr{F}$ in (163) is positive for all wave vectors q and it follows that the fluid is stable against long-wavelength fluctuations. On the other hand if $f_0''(\rho_u)<0$ (negative compressibility) $\Delta\mathscr{F}$ in (163) will be negative for $q<q_2$, where

$$q_2=(-f_0''(\rho_u)/2f_2(\rho_u))^{1/2} \tag{164}$$

is the 'critical' wave vector and the fluid will be unstable against such fluctuations. Whilst these results are of precisely the same form as those obtained by Cahn† [54] in his classic analysis we have now made a rigorous microscopic identification of f_2. In Cahn's theory, as in the van der Waals treatment of surface tension, there is usually no attempt to relate the coefficient of the square-gradient term to a particular microscopic quantity. The present analysis also shows that a proper generalization of Cahn's theory, which is not restricted to long wavelengths, exists and leads to a different critical wave vector q_c. The latter is the solution of

$$1=\rho_u c[\rho_u;q_c]. \tag{165}$$

The existence of a spinodal (the locus of points in the $\rho-T$ plane where $f_0''(\rho_u)=0$; (see fig. (3)) is, of course, dependent on the idea that the free energy density in the single-phase region has an analytic continuation into the two-phase region. This idea has not been proved [27]. In fact the argument [27, 53] in favour of it depends to a large extent on the strong experimental evidence for spinodal decomposition (see below). The analysis we have described above also requires that the Ornstein–Zernike direct correlation function has an analytic continuation into the two-phase region. There exist practical procedures for performing such a continuation [14].

The kinetics of spinodal decomposition may be analysed in an analogous fashion. We assume that the density satisfies the continuity equation

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=-\nabla\,.\,\mathbf{J}, \tag{166}$$

where $\mathbf{J}$ is the current density. If the departures from equilibrium are small, $\mathbf{J}$ should

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† Cahn considered concentration fluctuations in binary systems rather than density fluctuations in a single-component system. His free energy functional was of the Cahn–Hilliard square-gradient type which is analogous to the van der Waals approximation.

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be proportional to some driving force which will be associated with the effective one-body potential in the fluid, i.e.

$$\mathbf{J} = -B\rho(\mathbf{r},t)\nabla\mu_{\rm in}[\rho(\mathbf{r},t)], \tag{167}$$

where B is a positive constant of proportionality and $\mu_{\rm in}[\rho]$ is the intrinsic chemical potential defined in (15). In general, we require some prescription for $\mu_{\rm in}[\rho]$ or equivalently $\mathscr{F}[\rho]$. One way of proceeding is to assume $\rho(\mathbf{r},t)$ is slowly varying in space and use the gradient expansion (see (63))

$$\mu_{\rm in}[\rho]=f_0'(\rho)-f_2'(\rho)|\nabla\rho|^2-2f_2(\rho)\nabla^2\rho+\dots$$

Substituting the resultant $\mathbf{J}$ into (166) will give an explicit, but non-linear, partial differential equation for $\rho(\mathbf{r},t)$. This could then be linearized. It is preferable, however, to linearize directly, i.e. Taylor expand $\mathscr{F}[\rho]$ about some initial uniform density $\rho_{\rm u}$ as in (160) and then differentiate so that

$$\begin{aligned}\mu_{\rm in}[\rho]&=\mu(\rho_{\rm u})+\beta^{-1}\int d\mathbf{r}'\left(\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho_{\rm u}}-c[\rho_{\rm u};|\mathbf{r}-\mathbf{r}'|]\right)\tilde{\rho}(\mathbf{r}',t)+\dots\\&=\mu(\rho_{\rm u})+\frac{1}{\beta\mathscr{V}}\sum_{\mathbf{q}}\left(\frac{1}{\rho_{\rm u}}-c[\rho_{\rm u};q]\right)\tilde{\rho}(\mathbf{q},t)\exp(-i\mathbf{q}\cdot\mathbf{r})+\dots,\end{aligned}$$

where

$$\tilde{\rho}(\mathbf{q},t)=\int d\mathbf{r}\exp(i\mathbf{q}\cdot\mathbf{r})\tilde{\rho}(\mathbf{r},t).$$

Thus, to first order in $\tilde{\rho}$, the current density is

$$\mathbf{J}=\frac{B\rho_{\rm u}}{\beta\mathscr{V}}\sum_{\mathbf{q}}i\mathbf{q}\left(\frac{1}{\rho_{\rm u}}-c[\rho_{\rm u};q]\right)\tilde{\rho}(\mathbf{q},t)\exp(-i\mathbf{q}\cdot\mathbf{r}) \tag{168}$$

and substituting into (166) we have

$$\frac{\partial\tilde{\rho}(\mathbf{q},t)}{\partial t}=-\frac{B}{\beta}\rho_{\rm u}q^2\left(\frac{1}{\rho_{\rm u}}-c[\rho_{\rm u};q]\right)\tilde{\rho}(\mathbf{q},t) \tag{169}$$

The solution of (169) is of the form

$$\tilde{\rho}(\mathbf{q},t)=\tilde{\rho}(\mathbf{q},0)\exp(R(q)t) \tag{170}$$

with

$$R(q)=-\frac{B}{\beta}\rho_{\rm u}q^2\left(\frac{1}{\rho_{\rm u}}-c[\rho_{\rm u};q]\right). \tag{171}$$

For long-wavelength fluctuations we can again expand the direct correlation function in powers of q^2 and it follows that to $O(q^4)$:

$$R(q)=-B\rho_{\rm u}(q^2f_0''(\rho_{\rm u})+2q^4f_2(\rho_{\rm u})). \tag{172}$$

If the fluid is in the unstable region, i.e. $f_0''(\rho_{\rm u})<0$ (see fig. 3), the amplitude of the fluctuations will increase exponentially with time provided q is smaller than the critical wave vector q_2 as defined in (164). When $q>q_2$ the amplitude will decay exponentially with time. Equation (172) is identical in form to that derived by Cahn [54]. We now find, from our more general analysis, that $R(q)$ will be positive and the amplitude of the fluctuations will increase with time, provided $q<q_{\rm c}$ where $q_{\rm c}$ is defined by (165).

