Quantum statistical mechanical equations for inhomogeneous fluids II

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Abstract. A quantum analogue of the classical first BBGKY equation, derived in a previous paper for the ground-state liquid surface, is extended to finite temperatures. This 'force-expectation' equation expresses the vanishing of the spatial average value through the surface of the force experienced by a single particle. A companion 'pressure-expectation' equation, expressing the zero value of the averaged normal pressure, is also recognised. A test of the force-expectation equation for a boson liquid surface has proved successful, and suggests the value of the equation as a discriminant for approximations to the radial distribution function in the surface, rather than for the surface structure itself.

1. Introduction

In a previous paper (Buchan 1975, to be referred to as I), a proof was given for the existence of an exact ground-state quantum analogue of the classical first Bogolyubov–Born–Green–Kirkwood–Yvon (BBGKY) equation. This latter equation may be written:

$$G_c(z_1) = kT\frac{dn(z_1)}{dz_1} - \int d^3r_{12}\frac{z_{12}}{r_{12}}\frac{dV}{dr_{12}}n^{(2)}(z_1, r_{12}) = 0 \tag{1}$$

and is an expression of the static mechanical equilibrium of a plane fluid interface, in the normal (z) direction. In contrast, our quantum counterpart is the same equation in integral form, i.e.

$$\int dz\, G(z) = 0, \tag{2}$$

where $G(z)$ is the analogue of (1), and is defined below. Equation (2) can be interpreted (see I) as a 'force expectation-value' equation. That is, it states that the equivalence to zero of the *expectation* value of the force per particle, spatially averaged through the interface, is the new equilibrium condition.

In the present paper two new developments are reported. First the extension of the force-expectation equation to general (excited) states of the liquid–vapour system is given. The existence of a collateral pair of equations for the interface is then established. Their physical significances are discussed in the conclusions. Secondly we report in detail a successful test of the force-expectation equation for the ground state

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surface of a boson liquid. This test was carried out during a variational calculation of the surface energy of an artificial mass-3 boson liquid, required in the evaluation of the surface tension γ_3^F of ^{3}He (Buchan and Clark 1977b).

2. Extension of the force-expectation equation

In I the validity of the force-expectation equation ((2) above) was demonstrated only for the ground state $\psi_0(r_1, \ldots, r_N)$ of an N-particle system, with the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + U(r_1, \ldots, r_N) \tag{3}$$

where $U(N) = \sum_{i>j=1}^{N} V(r_{ij})$ contains only internal two-body interactions. The geometry assumed for the system was that of a simple cuboidal enclosure, thickness $2a$ in the z direction, with two free surfaces placed symmetrically about the mid-(x, y) plane.

The aim here is to show the validity of equation (2) applied to general, excited states $\psi_n(r_1, \ldots, r_N)$ of the system, for which the pressure $P_n \neq 0$ and a vapour of finite density exists. In order to avoid repetition of the proof given in I, we quote the following result (equation (16)) given there:

$$2P_n a = \int_{-a}^{a} P_{zz} \, dz \tag{4}$$

where

$$P_{zz}(z_1) = 2t_z(z_1) + z_1 f(z_1)$$

$$t_z(z_1) = N \int \psi_n^+ \left(-\frac{\hbar^2}{2m} \frac{\delta^2}{\delta z_1^2} \right) \psi_n \, d^3 r_{2\ldots N} \tag{5}$$

$$f(z_1) = \int \frac{z_{12}}{r_{12}} \frac{dV}{dr_{12}} n^{(2)}(z_1, r_{12}) \, d^3 r_{12}. \tag{6}$$

Here $n^{(2)}(z_1, r_{12})$ is the usual pair distribution function, $t_z(z_1)$ is the z component of the kinetic energy density, and $f(z_1)/n(z_1)$ may be interpreted as the net force on a particle at $z = z$ in the z direction, due to the interatomic potential $V(r)$. In order to simplify notation subscripts 'n' are omitted from functional quantities (e.g. $t_z(z)$) in the text.

Now partial integration of (4) gives

$$\int_{-a}^{a} dz \, zG(z) = 4at_z(a) - 2P_n a \tag{7}$$

where $t_z(a)$ is the bulk (isotropic) value of (5) in the vapour phase, and $z = 0$ locates the mid-plane of our slab-symmetrical system. Since $zG(z)$ is clearly a symmetric function, we derive for the upper half-slab:

$$\int_{0}^{a} dz \, zG(z) = (2t_z(a) - P_n)a. \tag{8}$$

Using arguments similar to those given in I, $G(z)$ may be written as a function $G(t)$ of a new variable $t = z - c$, where $t = 0$ is fixed with respect to the inhomogeneous

surface layers. We now hold 'a' fixed, but macroscopically large, so that the right-hand side of equation (8) is constant. By allowing the plane $z = c$ of the surface to vary, the arguments given in the appendix of I may again be applied. (This follows since the value of the function $h(c) = \int_0^a \mathrm{d}z \, z G(z - c)$ given there need only, in general, be a constant for the proof to remain valid.) Hence we have for a free surface on bulk fluid

$$\int \mathrm{d}z\left(\frac{\mathrm{d}}{\mathrm{d}z}(2t_z(z)) - f(z)\right) = 0 \tag{9}$$

where integration extends across the inhomogeneous layers.

