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Quantum statistical mechanical equations for inhomogeneous fluids

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Abstract. By adaptation and extension of the Brout–Nauenberg quantum surface tension theory, exact quantum statistical mechanical equations for inhomogeneous fluid regions are derived. For free helium surfaces and the ^3He – ^4He interface in the zero-pressure ground state, the equation appears as an analogue of the classical first BBGKY equation, in integral form. For thin films, a similar equation is derived containing a wall potential term. Such equations could be used to determine parameters relevant to the variation of the number density, or the z component of the kinetic energy density, with the normal coordinate z . Excited states and their ensemble averages are also considered and a quantum analogue of the classical virial equation of state is derived.

1. Introduction

Much recent interest has been shown in the surface phenomena of liquid ^4He , and of dilute solutions of ^3He in ^4He . Theories on the surface tension of ^4He (eg Brout and Nauenberg 1958, Bowley 1970, Chang and Cohen 1973) and on the surface states of adsorbed ^3He on ^4He (eg Lekner 1970) have shown clearly the need for fairly detailed knowledge of the variation of the number density $n(z)$ through the liquid–vapour interface (z is a coordinate perpendicular to the interface). This problem can be handled with reasonable success using parameterized forms for $n(z)$, the parameters being determined by applying variational techniques to the surface tension γ (see Shih and Woo 1973, Chang and Cohen 1973). However, to date no rigorous quantum theoretical equation useful in determining the density profile exists.

In this paper it is shown that a quantum analogue of the classical first Bogolyubov–Born–Green–Kirkwood–Yvon (BBGKY) equation

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

exists, in integral form, for the zero-pressure ground state ($T = 0$, pressure $P_0 = 0$) of a quantum fluid. Here $n^{(2)}(r_1, r_2)$ is the usual pair distribution function. We assume only the existence of an N -particle ground-state eigenfunction $\psi_0(r_1, \dots, r_N)$ of the Hamiltonian

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

The potential $U(N) = \sum_{i>j=1}^N V(r_{ij})$ includes only internal two-body interactions, in order to preserve the simple analogy with (1). The effect of an external potential of the form $w(z)$ per particle is also considered.

For excited eigenstates ψ_n with pressure $P_n \neq 0$ our equation does not apply, but a corresponding equation is derived. A quantum theoretic analogue of the classical virial equation of state

$$P = nkT - \frac{1}{6} \int d^3r r \frac{dV}{dr} n^{(2)}(r), \tag{3}$$

(two-body interactions only) where n is the bulk number density, is easily derived as a corollary. All equations are independent of particle statistics.

In the case of classical statistical mechanics, where particle momenta p_i are permitted to vary independently of position coordinates r_i in phase space, the probability of a given particle distribution is proportional to the Boltzmann factor $\exp(-U(N)/kT)$. Equation (1) is then obtained by simple differentiation of the expression

$$n(r_1) = \frac{N \int \exp(-U(N)/kT) d^3r_{2\dots N}}{\int \exp(-U/kT) d^3r_{1\dots N}} \tag{4}$$

and has been used by Berry and Reznik (1971) to determine $n(z)$ approximately. It can also be shown that (1) is equivalent to the condition $P = \text{constant}$ in the normal direction across the liquid-vapour interface, ie to mechanical equilibrium of the interface in the normal sense.

In the quantum statistical mechanical case, the momenta $p_i \equiv (\hbar/i)\nabla_i$ are uniquely determined by the system configuration via $\psi(r_1, \dots, r_N)$. Differentiation of the expression

$$n(r_1) = N \int \psi^\dagger \psi d^3r_{2\dots N} \tag{5}$$

(ψ is taken to be normalized such that $\int \psi^\dagger \psi d^3r_{1\dots N} = 1$ throughout the text) then leads to nothing new. Derivation of an analogue of (1) is a more complicated procedure, which we give below. In its simplest form our ground-state equation is applicable to the free surfaces of pure ^4He and ^3He . With suitable modifications it may be applied to the free surface of dilute (<6.4%) mixtures of ^3He in ^4He , and to the ^3He - ^4He interface. For thin films an independent equation is derived.

2. The pressure tensor equation

We consider a cuboidal enclosure with sides of length b , and thickness $2a$, containing N atoms in a configuration with slab symmetry about the mid-plane, as shown in figure 1.

