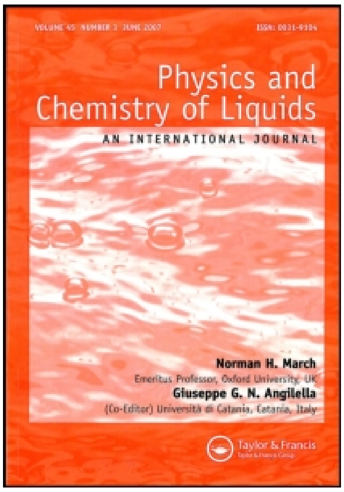

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A MICROSCOPIC GENERALIZATION OF BERNOULLI'S EQUATION TO INCLUDE LOW-ORDER DENSITY GRADIENTS

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A microscopic generalization of Bernoulli's equation is established by appealing to low-order density gradient theory of an inhomogeneous liquid. This theory, used earlier to relate surface energy, bulk compressibility and the thickness of the liquid surface, is here generalized to embrace the case in which the inhomogeneous fluid is subjected to a velocity gradient to simulate the case of steady flow. Finally the theory is extended to include non-steady flow and contact is again established with Bernoulli's equation.

KEY WORDS: Bernoulli equation, density gradients, non-steady flow.

1 INTRODUCTION

For problems of both fundamental and technological interest, such as the flow of liquids round obstacles, or the motion of bubbles in a molten mixture, the equations of hydrodynamics afford a valuable starting point. While they are known to provide, say in a bulk liquid, a correct description of liquid behaviour at long time and large distances (equivalent to small wavenumbers), they are not appropriate to treat phenomena which involve distances of the order of atomic dimensions. One such property is liquid surface energy σ. This has been known, since the early work of Frenkel, to relate to bulk liquid isothermal compressibility K_T via the thickness l of the liquid-vapour interface:

$$\sigma K_T \sim l. \tag{1.1}$$

The distance l, for liquids far from the critical point, is of the order of oneÅ, as is clear, for instance, from Table II of the paper by Egelstaff and Widom[1].

To give a microscopic derivation of the relation (1.1), Bhatia and March[2] (BM) therefore used low-order density gradient expansions, based on the atomic number density profile, $\rho(z)$ say, through the planar metal liquid-vapour interface. As background to the present study, let us rewrite their Eq. (7) for the chemical potential μ, with inclusion of an external potential energy $U(z)$, as

$$\mu - U(z) = \mu[\rho(z)] - A[\rho(z)]\rho''(z) - \tfrac{1}{2}A'[\rho(z)]\rho'(z)^2. \tag{1.2}$$

This equation stems from writing the free energy of a non-uniform assembly in terms of a local free energy density $\psi(\mathbf{r})$ as $F = \int \psi(\mathbf{r})d\mathbf{r}$. Gradient expansion of $\psi(\mathbf{r})$ then yields, for a flat interface of area a in the xy plane in the external potential energy $U(z)$:

$$F = \tilde{a}\left[\int_a^b \psi(z)\,dz + \int_a^b \rho(z)U(z)\,dz\right] \tag{1.3}$$

where, as in BM,

$$\left.\begin{aligned} \psi(z) &= \psi[\rho(z)] + \tfrac{1}{2}A[\rho(z)]\rho'(z)^2; \\ A(\rho) &= (k_BT/6)\int r^2 c(r,\rho)\,d\mathbf{r} \end{aligned}\right\} \tag{1.4}$$

In Eq. (1.3), a and b define the boundaries of the system of volume V say. The quantity $\psi(\rho)$ in Eq. (1.4) is the free energy density of a uniform system of density ρ, while $c(r,\rho)$ is the Ornstein-Zernike direct correlation function of such a homogeneous phase. One can usefully think of $c(r,\rho)$ as subsuming the essential information about the intermolecular forces into the quantity $A(\rho)$. This is what is then required to generate the inhomogeneous density profile $\rho(z)$ from the Euler-Lagrange equation (1.2) of the variation principle $\delta F = 0$. One can view the chemical potential μ in Eq. (1.2) as the Lagrange multiplier entering the variational problem in order to take care of the normalization of the density profile $\rho(z)$. Finally, in Eq. (1.2), $\mu(\rho)$ is the chemical potential of a uniform system of density ρ while

$$A'(\rho) = \frac{\partial A(\rho)}{\partial \rho}; \; \mu(\rho) = \frac{\partial \psi(\rho)}{\partial \rho}. \tag{1.5}$$

To complete this discussion of the background to the present work, let us note:

(i) For external potential $U(z)$ put to zero in Eq. (1.2), BM stress that this equation is then equivalent to the constancy of the pressure P across the inhomogeneity (see Eq. (2.5) below) and

(ii) That the surface energy σ, again for $U = 0$, is obtained by integrating the above equation expressing the constancy of P though the interface to find

$$\sigma = \int_a^b A[\rho(z)]\,\rho'(z)^2\,dz, \tag{1.6}$$

a result which can be traced back to van der Waals.

We turn immediately to effect the generalization of the above microscopic theory to include steady flow.