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It is possible, in principle, to test the predictions of this theory experimentally. X-ray or light scattering experiments measure an intensity $I(\mathbf{q},t)\propto|\tilde{\rho}(\mathbf{q},t)|^2$. The present theory predicts that the time derivative of the logarithm of the intensity should be time independent and equal to $2R(q)$. The quantity which is conveniently extracted from an experiment is

$$D(q)=q^{-2}\frac{d}{dt}\ln I(\mathbf{q},t)=2q^{-2}R(q). \tag{173}$$

Thus for very small wave vectors q, $D(q)$ should vary linearly with q^2. This would correspond to the light-scattering situation. For wave vectors corresponding to wavelengths $\lesssim 20\sigma$, where σ is a molecular diameter, (171) predicts deviations from a linear behaviour, since higher order terms in the expansion of $c[\rho_u; q]$ then become important. The critical wave vectors q_2 and q_c will lie in this range. Cahn's theory predicts that $D(q)$ varies linearly with q^2 for all q. Recently Abraham [33, 55] has used an approximate thermodynamic perturbation theory to treat this problem. He calculates substantial deviations from linear behaviour for $q\gtrsim q_2$. Our analysis provides a general explanation for such behaviour.

We stress that the theory of spinodal decomposition as described above is only valid for the initial stages of the decomposition when the amplitudes of the fluctuations are small. As the amplitudes grow non-linear effects become important and the present linear theory will be invalid [56, 57]. It has also been suggested [58, 57] that even in the early stages of decomposition the above theory is incomplete and that there should be a 'random-force' contribution to the current density in (167). The addition of such a term modifies the subsequent analysis and can lead to additional curvature effects in $D(q)$, i.e. this separate mechanism also acts to produce deviations from a linear variation with q^2. Abraham [55, 53] has commented on the present experimental and theoretical situations. Experiments are usually performed on binary alloys rapidly quenched from the melt into the unstable, solid-solution region. Consequently the relevant order parameter is not the density but the concentration. Whilst these experiments provide ample evidence that the early stages of spinodal decomposition are well described by the Cahn theory they frequently yield a $D(q)$ which is not proportional to q^2 for $q\gtrsim q_c$. Hence the current interest in this problem. Cahn's theory has also given a satisfactory explanation of light scattering measurements on some binary-fluids (see e.g. [53]). The interpretation of the various experiments and, in particular, the role of the non-linear terms and the 'random force' remain the subject of current investigation.

§ 10. CONCLUSIONS, PERSPECTIVES AND OTHER TOPICS

In this paper we have reviewed the general theory of the equilibrium statistical mechanics of non-uniform classical fluids and we have described the application of this theory to three different problems—the long-wavelength behaviour of the direct correlation function of a uniform fluid, the early stages of spinodal decomposition and the liquid–vapour interface. It might be useful to summarize some of our main conclusions and mention possible topics for future research in these areas.

The approximations described in § 7 for the long-wavelength behaviour of the direct correlation function or, equivalently, the liquid structure factor $S(q)$ are both physically revealing and sufficiently simple to warrant application in more complex fluids. $S(q)$ at small q contains information concerning the long-range part of the interatomic potential. Consequently we might expect $S(q\approx 0)$ to differ considerably between metals and insulators, reflecting the long-range oscillations and van der

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Waals attraction of the different pair potentials. Experimentally most liquid metals at their triple points are considerably less compressible than their equivalent hard-sphere reference system while insulators are roughly twice as compressible as their equivalent hard-sphere reference systems. Calculations based on the RPA and ERPA of § 7 give a good account of this trend in the compressibility [17]. The approximation schemes may also prove useful for the interpretation of small q diffraction data in both metals and insulators. The extension of the general theory to binary mixtures is straightforward [16] and the RPA and MDA have been used in a study of phase separation in binary alloys [16]. (Phase separation is concerned with the $q=0$ divergence of the partial structures factors.) The results for a single alloy system, Li–Na, are encouraging and this would appear to be a promising approach to what is traditionally regarded as a difficult problem. In a related, but somewhat less ambitious, vein the various approximations should throw considerable insight into the long-wavelength behaviour of the measured partial structure factors of binary systems near the triple point. We note that the $q=0$ limits of the partial structure factors are related to important thermodynamic quantities, i.e. the isothermal compressibility, partial molar volumes and activities (e.g., Bhatia [59]).

Our present treatment of spinodal decomposition has put Cahn's classic work on a proper theoretical basis and showed how to properly extend his approach to finite wavelengths. We have not attempted to go beyond the linear aspects of the problem or to deal with all the rather controversial aspects of the kinetics of spinodal decomposition. Calculations of the critical wave vectors q_2, q_c and the function $R(q)$ of § 9 have recently been performed for a Lennard–Jones fluid at various points in the unstable region [77]. We find that the small q expansion is inaccurate for $q \sim q_c$. The formal extension of our analysis to binary mixtures appears to be quite straightforward and it would be useful to develop tractable approximation schemes for this case since spinodal decomposition appears to be observed in various binary systems (see § 9).

In § 8 we saw that the general theory has proved extremely fruitful in its application to the liquid–vapour interface. It is probably safe to argue that the density profile and surface tension of simple, argon-like liquids is now quite well understood. One major theoretical problem remains, however, and this concerns the search for a proper microscopic model which will describe correlations in the interface. As discussed in § 8.4 and §8.5, while there is important recent work in this area, most existing models are based on capillary wave theory and lead to what we believe are unrealistic divergences in the width of the equilibrium density profile under certain limiting conditions. A second more technical problem concerns the relationship between the Kirkwood–Buff result (107) for the surface tension and the corresponding result in terms of the direct correlation function (128). As we mentioned in § 8.3 no direct proof of their equivalence has been given. Very recently, however, Jhon *et al.* [60] have shown that the Kirkwood–Buff result can be transformed to a formula involving a force–force correlation function and that the latter is equivalent to (128). Whilst this does not constitute a direct demonstration of the equivalence of the two approaches it certainly implies that a direct derivation should exist.†

Relatively little work has been done on the statistical theory of the liquid–vapour interface for more complex fluids (for a recent review see Croxton [61]). The formal

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† Schofield [79] *has* shown that the Kirwood–Buff result can be directly transformed to the formula involving the direct correlation function.