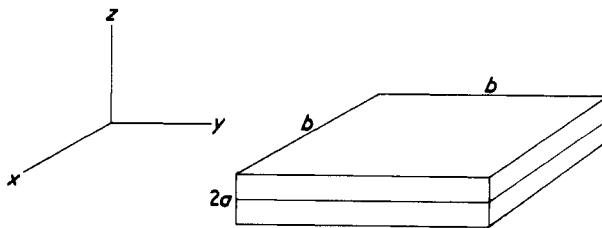


Figure 1. The slab enclosure containing N atoms, with two planar liquid-vapour interfaces and symmetry about the mid-plane. The origin of axes is arbitrary.

In the limit $b/a \rightarrow \infty$ (and $N \rightarrow \infty$) perimeter effects disappear and two planar surfaces of area b^2 result. Effectively, the lower half-slab contains a mirror image in the mid-plane of the system in the upper half-slab. The wavefunctions ψ contain all the information regarding bulk (liquid and vapour) and surface structure. Thus ψ_0 represents the ground state of the system ($T = 0, P_0 = 0$) with a vapour phase absent and two liquid–vacuum interfaces of area b^2 . The ψ_n represent excited states with non-zero vapour densities. The volume $V = 2ab^2$ will be considered fixed on passing from one state to another and N , of course, varies directly with b^2 to simulate physically real conditions. Where appropriate, the liquid slab will be assumed to be sufficiently thick for bulk liquid conditions to prevail around the mid-plane.

In principle some potential $w(z)$ per particle, symmetric about the mid-plane, should be included in the Hamiltonian (2) to force the system to take up the desired configuration. This is particularly true of the ‘ground state’, since otherwise a state of lower energy could always be attained by allowing the system to take up the configuration of a spherical drop of liquid. The effects of such a potential, and justification for its omission here, are considered in § 5.

The energy of the system is

$$E_n(V, A) = \int_V \psi_n^\dagger H \psi_n d^3r_{1\dots N} \quad (6)$$

where H is given by (2) and

$$V = 2ab^2, \quad A = 2b^2. \quad (7)$$

We define a variable scale factor λ such that $r_i = \lambda r'_i$ ($i = 1$ to N). It can then be shown that

$$\lambda \frac{dE_n}{d\lambda} = \int \psi_n^\dagger \lambda \frac{\partial H}{\partial \lambda} \psi_n d^3r_{1\dots N} = - \int_V d^3r_1 (p_{xx}(r_1) + p_{yy}(r_1) + p_{zz}(r_1)) \quad (8)$$

where

$$p_{xx}(r_1) = N \int \psi_n^\dagger \left(-\frac{2\hbar^2}{2m} \frac{\partial^2}{\partial x_1^2} - x_1 \frac{\partial U}{\partial x_1} \right) \psi_n d^3r_{2\dots N} \quad (9)$$

and the components p_{yy}, p_{zz} of the pressure tensor are similarly defined. Note that in order to simplify notation we have omitted the subscript ‘ n ’ on these components, and likewise for other quantities in the text. We also have:

$$\lambda \frac{dE_n}{d\lambda} = \left(\frac{\partial E_n}{\partial V} \right)_A \lambda \frac{dV}{d\lambda} + \left(\frac{\partial E_n}{\partial A} \right)_V \lambda \frac{dA}{d\lambda} = -3VP_n + 2A\gamma_n \quad (10)$$

where $P_n = -(\partial E_n / \partial V)_A$ is the system pressure, and $\gamma_n = (\partial E_n / \partial A)_V$ the coefficient of surface tension appropriate to state ψ_n .