In I (equation (23)), the existence of another identity was established for general states ψ_n of the system. This is written

$$\int \mathrm{d}z_1(P_n - 2t_z(z_1) + F(z_1)) = 0 \tag{10}$$

where

$$F(z_1) = \frac{1}{2}\int \mathrm{d}^3 r_{12}\frac{z_{12}^2}{r_{12}}\frac{\mathrm{d}V}{\mathrm{d}r_{12}}n^{(2)}(z_1, r_{12}). \tag{11}$$

Clearly at any finite temperature T, both (9) and (10) above apply with their integrand terms replaced by ensemble averages. Thus in the identities (9) and (10) we recognise a pair of equations valid for any state of the free liquid–vapour interface. The physical interpretation of these equations is discussed in the conclusions.

3. Testing the force-expectation equation

In a separate paper (Buchan and Clark 1977b) results have been reported for a calculation of the ground-state surface energy $\gamma_3^F(0)$ of ^{3}He. A prerequisite to the evaluation of γ_3^F was a variational theory for the ground-state surface of an artificial mass-3 boson (M3B) liquid. A description of the bulk M3B liquid may be found in Buchan and Clark (1977a); that of its free surface in Buchan and Clark (1977b). Briefly the results are as follows.

The bulk liquid was found to have a variational minimum energy $\epsilon_3 = -3 \cdot 82$ K at a density $n_b = 0 \cdot 0164$ Å^{-3}, using a Jastrow product wavefunction. A Lennard-Jones potential was employed with modified strength and range parameters. For the free surface γ_3^B was minimised with respect to the parameter β in a simple Fermi profile $n(z) = n_b[1 + \exp(\beta z)]^{-1}$; and the parameters β_1, β_2, γ in a generalised Fermi profile:

$$n(z) = n_b(1 + \exp P(z))^{-1}$$
$$P(z) = \left(\frac{\beta_1\, e^{\gamma z} + \beta_2\, e^{-\gamma z}}{e^{\gamma z} + e^{-\gamma z}}\right)z \tag{12}$$

The simple Fermi profile gave $\gamma_3^B = 0 \cdot 195$ erg cm^{-2} at $\beta = 0 \cdot 7$ Å^{-1}, while for (12) we obtained $\gamma_3^B = 0 \cdot 191$ erg cm^{-2}, with $\beta_1 = 0 \cdot 9$ Å^{-1}, $\beta_2 = 0 \cdot 48$ Å^{-1}, $\gamma = 0 \cdot 39$ Å^{-1}.

Simultaneous with the computation of γ_3^B itself, the opportunity was taken to test equation (9). Rather than evaluate $\mathrm{d}(2t_z(z))/\mathrm{d}z$ through the interface, which would necessitate computation of complicated third-order derivatives, direct integration can

be performed on the first term of equation (9), casting it in the form

$$\int_{-\infty}^{\infty} dz\, f(z) = \int_{-\infty}^{\infty} dz\, \frac{d}{dz}(2t_z(z)) = -2t_b. \tag{13}$$

Here t_b is a component of the bulk liquid kinetic energy density, and can easily be shown to satisfy $t_b = \frac{1}{3}n_b\langle T\rangle/N$, where $\langle T\rangle/N$ is the expectation value of the kinetic energy per particle in bulk liquid, and has the value $\langle T\rangle/N = 10\cdot34\,K/N$ in the present calculation (Buchan and Clark 1977a). Hence our equation predicts

$$\int_{-\infty}^{\infty} dz\, f(z) = -0\cdot1131\ K\ \text{Å}^{-3}. \tag{14}$$

Integration of the left-hand side of (14) was performed numerically, using equation (6) and the *ansatz*

$$n^{(2)}(r_1, r_2) = n(r_1)n(r_2)g_b(r_{12}; \tfrac{1}{2}(n(z_1)+n(z_2))) \tag{15}$$

i.e. the radial distribution function $g(r; n)$ is that appropriate to the mean of the densities at r_1 and r_2. In practice $g_b(r)$ was computed for a mesh of densities, spacing $n_b/20$, through the interface, using the α equation of Chang and Cohen (1973), with a constant value of α. Further details may be found in Buchan (1976).