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extension of the theory to multi-component systems is straightforward [29] but there have been few calculations. Chapela *et al.* [49] have carried out a computer simulation of the surface of a Lennard–Jones binary mixture. This calculation shows the expected adsorption of the component of higher vapour pressure. It is clear that in binary fluids the surface tension is very sensitive to the form of the density profiles of each component, so one requires fairly accurate, yet tractable, approximate theories in order to understand experimental data. Recently Pastor and Goodisman [62] have stressed this point for molten salts; there is little theoretical understanding of these important systems. For mixtures of neutral atoms, thermodynamic perturbation theories would appear to be useful and Abraham [63] has discussed this. While liquid metals lie outside the scope of this paper we should mention that Lu and Rice [78] have recently reported experimental results for the ion-density profile of liquid Hg using X-ray techniques. This would appear to be the first successful experimental determination of a density profile for *any* liquid near its triple point. The width of the measured profile is about two or three atomic diameters, i.e. similar to that which would be expected from theoretical work on *insulating* liquids. However, this width is much larger than that predicted by the theoretical work of Rice and co-workers (see [78] for details) on metals. It is also larger than widths predicted by the present author [64] who developed a 'pseudoatom' model to describe the free surface of a liquid metal. This model takes into account both electronic and ionic contributions to the surface tension and involves both the averaged conduction electron density and the ion-density profile. Calculations for a few metals near their melting points yield surface tensions which are in fair agreement with experiment and predict ion-density profiles with substantially smaller widths than those obtained for insulating, argon-like liquids at their triple points [35]. It might also be interesting to examine the horizontal correlation functions at the surface of binary liquids—especially for charged fluids. Gray and Gubbins [65] have generalized the Kirkwood–Buff theory to molecular fluids in which the interaction potential depends on the relative orientation of the molecules and Haile *et al.* [66] have developed a thermodynamic perturbation theory for the surface properties of such fluids.

The statistical thermodynamics of the surface of superfluid ^{4}He has received a great deal of attention in recent years. Much of the theoretical work in this field is based on density functional techniques which are quantum-mechanical analogues of those described in this paper (see, e.g. Ebner and Saam [67] and references therein). There are also models which build up the equilibrium density profile and calculate the surface tension by unfreezing 'ripplons' in a 'bare' surface [68, 67]. These 'ripplons' are analogous to capillary waves but possess a large zero-point energy. They lead to a considerable broadening of the surface profile and give a very large contribution to the surface tension. It would also appear that these models should lead to troublesome divergences in the limit $g \to 0$ or A, the area of the interface, $\to \infty$.

One important area of research, where the general theory of non-uniform fluids can make an impact is that concerned with the liquid–solid interface. Several authors have developed theories of the density profile of a simple liquid in contact with a structureless, repulsive wall (see, e.g. Sullivan and Stell [69] and references therein). These theories solve the appropriate Ornstein–Zernike equation, usually within a Percus–Yevick type of approximation. Saam and Ebner [70] have criticized some aspects of the approximation scheme. In particular they argue it cannot predict the formation and growth of unsaturated liquid films near the fluid–solid

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interface and that the density functional technique of Ebner *et al.* (see § 6.4) is much superior in this respect. Singh and Abraham [71] have applied their thermodynamic perturbation theory (see § 8.1) to the determination of the density profile for a hard-sphere liquid in contact with a soft repulsive wall. While replacing the actual 'structured' wall by some average external potential may turn out to be a rather crude approximation for a real solid–liquid interface [72] such model calculations should prove useful for understanding interfacial tension, wetting, contact-angle, etc. The molecular theory of such phenomena is still in its infancy; for a recent review see Navascués [73].

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APPENDIX 1

THE PROOF THAT $V_{\text{ext}}(\mathbf{r})$ IS UNIQUELY DETERMINED BY THE EQUILIBRIUM DENSITY $\rho_0(\mathbf{r})$

We follow the Hohenberg–Kohn–Mermin argument which proceeds by *reductio ad absurdum*. Suppose another potential exists which gives rise to the same density $\rho_0(\mathbf{r})$. Let this potential be $V'_{\text{ext}}(\mathbf{r})$ corresponding to the hamiltonian $H'_N = T + U + V'$. The corresponding equilibrium probability density f' and the grand potential Ω' refer to the original temperature and chemical potential. It is easy to show that even if the two external potentials differ by only a constant, the grand canonical probability densities are different, i.e. $f' \neq f_0$.

From (5) we have

$$\Omega' = \mathrm{Tr}_{\text{cl}} f'(H'_N - \mu N + \beta^{-1} \ln f')$$

$$< \mathrm{Tr}_{\text{cl}} f_0(H'_N - \mu N + \beta^{-1} \ln f_0)$$

The r. h. s. of this inequality is $\Omega + \mathrm{Tr}_{\text{cl}} f_0(V' - V)$ so

$$\Omega' < \Omega + \int d\mathbf{r}\, \rho_0(\mathbf{r})(V'_{\text{ext}}(\mathbf{r}) - V_{\text{ext}}(\mathbf{r})). \tag{A 1}$$

Interchanging primed and unprimed quantities we find

$$\Omega < \Omega' + \mathrm{Tr}_{\text{cl}} f'(V - V'),$$

but since f' is assumed to give rise to $\rho_0(\mathbf{r})$ this can be written as

$$\Omega < \Omega' + \int d\mathbf{r}\, \rho_0(\mathbf{r})(V_{\text{ext}}(\mathbf{r}) - \mathrm{V}'_{\text{ext}}(\mathbf{r})). \tag{A 2}$$

Adding (A 1) and (A 2) leads to a contradiction

$$\Omega + \Omega' < \Omega' + \Omega.$$

Consequently for a given chemical potential there is a unique $V_{\text{ext}}(\mathbf{r})$ which will determine a given equilibrium density. If we allow the chemical potential in the system with hamiltonian H'_N to be different from μ we can then prove that the combination $\mu - V_{\text{ext}}(\mathbf{r}) = u(\mathbf{r})$ is a unique functional of the density. The proof that f_0 is a functional of $\rho_0(\mathbf{r})$ then follows straightforwardly and the subsequent analysis follows that of § 2.