A separate expression for the surface tension coefficient γ_n is now derived, in the limit $b/a \rightarrow \infty$:

$$\gamma_n = \lim_{b/a \rightarrow \infty} \left(\frac{\partial E_n}{\partial b} \right)_V \left(\frac{\partial A}{\partial b} \right)_V^{-1} = \frac{1}{4b} \int \psi_n^\dagger \left(\frac{\partial H(b, V)}{\partial b} \right) \psi_n d^3r_{1\dots N} \quad (11)$$

where (7) has been used to re-express E_n and A as functions of b and V . We have also used the coordinate transformation: $x_i = bx'_i, y_i = by'_i, z_i = 2az'_i = (V/b^2)z'_i$ to express H as

a function of b and V . With these scale factors the primed coordinates range over a unit cube. Hence

$$\gamma_n = \frac{1}{2b^2} \int d^3r [p_{zz}(\mathbf{r}) - \frac{1}{2}(p_{xx}(\mathbf{r}) + p_{yy}(\mathbf{r}))]. \quad (12)$$

Using (8), (10) and (12) we find

$$P_n V = \int_V p_{zz}(\mathbf{r}_1) d^3r_1. \quad (13)$$

A corresponding equation for a spherical volume of fluid has been derived by Brout and Nauenberg (1958), whose work has provided much of the stimulus for this research. In their case, however, the choice of a spherically-symmetric system impeded progress beyond their equation (25) (the equation corresponding to (13)). Indeed their planar surface tension expression is somewhat more easily derived from (11) above (see Buchan 1974).

Now

$$p_{zz}(\mathbf{r}_1) = p_{zz}(z_1) = 2t_z(z_1) + z_1 f(z_1)$$

where

$$t_z(z_1) = N \int \psi_n^\dagger \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z_1^2} \right) \psi_n d^3r_{2\dots N} \quad (14)$$

is the z component of the kinetic energy density, and

$$f(z_1) = -N \int \psi_n^\dagger \frac{\partial U}{\partial z_1} \psi_n d^3r_{2\dots N} = \int \frac{z_{12}}{r_{12}} \frac{dV}{dr_{12}} n^{(2)}(z_1, \mathbf{r}_{12}) d^3r_{12}. \quad (15)$$

The identity $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int \psi_n^\dagger \psi_n d^3r_{3\dots N}$ has been used in (15). Using $V = \int_V d^3r_1$, (13) becomes

$$2P_n a = \int p_{zz} dz \quad (16)$$

where integration extends across the thickness $2a$ of the slab.

3. The ground state

For the ground state with pressure $P_0 = 0$, corresponding to the end-point of the liquid-vapour coexistence line for ${}^3\text{He}$ and ${}^4\text{He}$, (16) gives

$$\int_{-\infty}^{\infty} dz z G(z) = 0 \quad (17)$$

where $G(z) = d/dz(2t_z(z)) - f(z)$, by partial integration of the first term in p_{zz} . The limits of integration have been extended since both terms in $G(z)$ vanish outside the fluid; they also vanish deep inside the fluid. We note now that nowhere have we specified the origin of axes, ie $z = 0$ is arbitrary. Choosing the mid-plane as the plane $z = 0$, it is clear that $G(z)$ is an antisymmetric function for the slab. Thus $zG(z)$ is symmetric and so we derive for the upper half-slab

$$\int_0^{\infty} dz z G(z) = 0. \quad (18)$$

Further, it is physically evident that $G(z)$ is a function whose value in the plane $z = z_1$ is determined *not* by the absolute value of z_1 but by the location of that plane relative to the rest of the surface layers. Hence $G(z)$ may be written as a function $G(t)$ of a new variable t , where $t = 0$ is a plane fixed with respect to the inhomogeneous surface layers. It can then be shown, using the arbitrariness of the thickness of the slab of fluid, while assuming this to be sufficiently macroscopic for bulk conditions to prevail at $z = 0$, that (18) implies $\int_0^\infty dz G(z) = 0$. A proof is given in the appendix. Hence we have for a free surface on bulk fluid

$$\int dz \left(\frac{d}{dz} (2t_z(z)) - f(z) \right) = 0 \quad (19)$$

where integration extends across the inhomogeneous layers, ie those regions where $G(z) \neq 0$.

This equation represents a quantum analogue of (1), in integral form, with $d/dz(2t_z(z))$ the analogue of $d/dz(n(z)kT)$. We note that by simple intuition an equation $G(z) = 0$ might be written as the analogue of (1). However, while such an equation satisfies (19), it is in no way implied by it. This point is further discussed in our conclusions.