2 GENERALIZATION OF CHEMICAL POTENTIAL AND PRESSURE EQUATIONS TO INCLUDE STEADY FLOW, CHARACTERIZED BY VELOCITY $v(z)$ PARALLEL TO (xy) PLANE OF INTERFACE

We turn from the above summary of the treatment of a system in equilibrium to deal with a steady state situation. This implies that there are mechanisms to remove momentum and energy from the system, when a steady flow is imposed by external means.

To be quite specific, we consider steady flow parallel to the (xy) plane of the interface of the inhomogeneous system under consideration. Then we must add a kinetic energy K, written in terms of a local kinetic energy $k(\underset{\sim}{r})$ as $K=\int k(\underset{\sim}{r})\,d\underset{\sim}{r}$, or for the flat interface considered:

$$K=\tilde{a}\tfrac{1}{2}M\int \rho(z)\,v(z)^2\,dz \tag{2.1}$$

where M is the molecular mass. Here we have simulated steady flow parallel to the interface by the velocity $v(z)$ in Eq. (2.1).

It is clear that minimizing $F+K$ with respect to variations in the density profile then yields a new equation for the Lagrange multiplier μ accounting for the constraint of normalization of $\rho(z)$ in the permitted density variations: namely

$$\mu=U(z)+\tfrac{1}{2}Mv^2(z)+\mu[\rho(z)]-\tfrac{1}{2}(\rho'(z))^{-1}\frac{d}{dz}[A[\rho(z)]\,\rho'(z)^2], \tag{2.2}$$

the last term in Eq. (2.2) involving rewriting the terms in Eq. (1.2) in A and A' as shown. In Eq. (2.2) $A(\rho)$ is as defined in Eq. (1.5), the inhomogeneous density $\rho(z)$ now replacing ρ.

Multiplying Eq. (2.2) by $\rho'(z)$ we now rewrite the various terms as follows:

$$\rho'\mu=\frac{d}{dz}(\mu\rho(z)):\rho'U(z)=\frac{d}{dz}(\rho U)-\rho\frac{dU}{dz}:$$

$$\tfrac{1}{2}M\rho' v^2(z)=\tfrac{1}{2}M\left[\frac{d}{dz}(\rho v^2)-\rho\frac{d}{dz}v^2(z)\right]:$$

$$\rho'\mu[\rho(z)]=\rho'(z)\frac{d\psi(\rho)}{d\rho}=\frac{d}{dz}\psi(\rho(z)), \tag{2.3}$$

and hence, from Eq. (2.2) times $\rho'(z)$ one finds

$$\frac{d}{dz}[\mu\rho(z) - \rho U - \tfrac{1}{2}M\rho v^2 - \psi(\rho(z)) + \tfrac{1}{2}A[\rho(z)]\rho'(z)^2] = -\rho(z)\frac{dU(z)}{dz} - \tfrac{1}{2}\rho M\frac{d}{dz}v^2(z). \qquad (2.4)$$

One immediately has a limiting check on Eq. (2.4) in that, if one puts the external potential energy $U(z)$ and the flow term $v(z)$ to zero simultaneously then evidently the RHS is zero and one has

$$\frac{d}{dz}[\mu\rho(z) - \psi(\rho(z)) + \tfrac{1}{2}A[\rho(z)]\rho'(z)^2] = 0. \qquad (2.5)$$

The expression in the square bracket in Eq. (2.5) is the pressure P in Eq. (9) of BM and evidently Eq. (2.5) is a statement of the constancy of P across the interface.

It seems then natural to define a generalized pressure $P(z; U, v)$ as the square bracket in Eq. (2.4) and therefore to write

$$\frac{d}{dz}P(z; U, v) = -\rho(z)\frac{dU(z)}{dz} - \tfrac{1}{2}\rho M\frac{d}{dz}v^2(z). \qquad (2.6)$$

It can now be noted that in the limit of an incompressible fluid, for which ρ is maintained constant, the RHS of Eq. (2.6) becomes the exact differential $-d/dz\,[\rho U + \tfrac{1}{2}\rho M v^2]$, and Eq. (2.6) reduces to

$$\frac{d}{dz}\{P[z; U, v] + \rho U(z) + \tfrac{1}{2}\rho M v^2(z)\} = 0 \qquad (2.7)$$

which is a statement of Bernoulli's theorem.

Evidently then, in the present microscopic framework, Eq. (2.4), or equivalently Eq. (2.6), represents the desired generalization of Bernoulli's theorem.

Let us finally effect the extension to a non-steady flow. The hydrodynamic generalization to this situation is set out by Sommerfeld[3].

3 GENERALIZATION TO INCLUDE NON-STEADY FLOW

Let us follow Sommerfeld and work with a velocity potential ϕ defined by

$$v = -\operatorname{grad}\phi. \qquad (3.1)$$

We next adopt the procedure of Bloch[4,5] who, however, it should be stressed, was concerned with the hydrodynamic theory of an inhomogeneous degenerate electron gas. Nevertheless, his method is readily adapted to the present classical inhomogeneous fluid.