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APPENDIX 2

DISTRIBUTION FUNCTIONS IN THE GRAND CANONICAL ENSEMBLE

The grand partition function (2) can be written in terms of $u(\mathbf{r})=\mu-V_{\text{ext}}(\mathbf{r})$:

$$\Xi=\sum_{N=0}^{\infty}\frac{\lambda^{-3N}}{N!}\int d\mathbf{r}_1\ldots d\mathbf{r}_N\exp\left(\beta\int d\mathbf{r}\,u(\mathbf{r})\hat{\rho}(\mathbf{r})-\beta U\right) \tag{A 3}$$

Thus

$$\begin{aligned}\frac{\delta\Omega}{\delta u(\mathbf{r})}&=-\Xi^{-1}\sum_{N=0}^{\infty}\frac{\lambda^{-3N}}{N!}\int d\mathbf{r}_1\ldots d\mathbf{r}_N\,\hat{\rho}(\mathbf{r})\exp\left(\beta\int d\mathbf{r}u(\mathbf{r})\hat{\rho}(\mathbf{r})-\beta U\right)\\&=-\mathrm{Tr}_{\mathrm{cl}}f_0\hat{\rho}(\mathbf{r})\\&=-\langle\hat{\rho}(\mathbf{r})\rangle\\&=-\rho_0(\mathbf{r}),\end{aligned}$$

which is (25). Differentiating again we have

$$\mathscr{G}(\mathbf{r}_1,\mathbf{r}_2)\equiv\beta^{-1}\frac{\delta\rho_0(\mathbf{r}_1)}{\delta u(\mathbf{r}_2)}=\beta^{-1}\left(\frac{-\delta\ln\Xi}{\delta u(\mathbf{r}_2)}\rho_0(\mathbf{r}_1)+\beta\,\mathrm{Tr}_{\mathrm{cl}}f_0\hat{\rho}(\mathbf{r}_1)\hat{\rho}(\mathbf{r}_2)\right)$$

or

$$\mathscr{G}(\mathbf{r}_1,\mathbf{r}_2)=-\rho_0(\mathbf{r}_2)\rho_0(\mathbf{r}_1)+\langle\hat{\rho}(\mathbf{r}_1)\hat{\rho}(\mathbf{r}_2)\rangle, \tag{A 4}$$

which is equivalent to (26)

The hierarchy of configurational distribution functions is defined as usual by

$$\rho^{(m)}(\mathbf{r}_1\ldots\mathbf{r}_m)=\Xi^{-1}\sum_{N\geqslant m}^{\infty}\frac{z^N}{(N-m)!}\int d\mathbf{r}_{m+1}\ldots d\mathbf{r}_N\exp\left(-\beta(V+U)\right) \tag{A 5}$$

Clearly, $\rho^{(1)}(\mathbf{r})\equiv\rho_0(\mathbf{r})$ and it is straightforward to show

$$\begin{aligned}\langle\hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}')\rangle&=\Big\langle\sum_{i\neq j}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)\Big\rangle+\Big\langle\sum_{i}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_i)\Big\rangle\\&=\rho^{(2)}(\mathbf{r},\mathbf{r}')+\rho_0(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\end{aligned} \tag{A 6}$$

Combining this result with (A 4) we obtain (27) for $\mathscr{G}(\mathbf{r}_1,\mathbf{r}_2)$.

If the interaction potential U can be written as a sum of pairwise potentials as in (49) we can obtain $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ by functional differentiation of Ξ w.r.t. to the pairwise potential $\phi(\mathbf{r},\mathbf{r}')$. We write

$$\Xi=\sum_{N=0}^{\infty}\frac{\lambda^{-3N}}{N!}\int d\mathbf{r}_1\ldots d\mathbf{r}_N\exp\left(\beta\int d\mathbf{r}\,u(\mathbf{r})\hat{\rho}(\mathbf{r})-\frac{\beta}{2}\int\int d\mathbf{r}d\mathbf{r}'\hat{I}(\mathbf{r},\mathbf{r}')\phi(\mathbf{r},\mathbf{r}')\right),$$

where

$$\hat{I}(\mathbf{r},\mathbf{r}')=\sum_{i\neq j}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j).$$

Equation (50) then follows immediately since, for fixed $u(\mathbf{r})$

$$\frac{\delta\Omega}{\delta\phi(\mathbf{r},\mathbf{r}')}=-\beta^{-1}\frac{\delta\ln\Xi}{\delta\phi(\mathbf{r},\mathbf{r}')}=\tfrac{1}{2}\langle\hat{I}(\mathbf{r},\mathbf{r}')\rangle=\tfrac{1}{2}\rho^{(2)}(\mathbf{r},\mathbf{r}'),$$

where we have used (A 6).

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APPENDIX 3

Relation to linear response theory

Consider a non-uniform fluid of equilibrium density $\rho_0(\mathbf{r})$ and potential $u_0(\mathbf{r})$. Suppose this system is perturbed by an infinitesimal change in the external potential so that the new equilibrium density is $\rho(\mathbf{r})$ and the corresponding potential is $u(\mathbf{r})$.

The (static) linear density response function χ relates the change in density to the change in external potential:

$$\tilde{\rho}(\mathbf{r}) \equiv -\int d\mathbf{r}'\, \chi(\mathbf{r},\mathbf{r}')\tilde{u}(\mathbf{r}'), \tag{A 7}$$

where $\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0(\mathbf{r})$ and $\tilde{u}(\mathbf{r}) = u(\mathbf{r}) - u_0(\mathbf{r}) = -\Delta V_{\mathrm{ext}}(\mathbf{r})$, if the chemical potential is fixed. From (26) it follows that

$$\mathscr{G}(\mathbf{r}_1,\mathbf{r}_2) = -\beta^{-1}\chi(\mathbf{r}_1,\mathbf{r}_2). \tag{A 8}$$

For a uniform fluid of density ρ_0, $\mathscr{G}(\mathbf{r}_1,\mathbf{r}_2) = \rho_0^2(g(r_{12})-1) + \rho_0\delta(r_{12})$, so on Fourier transforming we have

$$\chi(q) = -\beta\rho_0(1 + \rho_0 \int d\mathbf{r} \exp(\mathrm{i}\mathbf{q}\,.\,\mathbf{r})(g(r)-1)) \equiv -\beta\rho_0 S(q), \tag{A 9}$$

where $S(q)$ is the liquid structure factor. The direct correlation function of the uniform fluid $c^{(2)}(q)$ is related to the inverse of $S(q)$:

$$\rho_0 c^{(2)}(q) = 1 - 1/S(q), \tag{A 10}$$

which follows from Fourier transforming (32), the Ornstein–Zernike equation. Combining (A 9) and (A 10) we find

$$c^{(2)}(q) - 1/\rho_0 = \beta/\chi(q),$$

which is the result quoted in (68).