4. Excited states of the system

For states ψ_n with non-zero pressure P_n , the right-hand side of (13) contains the term

$$\begin{aligned} \int_V d^3r_1 z_1 f(z_1) &= \iint d^3r_1 d^3r_2 z_1 \frac{z_{12}}{r_{12}} \frac{dV}{dr_{12}} n^{(2)}(z_1, r_{12}) \\ &= \iint d^3r_2 d^3r_1 z_2 \frac{z_{21}}{r_{21}} \frac{dV}{dr_{21}} n^{(2)}(z_2, r_{21}) \\ &= - \iint d^3r_1 d^3r_2 z_2 \frac{z_{12}}{r_{12}} \frac{dV}{dr_{12}} n^{(2)}(z_1, r_{12}). \end{aligned} \quad (20)$$

Hence

$$\int_V d^3r_1 z_1 f(z_1) = - \int_V d^3r_1 F(z_1)$$

where

$$F(z_1) = \frac{1}{2} \int d^3r_{12} \frac{z_{12}^2}{r_{12}} \frac{dV}{dr_{12}} n^{(2)}(z_1, r_{12}). \quad (21)$$

Thus (13) becomes

$$\int_V d^3r_1 P_n = \int_V d^3r_1 (2t_z(z_1) - F(z_1)). \quad (22)$$

The integrand terms are even functions of z for our slab-symmetric system when $z = 0$ locates the mid-plane, and so

$$\int dz_1 (2t_z(z_1) - F(z_1) - P_n) = 0 \quad (23)$$

where integration extends across a single liquid-vapour interface. At any finite temperature T this relation clearly obtains if the terms of the integrand are replaced by their ensemble averages.

In the case of a homogeneous system, ie when ψ_n describes a uniform distribution of matter, we may remove the integral signs from (22). Further, owing to isotropy, z_{12} may equally well be replaced by x_{12} or y_{12} in $F(r_1)$. Hence

$$P_n = 2t_B - \frac{1}{6} \int d^3r r \frac{dV}{dr} n^{(2)}(r) \quad (24)$$

where

$$t_B = \frac{1}{3} N \int \psi_n^\dagger \left(-\frac{\hbar^2}{2m} \nabla_1^2 \right) \psi_n d^3r_{2\dots N}$$

is a component of the bulk kinetic energy density. Expressing (24) as an ensemble average we obtain our quantum analogue of (3):

$$P = \langle P_n \rangle = \langle 2t_B \rangle - \frac{1}{6} \int d^3r r \frac{dV}{dr} \langle n^{(2)}(r) \rangle. \quad (25)$$

This equation has been derived independently by McLellan (1974). Similar techniques were employed there, but the arguments were confined to homogeneous systems.

5. Inclusion of external potential

We consider the effects of an external potential per particle of the form $w(z)$, where $z = 0$ locates the mid-plane of the slab. $w(z)$ will be an even function of z , so that the upper and lower half-slabs remain 'mirror image' systems. Thus $w(z) = mg|z|$ is the gravitational potential, and $w(z) = -m\alpha/|z|^3$ represents the van der Waals potential in the field of a solid substrate at $z = 0$.

The extra term $\sum_{k=1}^N w(z_k)$ in the Hamiltonian (2) results in the addition of a term $-zn(z) dw/dz$ to $p_{zz}(r)$ in both (8) and (12). For the ground state (§ 3), (18) remains valid, with $G(z)$ now containing $n(z) dw/dz$. However, $G(z)$ may only be written as a function $G(t)$ if dw/dz is independent of z . Thus a modified form of (18) may only be derived for the gravitational potential. The equation is, for the upper half-slab:

$$\int dz \left(\frac{d}{dz} (2t_z(z)) - f(z) + mgn(z) \right) = 0 \quad (26)$$

where integration extends now across the entire system, since the effect of $w(z)$ will be to render even the 'bulk' inhomogeneous, with the integrand of (26) non-zero not only in the surface layers.

We stated in § 2 that a potential $w(z)$ was required to force the system to take up the assumed slab-symmetric configuration. In that case, assuming a gravitational-type potential, the correct equation is of the form (26) rather than of the form (19). However, the external force field need only be sufficiently strong to give the slab-symmetric configuration less energy than any other configuration with lower surface area. Clearly, in the case of an arbitrarily large system the external potential may be made arbitrarily weak, since we may allow the surface to volume ratio to become vanishingly small (by using the limits $a, b \rightarrow \infty$, while simultaneously permitting $b/a \rightarrow \infty$ as required for (11)).