The result obtained for the simple Fermi profile is

$$\int dz\, f(z) = -0\cdot1175\ K\ \text{Å}^{-3} \tag{16}$$

which differs from (14) by less than 4%. While this agreement is good, a more striking feature of our computations was that (16) remained constant (to within $\sim0\cdot002\%$) as the profile shape was varied. Thus moving from the variational minimum of the simple Fermi to that of the generalised Fermi profile, a drop of only $0\cdot002\%$ was observed.

Simultaneously, however, significant changes in $f(z)$ itself occurred. These effects are illustrated in figure 1, which shows $\bar{n}(z) = n(z)/n_b$ and $f(z)$ for the minimum of the
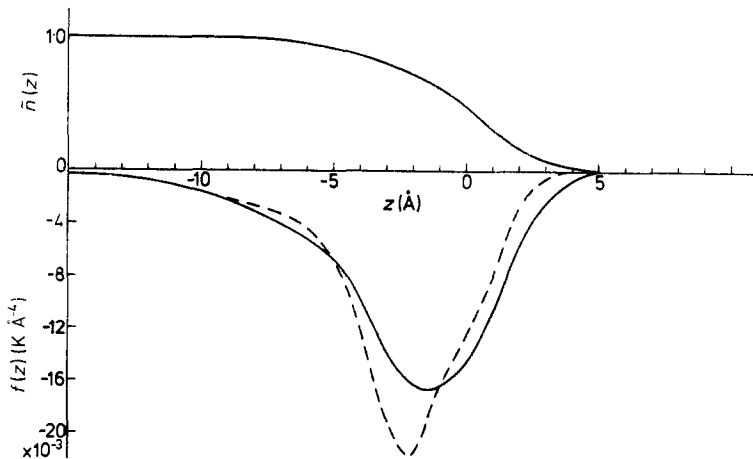

Figure 1. Various functions through the M3B surface with generalised Fermi profile. Upper and lower full curves: $\bar{n}(z)$ and $f(z)$, respectively, at surface energy minimum. Broken curve: $f(z)$, with β_1 increased to $1\cdot5\ \text{Å}^{-1}$.

generalised Fermi profile. Also shown is $f(z)$ for the same profile, but with β_1 displaced from $0.9\,\text{Å}^{-1}$ to $1.5\,\text{Å}^{-1}$. For this displacement (16) remained true to within about 0.002%, which is certainly better than any error in our calculations resulting from solution of the α equation for $g(r; n)$. But at the same time the minimum in $f(z)$ dropped from $-0.0167\,\text{K Å}^{-4}$ to $-0.0215\,\text{K Å}^{-4}$, i.e. by about 30%.

The conclusion then is that as the profile is varied, $f(z)$ restructures itself significantly in the surface in order to keep (16) fixed. This result was not anticipated, since we expected the difference between the left- and right-hand sides of (14) to be zero (or very small) only in the region of the surface energy minimum. Thus our equation is not, apparently, useful as an alternative method of locating values for structural parameters (e.g. β) of the surface. However, the degree of agreement between (14) and (16) should serve as an overall indication of the accuracy of the distribution functions $g(r_1, r_2)$ used through the surface. Thus only (16) suffers from errors in the latter. For example, the difference of only around 4% between (14) and (16) above suggests the satisfactory nature of the *ansatz* (15) when combined with $g(r, n)$ derived from solution of the α equation at all densities n through the interface.

4. Conclusions

In I a physical interpretation of equation (2) above was given in terms of the expectation value of a force per particle. This equation has now been shown to apply to any (finite temperature) state of a liquid–vapour interface, thus completing the quantum analogy of equation (1). Simultaneous with equation (2), however, we recognise the validity of a companion identity, namely equation (10) above.

It is possible to place a similar interpretation on equation (10), but expressed in terms of the components of pressure, rather than the components of force exerted on an individual particle. Thus $2t_z(z)$ is analogous to $n(z)\,kT$, the kinetic component of the pressure at a point z; and $F(z)$ is identical with the interparticle potential term in the classical pressure tensor (see Kirkwood and Buff 1949, equation (10)). In other words the integrand of (10) may be interpreted as a quantum underpressure in the normal direction. Then whereas in the classical case the underpressure vanishes everywhere, our equation implies that in the quantum case only its expectation value vanishes.

A test of the force-expectation equation (equation (9)) has shown that its value is invariant under quite large changes in surface structure, and hence that the equation is not a useful determinant of surface profile shape. It does nevertheless serve as an overall indicator of the accuracy of proposed approximations for $g(r_1, r_2)$ through the interface, and could be used to discriminate between different approximation schemes. It would be interesting to conduct a similar trial on the 'pressure-expectation equation' (equation (10)), though this would necessitate direct evaluation of $t_z(z)$ through the surface. With the Jastrow approximation for the boson surface (e.g. Buchan and Clark 1977b) this would involve the three-particle distribution function ($g(r_1, r_2, r_3)$), thus implicating further approximations in the calculation.

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