APPENDIX 4

Analysis of correlations in the interface

Equation (135) for the equilibrium density profile in a gravitational field can be written as

$$\frac{d\rho_0(z_1)}{dz_1} = -\beta mg \int dz_2\, \mathscr{G}_0(z_1,z_2), \tag{A 11}$$

where $\mathscr{G}_0(z_1,z_2) = \int d\mathbf{R}_{12}\,\mathscr{G}(R_{12},z_1,z_2)$. This is the 'inverse' equation to (55). The latter can be re-expressed as

$$-\beta mg = \int dz_2 \frac{d\rho_0(z_2)}{dz_2} C_0(z_1,z_2), \tag{A 12}$$

where $C_0 = \int d\mathbf{R}_{12}\, C^{(2)}(R_{12},z_1,z_2)$. We recall that since $C^{(2)}$ is the inverse of $\mathscr{G}$ i.e.

$$\int d\mathbf{r}_3\, C^{(2)}(\mathbf{r}_1,\mathbf{r}_3)\mathscr{G}(\mathbf{r}_3,\mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{A 13}$$

their horizontal Fourier components also satisfy an inverse relation:

$$\int dz_3\, C^{(2)}(Q,z_1,z_3)\mathscr{G}(Q,z_3,z_2) = \delta(z_1 - z_2) \tag{A 14}$$

and in particular the zeroth components satisfy

$$\int dz_3 C_0(z_1,z_3)\mathscr{G}_0(z_3,z_2) = \delta(z_1 - z_2). \tag{A 15}$$

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This last result is, of course, consistent with (A 11) and (A 12).

It is convenient to analyse (A 12) using matrix methods [10]. Since $C^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is non-negative and symmetric w.r.t. the interchange of $\mathbf{r}_1$ and $\mathbf{r}_2$ (see (22)), $C_0(z_1, z_2)$ can be represented by a symmetric, non-negative, continuous matrix. Such a matrix can be decomposed into its spectral form

$$C_0(z_1, z_2) = \sum_i \lambda_i \varepsilon_i^*(z_1)\varepsilon_i(z_2), \tag{A 16}$$

where λ_i are the eigenvalues and $\varepsilon_i(z)$ are an orthonormal set of eigenvectors. Equation (A 12) asserts that, if $g=0$, $d\rho_0(z_1)/dz_1$ is an eigenvector of $C_0(z_1, z_2)$ with eigenvalue zero. Consequently, following Wertheim [10], we separate out the set of eigenvalues which go to zero linearly with g. This set is denoted by $\lambda_j = \beta m g \nu_j$. We assume that all eigenvalues and eigenvectors go to a limit as g goes to zero and that no eigenvalue goes to zero faster than g.

Equation (A 15) implies

$$\mathscr{G}_0(z_1, z_2) = \sum_i \lambda_i^{-1} \varepsilon_i^*(z_1)\varepsilon_i(z_2) \tag{A 17}$$

which will have contributions which diverge as g^{-1} for all z_1 and z_2 so we write

$$\mathscr{G}_0(z_1, z_2) = \sum_j (\beta m g \nu_j)^{-1} \varepsilon_j^*(z_1)\varepsilon_j(z_2) + \text{less singular terms}. \tag{A 18}$$

Since (A 11) indicates that the integral of $\mathscr{G}_0(z_1, z_2)$ over z_2 has the same g^{-1} divergence, the long-ranged correlations cannot be in the z direction. Furthermore since $\mathscr{G}(\mathbf{r}_1, \mathbf{r}_2)$ is not pointwise divergent, these correlations must originate from integrating in the x and y directions.

Inserting (A 17) into (A 11) we find

$$\frac{d\rho_0(z_1)}{dz_1} = -\beta m g \int_{-\infty}^{\infty} dz_2 \sum_i \lambda_i^{-1} \varepsilon_i^*(z_1)\varepsilon_i(z_2)$$

and in the limit when g goes to zero, this reduces to

$$\frac{d\rho_0(z)}{dz} = -\sum_j \nu_j^{-1} \varepsilon_j^*(z) E_j \tag{A 19}$$

where $E_j = \int_{-\infty}^{\infty} dz\, \varepsilon_j(z)$ and the $\varepsilon_j(z)$ are to be evaluated at $g=0$.

Integrating (A 19) through the fluid we obtain

$$\rho_l - \rho_v = \sum_j \nu_j^{-1} |E_j|^2 \tag{A 20}$$

and using the orthonormality of the $\varepsilon_j(z)$ we find

$$\int_{-\infty}^{\infty} dz \left| \frac{d\rho_0(z)}{dz} \right|^2 = \sum_j \nu_j^{-2} |E_j|^2. \tag{A 21}$$

Wertheim points out that while there may be large continuum contributions to the summation in (A 19) it is more likely, since $d\rho_0(z)/dz$ is a sharply peaked function, that the eigenvalues form a discrete spectrum and that the contribution from the smallest value ν_0 is the dominant one. If we make this conjecture and retain only the lowest term in each of (A 18), (A 19) and (A 20) we find, in the limit g goes to zero,

$$\mathscr{G}_0(z_1,z_2)\approx\frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}((\rho_l-\rho_v)\beta mg)^{-1}+\text{less singular terms},$$

which is the result quoted in (136).

A similar analysis can be carried through for $\mathscr{G}(Q,z_1,z_2)$ at small finite Q. We suppose that

$$C^{(2)}(Q,z_1,z_2)=\sum_i\lambda_i(Q)\varepsilon^*(Q,z_1)\varepsilon_i(Q,z_2), \tag{A 22}$$

where the eigenvalues $\lambda_i(Q)$ and the eigenvectors $\varepsilon_i(Q,z)$ now depend on the wave vector Q. The inverse quantity is then given by

$$\mathscr{G}(Q,z_1,z_2)=\sum_i\lambda_i(Q)^{-1}\varepsilon_i^*(Q,z_1)\varepsilon_i(Q,z_2). \tag{A 23}$$

The idea is to use perturbation theory to express $\lambda_i(Q)$ in terms of λ_i, the eigenvalue corresponding to $Q=0$. We begin by expanding $C^{(2)}(Q,z_1,z_2)$ for small Q as in (125) so that

$$\begin{aligned}\lambda_i(Q)&=\int\!\!\int dz_1dz_2\,\varepsilon_i(Q,z_1)\varepsilon_i^*(Q,z_2)C^{(2)}(Q,z_1,z_2)\\&=\int\!\!\int dz_1dz_2\,\varepsilon_i(Q,z_1)\varepsilon_i^*(Q,z_2)(C_0(z_1,z_2)+Q^2C_2(z_1,z_2)+\dots).\end{aligned}$$