Hence in the thermodynamic limit ($N \rightarrow \infty$), we may neglect the external potential ($g \rightarrow 0$) and retrieve equation (19).

In the case where g is considered to remain finite (eg the earth's gravitational potential), (26) is the relevant equation; but then the corresponding classical equation (1) also contains the term $mg n(z)$ and the analogy is sustained. Even then, when the surface thickness is of the order of a few atomic diameters, the quantity $f(z)/n(z)$, representing the net pull on a particle due to the van der Waals forces, will be considerably larger in the surface regions than mg , so that the latter force may to good approximation be neglected.

The van der Waals potential, representing the attractive effects of a wall at $z = 0$ for the upper half-slab, is important in the case of helium films (here, of unspecified thickness). For such a potential, with $dw(z)/dz$ a function of z , we must content ourselves with the equation (17), since an equation of the type (26) cannot be derived. Thus for the ground state of a helium film on a wall at $z \leq 0$ giving rise to a potential $w(z)$ per particle:

$$\int_0^{\infty} dz z \left(\frac{d}{dz} (2t_z(z)) - f(z) + n(z) \frac{dw}{dz} \right) = 0. \quad (27)$$

For excited states, we add the term $-zn(z) dw/dz$ to the integrand of (23).

6. Application to ^3He - ^4He mixtures

For a system containing N_3 ^3He and N_4 ^4He atoms ($N_3 + N_4 = N$) the Hamiltonian becomes

$$H = -\frac{\hbar^2}{2m_4} \sum_{i=1}^{N_4} \nabla_i^2 - \frac{\hbar^2}{2m_3} \sum_{j=N_4+1}^N \nabla_j^2 + \sum_{i>j=1}^N V(r_{ij}). \quad (28)$$

All of the results of § 2 can be shown to apply, with appropriate quantities split into their 'partial' components. Thus $p_{zz}(\mathbf{r})$ becomes $p_{zz,4}(\mathbf{r}) + p_{zz,3}(\mathbf{r})$ where the partial pressure tensor component $p_{zz,4}(\mathbf{r})$ is defined as:

$$\begin{aligned} p_{zz,4}(\mathbf{r}) &= 2t_{z,4}(\mathbf{r}) + zf_4(z) \\ t_{z,4}(z_1) &= N_4 \int \psi_n^\dagger \left(-\frac{\hbar^2}{2m_4} \frac{\partial^2}{\partial z_1^2} \right) \psi_n d^3 r_{2\dots N} \\ f_4(z_1) &= \int d^3 r_{12} \frac{z_{12}}{r_{12}} \frac{dV}{dr_{12}} (n_{44}^{(2)}(z_1, \mathbf{r}_{12}) + n_{43}^{(2)}(z_1, \mathbf{r}_{12})) \end{aligned} \quad (29)$$

and $p_{zz,3}(\mathbf{r})$ is similarly defined.

$\psi_n(\mathbf{r}_1, \dots, \mathbf{r}_{N_4}; \mathbf{r}'_1, \dots, \mathbf{r}'_{N_3})$ describes the appropriate configuration of the system and must, of course, in principle be written in a form which is symmetric with respect to the interchange of bosons, and antisymmetric for the fermions. Choice of ψ_n by itself poses a fundamental problem. Note that in the pair distribution function $n_{\alpha\beta}(r_i, r_j)$ the first coordinate r_i is that of the atomic species α , and r_j that of atomic species β .

For the ground state of the system, with $P_0 = 0$, there are two distinct cases of interest. The first occurs for $x = N_3/N < 6.4\%$, when mixing is complete; and the second for $x > 6.4\%$ when phase separation occurs. In the unseparated case, it is easily shown that all of the considerations of § 3 apply, and hence equation (19), the terms of the integrand being expressed as sums of partial terms.