Bloch obtained the equation of motion for the fluid, again from a variation principle, by writing

$$\delta \int_{t_1}^{t_2} L\,dt = 0 \tag{3.2}$$

with the Lagrangian L given by

$$L = M \int \rho \frac{\partial \phi}{\partial t} d\underset{\sim}{r} - H \tag{3.3}$$

where H is the energy of the fluid in motion. H involves the kinetic energy $K = \int k(\underset{\sim}{r})\,d\underset{\sim}{r}$ introduced above, and with the appropriate adaptation to the classical liquid one then finds, in the non-steady state:

$$M \frac{\partial \phi}{\partial t} = \tfrac{1}{2} M\,(\mathrm{grad}\,\phi)^2 + \text{chemical potential terms as before} \tag{3.4}$$

The equation of continuity has evidently also to be obeyed, and reads

$$\frac{\partial \rho}{\partial t} = \mathrm{div}\,(\rho\,\mathrm{grad}\,\phi) \tag{3.5}$$

In the steady state it is evident that $\partial\rho/\partial t = 0$. Also, if we then take the limit of an incompressible fluid in the steady state we find

$$\mathrm{div}(\mathrm{grad}\,\phi) = 0 \tag{3.6}$$

since the density ρ in this limit is constrained to be constant.

It remains only to make contact with the Bernoulli equation for non-steady flow, as formulated, for instance, in the book by Sommerfeld[3]. His Eq. (14) on page 89 reads

$$\mathrm{grad}\left(-\rho \frac{\partial \phi}{\partial t} + \frac{M\rho v^2}{2} + P + U\rho \right) = 0 \tag{3.7}$$

where we have here again used U as an external potential energy, in contrast to his definition. This requires then the factor multiplying U in Eq. (3.7).

Instead of the Sommerfeld result (3.7) the desired microscopic extension of the Bernoulli equation for non-steady flow reads, as a generalization of Eq. (2.6):

$$\frac{d}{dz} P(z; U, v) = -\rho(z) \frac{dU(z)}{dz} - \tfrac{1}{2}\rho M \frac{d}{dz}(\mathrm{grad}\,\phi)^2 + \frac{d}{dz}\left\{ \rho(z) \frac{\partial \phi(z,t)}{\partial t} \right\}. \tag{3.8}$$

For the case when ρ is the held constant, Eq. (3.8) reduces to

$$\frac{d}{dz}\left\{ -\rho \frac{\partial \phi(z,t)}{\partial t} \right\} + \frac{M\rho}{2}\left(\frac{\partial \phi}{\partial z} \right)^2 + U\rho + P = 0, \tag{3.9}$$

which corresponds to the special case of Sommerfeld's generalization of Bernoulli's result in Eq. (3.7) above when one is dealing with planar geometry and density variations restricted to be perpendicular to the (xy) plane.

4 SUMMARY

The present microscopic theory is based on a low-order density gradient expansion. This is expressed in terms of (a) the bulk classical liquid Ornstein-Zernike direct correlation function $c(r, \rho)$, determining the function $A(\rho)$ through Eq. (1.4) and (b) the density profile $\rho(z)$ in the inhomogeneous fluid under discussion. This leads to Eq. (2.4), which represents the appropriate generalization of Bernoulli's equation, which is for an incompressible liquid under steady flow conditions. Equation (2.4) is a direct consequence of the chemical potential Eq. (2.2), which is in turn characterized by the bulk liquid chemical potential $\mu(\rho)$ and the function $A(\rho)$ discussed immediately above.

In principle, therefore, $\rho(z)$ can be calculated for the inhomogeneous fluid from knowledge of bulk fluid properties plus the vapour density; from Eq. (2.2) with $U = v = 0$. In steady flow, the above information must, of course, be supplemented by knowledge of $v(z)$, connected to the new profile, $\rho(z; v)$ say, by the continuity equation (3.5) in the case when $\partial\rho/\partial t$ is put equal to zero.

Since we referred to Bloch's hydrodynamic theory of an inhomogeneous degenerate electron gas in setting up the generalization of Eq. (2.2) for non-steady flow conditions, it is relevant as an example in that same context to note that Brown and March[6] were able to solve the analogue of Eq. (2.2) for $U = v = 0$ for the electron density profile. This in turn enabled the surface tension σ of a simple liquid metal to be calculated from the analogue of Eq. (1.6), Eq. (1.1) thereby being regained, with an explicit, though naturally approximate, expression for the surface thickness of the electronic spill-out from the liquid metal surface.

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References

1. P. A. Egelstaff and B. Widom, *J. Chem. Phys.*, **53**, 2667 (1970).
2. A. B. Bhatia and N. H. March, *J. Chem. Phys.*, **68**, 1999 (1978).
3. A. Sommerfeld, Mechanics of Deformable Bodies (Academic: New York) 1950.
4. F. Bloch, *Zeits für Physik*, **81**, 363 (1933).
5. See, for instance, the summary in N. H. March, Self-Consistent Fields in Atoms (Pergamon:Oxford) 1975, page 118.
6. R. C. Brown and N. H. March, *J. Phys.*, **C6**, L363 (1973); see also *Physics Reports*, **24C**, 77 (1976).