To lowest order we can replace $\varepsilon_i(Q,z)$ by $\varepsilon_i(z)$, the eigenvector corresponding to $Q=0$, and we then obtain

$$\lambda_i(Q)=\lambda_i+Q^2\int\!\!\int dz_1dz_2\,\varepsilon_i(z_1)\varepsilon_i^*(z_2)C_2(z_1.z_2). \tag{A 24}$$

Substituting into (A 23) we note that the eigenvalues of interest are those associated with $\lambda_j=\beta mgv_j$ so we separate these out

$$\mathscr{G}(Q,z_1,z_2)=\sum_j\varepsilon_j^*(Q,z_1)\varepsilon_j(Q,z_2)(\beta mgv_j+Q^2\int\!\!\int dz_1dz_2\,\varepsilon_j(Q,z_1)\varepsilon_j^*(Q,z_2)C_2(z_1,z_2))^{-1}$$
$$+\text{less singular terms}.$$

If we make the same one eigenvalue conjecture as previously we find

$$\begin{aligned}\mathscr{G}(Q,z_1,z_2)&\sim\frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}\left((\rho_l-\rho_v)\beta mg+Q^2\int\!\!\int dz_1dz_2\frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}C_2(z_1,z_2)\right)^{-1}\\&=\beta^{-1}\frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}((\rho_l-\rho_v)mg+\gamma Q^2)^{-1}+\text{ less singular terms},\end{aligned}$$

where we have used (128) for the surface tension γ and worked to O (Q^2). This result (138) has been derived by Weeks [12] and with $g=0$, by Kalos *et al.* [11] and is implicit in Wertheim's paper. It is consistent with an exact result for $\mathscr{G}_2(z_1,z_2)$, the coefficient of Q^2 in the expansion of $\mathscr{G}(Q,z_1,z_2)$. To prove this we use (A 14):

$$\int dz_3\,(C_0(z_1,z_3)+Q^2C_2(z_1,z_3)+\dots)\,(\mathscr{G}_0(z_3,z_2)+Q^2\mathscr{G}_2(z_3,z_2)+\dots)=\delta(z_1-z_2)$$

Equating coefficients of Q^2 implies

$$\int dz_3C_2(z_1,z_3)\mathscr{G}_0(z_3,z_2)=-\int dz_3\,C_0(z_1,z_3)\mathscr{G}_2(z_3,z_2)$$

which, on using (A 15), yields two equivalent symmetrical forms [10]

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$$\mathscr{G}_2(z_1,z_2)=-\int\int dz_4dz_3\,\mathscr{G}_0(z_1,z_4)C_2(z_4,z_3)\mathscr{G}_0(z_3,z_2) \qquad \text{(A 25)}$$

and

$$C_2(z_1,z_2)=-\int\int dz_4dz_3\,C_0(z_1,z_3)\mathscr{G}_2(z_3,z_4)C_0(z_4,z_2). \qquad \text{(A 26)}$$

If we substitute (136) for $\mathscr{G}_0$ into the r. h. s. of (A 25) we find

$$\mathscr{G}_2(z_1,z_2)\approx-\gamma\beta^{-1}\frac{d\rho_0(z_1)}{dz_1}\frac{d\rho_0(z_2)}{dz_2}((\rho_l-\rho_v)mg)^{-2} \qquad \text{(A 27)}$$

which is identical to $\mathscr{G}_2$ as obtained from (138).

We can use (A 26) to transform the r. h. s. of (128) into

$$-\beta^{-1}\int\int dz_3dz_4\,\mathscr{G}_2(z_3,z_4)\int dz_1\frac{d\rho_0(z_1)}{dz_1}C_0(z_1,z_3)\int dz_2\frac{d\rho_0(z_2)}{dz_2}C_0(z_4,z_2)$$

which, using (A 12), reduces to $-\beta(mg)^2\int\int dz_1dz_2\,\mathscr{G}_2(z_1,z_2)$. We must now ask whether it is valid to identify this quantity with the surface tension, i.e. if

$$\gamma=-\lim_{g\to 0}\beta(mg)^2\int\int dz_1dz_2\,\mathscr{G}_2(z_1,z_2). \qquad \text{(A 28)}$$

For γ to be finite and independent of g, $\mathscr{G}_2(z_1,z_2)$ must therefore diverge as g^{-2}. Since this is precisely the behaviour indicated in (A 27), eqn. (A 28) would appear to be a valid result for the surface tension [10].

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APPENDIX 5

THE CAPILLARY WAVE MODEL

This model is based on the analysis leading to (140) except now we consider fluctuations about some 'bare' density profile (not the equilibrium density) which is characterized by a surface tension γ_{bare}. We set $V_{\text{ext}}=0$. The free energy functional associated with the distortion z_G of the Gibbs surface is conventionally taken to be

$$F_{\text{CW}}[z_G]=\tfrac{1}{2}\int d\mathbf{R}\,(\gamma_{\text{bare}}|\nabla_R z_G(\mathbf{R})|^2+(\rho_l-\rho_v)mg|z_G(\mathbf{R})|^2), \qquad \text{(A 29)}$$

i.e. as in § 8.4, it is assumed that $\rho(\mathbf{R},z)=\rho_{\text{bare}}(z-z_G(\mathbf{R}))$ and that all higher-order terms in the expansion of both the gravitational and 'surface' terms can be ignored.

The partition function for this model is given by the functional integral

$$Z=\mathscr{M}\int\delta z_G(\mathbf{R})\exp(-\beta F_{\text{CW}}[z_G]) \qquad \text{(A 30)}$$

where $\mathscr{M}$ is a normalization factor. Equation (A 29) is of the form of the gaussian model which is employed in field theoretical formulations of statistical mechanics. Consequently the partition function can be evaluated by Fourier transform techniques. We set

$$z_G(\mathbf{R})=\frac{1}{A}\sum_{\mathbf{Q}}a(\mathbf{Q})\exp(-i\mathbf{Q}.\mathbf{R}),$$

where A is the area of the interface and the partition function becomes

$$Z=\mathscr{M}\int\prod_{\mathbf{Q}}da(\mathbf{Q})\exp\left[-\frac{\beta}{2A}\sum_{\mathbf{Q}}|a(\mathbf{Q})|^2((\rho_l-\rho_v)mg+\gamma_{\text{bare}}Q^2)\right] \qquad \text{(A 31)}$$

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Since the different Fourier coefficients decouple, the integrals can be immediately solved:

$$Z = \mathscr{M} \prod_{\mathbf{Q}} \left[\frac{\beta((\rho_l - \rho_v)mg + \gamma_{\text{bare}} Q^2)}{2A\pi} \right]^{-1/2}. \tag{A 32}$$

The Helmholtz free energy is given by

$$\beta F = -\ln \mathscr{M} + \tfrac{1}{2} \sum_{\mathbf{Q}} \ln \left[\frac{\beta((\rho_l - \rho_v)mg + \gamma_{\text{bare}} Q^2)}{2A\pi} \right]. \tag{A 33}$$

The average value of $|a(\mathbf{Q})|^2$ is easily obtained from (A 32):

$$\langle |a(\mathbf{Q})|^2 \rangle = A[\beta((\rho_l - \rho_v)mg + \gamma_{\text{bare}} Q^2)]^{-1}.$$

It is possible to calculate the capillary wave contribution to the surface tension using the formula $\gamma_{\text{cw}} = (\partial F/\partial A)_T$. Since each wave vector Q scales with area as $A^{-1/2}$ we find from (A 33) that

$$\gamma_{\text{cw}} = \frac{1}{2\beta A} \sum_{\mathbf{Q}} \left[\frac{(\rho_l - \rho_v)mg}{(\rho_l - \rho_v)mg + \gamma_{\text{bare}} Q^2} - 2 \right]. \tag{A 34}$$

Thus, in the absence of the gravitational field, each normal mode 'reduces' the 'surface' free energy by an amount $k_B T$. When g is finite there is an additional positive contribution representing the work which must be done against the external field. This contribution is proportional to σ_G^2, the mean square fluctuation in the average location of the dividing surface (see (154)) so that the surface tension in this model of the interface can be written

$$\gamma = \gamma_{\text{bare}} - \frac{(Q_{\max}^2 - Q_{\min}^2)}{4\pi\beta} + \frac{(\rho_l - \rho_v)mg}{2} \sigma_G^2, \tag{A 35}$$

where $Q_{\max}$ and $Q_{\min}$ are the upper and lower cut-off as described in § 8.5. If we set $A = \infty$ and let $g \to 0$ we find

$$\gamma = \gamma_{\text{bare}} - \frac{Q_{\max}^2}{4\pi\beta} + \frac{\ln(\xi_{\text{bare}}^2 Q_{\max}^2)}{8\pi\beta\, \xi_{\text{bare}}^2}, \tag{A 36}$$

where the last term goes to zero as $g \ln g$. Consequently the surface tension goes to a well-defined limit in a vanishing external field. There remains, of course, the problem of choosing $Q_{\max}$ but if we take, as earlier, $Q_{\max} = 2\pi/\sigma$ where σ is a molecular diameter we can estimate the magnitude of the various terms in (A 36). Using parameters appropriate to argon near its triple point and in the earth's gravitational field (see § 8.5) we find

$$\gamma = 14 - 31{\cdot}9 + 8 \times 10^{-13}\,\text{dyn cm}^{-1}.$$

Clearly the surface tension depends crucially on the choice of γ_{bare} and $Q_{\max}$! More sophisticated versions of the capillary wave model [12, 21] attempt to provide proper prescriptions for these quantities.

We should note that attempts to improve upon the model of (A 29) by including higher-order terms rapidly run into difficulties and only approproximate solutions are available [76].

References

[1] Morita, T., and Hiroike, K., 1961, *Prog. theort. Phys., Osaka*, **25**, 537.

[2] De Dominicis, C., 1962, *J. Math. Phys.*, **3**, 983.

[3] Stillinger, F. H., and Buff, F. P., 1962, *J. chem. Phys.*, **37**, 1.

[4] Lebowitz, J. L., and Percus, J. K., 1963, *J. Math. Phys.*, **4**, 116.

[5] Percus, J. K., 1964, *The Equilibrium Theory of Classical Fluids* edited by H. L. Frisch and J. L. Lebowitz (Benjamin), p. II 33.

[6] Stell, G., 1964, *The Equilibrium Theory of Classical Fluids* edited by H. L. Frisch and J. L. Lebowitz (Benjamin), p. II 171.

[7] Triezenberg, D. G., and Zwanzig, R., 1972, *Phys. Rev. Lett.*, **28**, 1183.

[8] Lovett, R. A., Dehaven, P. W., Vieceli, J. J., and Buff, F. P., 1973, *J. chem. Phys.*, **58**, 1880.

[9] Lovett, R. A., Mou, C. Y., and Buff, F. P., 1976, *J. chem. Phys.*, **65**, 570.

[10] Wertheim, M. S., 1976, *J. chem. Phys.*, **65**, 2377.

[11] Kalos, M. H., Percus, J. K., and Rao, M., 1977, *J. statist. Phys.*, **17**, 111.

[12] Weeks, J. D., 1977, *J. chem. Phys.*, **67**, 3106.

[13] Mermin, N. D., 1965, *Phys. Rev.*, **137**, A1441.

[14] Ebner, C., Samm, W. F., and Stroud, D., 1976, *Phys. Rev.* A, **14**, 2264.

[15] Yang, A. J. M., Fleming, P. D., and Gibbs, J. H., 1976, *J. chem. Phys.*, **64**, 3732.

[16] Henderson, R. L., and Ashcroft, N. W., 1976, *Phys. Rev.* A, **13**, 859.

[17] Evans, R., and Schirmacher, W., 1978, *J. Phys.* C, **11**, 2437.

[18] Toxvaerd, S., 1971, *J. chem. Phys.*, **55**, 3116.

[19] Singh, Y., and Abraham, F. F., 1977, *J. chem. Phys.*, **67**, 537.

[20] Kirkwood, J. G., and Buff, F. P., 1949, *J. chem. Phys.*, **17**, 338.

[21] Davis, H. T., 1977, *J. chem. Phys.*, **67**, 3636.

[22] Hansen, J-P., and McDonald, I. R., 1976, *Theory of Simple Liquids* (Academic Press).

[23] Kohn, W., and Sham, L. J., 1965, *Phys. Rev.*, **140**, A1133.

[24] Saam, W. F., and Ebner, C., 1977, *Phys. Rev.* A, **15**, 2566.

[25] Hohenberg, P., and Kohn, W., 1964, *Phys. Rev.*, **136**, B864.

[26] Weeks, J. D., Chandler, D., and Andersen, H. C., 1971, *J. chem. Phys.*, **54**, 5237.

[27] Widom, B., 1972, *Phase Transitions and Critical Phenomena*, Vol. 2., edited by C. Domb and M. S. Green (Academic Press), p. 79.

[28] Buff, F. P., Lovett, R. A., and Stillinger, F. H., 1965, *Phys. Rev. Lett.*, **15**, 621.

[29] Ono, S., and Kondo, S., 1960, *Handbuch der Physik*, Vol. X, edited by S. Flügge (Springer Verlag), p. 134.

[30] van der Waals, J. D., 1894, *Z. phys. Chem.*, **13**, 657†.

[31] Lord Rayleigh, 1892, *Phil. Mag.*, **33**, 209.

[32] Bongiorno, V., and Davis, H. T., 1975, *Phys. Rev.* A, **12**, 2213.

[33] Abraham, F. F., 1975, *J. chem. Phys.*, **63**, 157.

[34] Salter, S. J., and Davis, H. T., 1975, *J. chem. Phys.*, **63**, 3295.

[35] Evans, R., and Kumaravadivel, R., 1976, *J. Phys.* C, **9**, 1891.

[36] Barker, J. A., and Henderson, D., 1967, *J. chem. Phys.*, **47**, 4714.

[37] Upstill, C. E., and Evans, R., 1977, *J. Phys.* C, **10**, 2791.

[38] Lee, J. K., Barker, J. A., and Pound, G. M., 1974, *J. chem. Phys.*, **60**, 1976.

[39] Telo da Gama, M. M., and Evans, R., 1979, *Molec. Phys* (in the press).

[40] Buff, F. P., and Lovett, R. A., 1968, *Simple Dense Fluids* edited by H. L. Frisch and Z. W. Salsburg (Academic Press), p. 17.

[41] Buff, F. P., 1955, *J. chem. Phys.*, **23**, 419.

[42] Toxvaerd, S., 1975, *Statistical Mechanics*, Vol. 2, edited by K. Singer (The Chemical Society), p. 256.

[43] Co, K. U., Kozak, J. J., and Luks, K. D., 1977, *J. chem. Phys.*, **66**, 1002.

[44] Toxvaerd, S., 1976, *J. chem. Phys.*, **64**, 2863.

[45] Leng, C. A., Rowlinson, J. S., and Thompson, S. M., 1977, *Proc. R. Soc.* A, **358**, 267.

[46] Lekner, J., and Henderson, J. R., 1977, *Molec. Phys.*, **34**, 333.

[47] Miyazaki, J., Barker, J. A., and Pound, G. M., 1976, *J. chem. Phys.*, **64**, 3364.

[48] Rao, M., and Levesque, D., 1976, *J. chem. Phys.*, **65**, 3233.

[49] Chapela, G. A., Saville, G., Thompson, S. M., and Rowlinson, J. S., 1977, *J. chem. Soc. Faraday Trans.* II, **73**, 1133.

[50] Hill, T. L., 1956, *Statistical Mechanics* (McGraw-Hill), section 39.

[51] Barker, J. A., and Henderson, D., 1976, *Rev. mod. Phys.*, **48**, 587.

[52] Abraham, F. F., Schreiber, D. E., and Barker, J. A., 1975, *J. chem. Phys.*, **62**, 1958.

[53] Abraham, F. F., 1977, *Comments in Solid St. Phys.*, **7**, 159.

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† J. S. Rowlinson has translated the original van der Waals paper into English. This will appear in: *J. statist. Phys.*

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[54] Cahn, J. W., 1961, *Acta metall.*, **9**, 795.
[55] Abraham, F. F., 1976, *J. chem. Phys.*, **64**, 2660.
[56] Cahn, J. W., 1966, *Acta metall.*, **14**, 1685.
[57] Langer, J. S., Bar-on, M., and Miller, H. D., 1975, *Phys. Rev.* A, **11**, 1417.
[58] Cook, H. E., 1970, *Acta metall.*, **18**, 297.
[59] Bhatia, A. B., 1977, in *Liquid Metals, 76*, edited by R. Evans and D. A. Greenwood (Inst. of Phys. Conf. Series No. 30), p. 21.
[60] Jhon, M. S., Desai, R. C., and Dahler, J. S., 1978, *Chem. Phys. Lett.*, **56**, 151.
[61] Croxton, C. A., 1978, in *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley), p. 42.
[62] Pastor, R. W., and Goodisman, J., 1978, *J. chem. Phys.*, **68**, 3654.
[63] Abraham, F. F., 1975, *J. chem. Phys.*, **63**, 1316.
[64] Evans, R., 1974, *J. Phys.* C, **7**, 2808.
[65] Gray, C. G., and Gubbins, K. E., 1975, *Molec. Phys.*, **30**, 179.
[66] Haile, J. M., Gray, C. G., and Gubbins, K. E., 1976, *J. chem. Phys.*, **64**, 2569.
[67] Ebner, C., and Saam, W. F., 1975, *Phys. Rev.* B, **12**, 923.
[68] Atkins, K. R., 1953, *Can. J. Phys.*, **31**, 1165.
[69] Sullivan, D. E., and Stell, G., 1977, *J. chem. Phys.*, **67**, 2567.
[70] Saam, W. F., and Ebner, C., 1978, *Phys. Rev.* A, **17**, 1768.
[71] Singh, Y., and Abraham, F. F., 1977, *J. chem. Phys.*, **67**, 5960.
[72] Abraham, F. F., 1978, *J. chem. Phys.*, **68**, 3713.
[73] Navascués, G., 1979, *Rep. Prog. Phys.* (to be published).
[74] Yang, A. J. M., Fleming, P. D., and Gibbs, J. H., 1977, *J. chem. Phys.*, **67**, 74.
[75] Jhon, M. S., Desai, R. C., and Dahler, J. S., 1978, *J. chem. Phys.*, **68**, 5615.
[76] Zittartz, J., 1967, *Phys. Rev.*, **154**, 529.
[77] Evans, R., and Telo da Gama, M. M., 1979, *Molec. Phys.* (in the press).
[78] Lu, B. C., and Rice, S. A., 1978, *J. chem. Phys.*, **68**, 5558.
[79] Schofield, P., *Chem. Phys. Lett.* (in the press).

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