In the phase-separated case, equation (17) applies. $\psi_0(r_1, \dots, r_{N_4}; r'_1, \dots, r'_{N_3})$ then describes a configuration of the system with a dilute (6.4%) ^3He -in- ^4He layer sandwiched symmetrically between two pure ^3He layers. Thus we have in the upper half-slab a ^3He - ^4He interface, and a free liquid-vacuum interface on pure ^3He . Equation (19) is already known to apply to the latter. If x is sufficiently large, we may assume both the mixed layer and the pure ^3He layer to be sufficiently macroscopic for bulk conditions to prevail well inside each, ie $G(z) = 0$. Then we have

$$\int_0^c dz z G(z) = 0$$

where $z = c$ is a plane deep in the pure ^3He layer where $G(z) \simeq 0$. The same arguments outlined above, after equation (18), can then be used to show that (19) also applies to the interface between the separated phases.

For excited states of the two-component system, (23) is valid in the inhomogeneous case if the pair distribution function in $F(z_1)$ is expressed as the sum over species

$$n^{(2)}(z_1, r_{12}) = \sum_{\alpha, \beta} n_{\alpha\beta}^{(2)}(z_1, r_{12}).$$

For a homogeneous mixture, (25) again obtains with the same condition on $n^{(2)}(r)$, ie $n^{(2)}(r) = \sum_{\alpha, \beta} n_{\alpha\beta}^{(2)}(r)$.

7. Conclusions

A quantum analogue of the classical first BBGKY integro-differential equation has been derived, and has been shown to apply to the liquid-vacuum interface of pure ^3He and ^4He , and of ^3He - ^4He mixtures, in the ground state. It is also valid for the interface of phase-separated mixtures at $T = 0$. The equation appears in integral form, ie if the classical equation is written $G_c(z) = 0$ for all z through the interface, then our equation is written $\int G(z) dz = 0$ where $G(z)$ is a quantum statistical mechanical counterpart of $G_c(z)$, and integration extends across the inhomogeneous layers. We pointed out in §3 that an equation $G(z) = 0$ was in no way implied by our arguments regarding the zero-pressure ground state. It might nevertheless be speculated by the reader that even in the quantum case the particles should distribute themselves in the interface such that 'mechanical equilibrium' is attained, ie $G(z) = 0$ everywhere. However, the correct distribution of particles must be that which, first and foremost, yields the minimum surface free energy.

In the classical case ($T \neq 0$), minimization of the surface free energy is assured by use of the Boltzmann factor $\exp(-U/kT)$. The equation (1), representing mechanical equilibrium, is consistent with the use of this distribution factor. In the quantum-mechanical case, the correct distribution of particles in the ground state, given by ψ_0 , is obtained by solving the many-particle wave equation :

$$H\psi_0 = E_0\psi_0 \tag{30}$$

with the appropriate boundary conditions. Thus (30) together with the correct ground-state boundary conditions must yield the ground-state wavefunction ψ_0 , and the corresponding distribution of particles must be that which yields the minimum surface energy. But our equations (19) and (26) were derived by equating two expressions for

the surface energy, namely (8) and (12). Built into both these expressions was the eigenvalue equation (30), and the subsequent development to equations (19) and (26) employed the correct ground-state boundary conditions, ie $\psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \rightarrow 0$ whenever any of $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ range well outside the liquid; and $P_0 = 0$.

Thus we see that the ground-state distribution of particles $\psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is implicitly included in our equations. Working within the framework of quantum theory, we have shown that $\int dz G(z) = 0$ is proven for the ground state, but that the classical-like condition of 'mechanical equilibrium' ($G(z) = 0$) is not necessarily true.

Indeed the nature of our result conforms with the familiar pattern of quantum mechanics, in which classical relations among dynamical variables, other than those having purely the significance of energy, become relations among corresponding expectation values. For, writing our equation (26) in the form $N^{-1} \int dz G(z) = 0$, we see that it becomes a relation among expectation values. Thus $\int dz mgn(z)/N$ represents the expectation value of the external force per particle, and $N^{-1} \int dz f(z)$ the expectation value of the net internal force per particle. The latter follows since $f(z)/n(z)$ is interpretable as the net van der Waals force on a particle at $z = z$ in the z direction. Similarly $N^{-1} \int dz (d/dz)(2t_z(z))$ may be interpreted as the expectation value of the net 'kinetic' force per particle.

This type of parallelism between classical and quantum mechanics is found, in the context of dynamics, in the laws of motion of a quantum system, given by Ehrenfest's theorem (eg Messiah 1958). Thus while the classical laws of motion of a particle are purely local, ie apply *at each point* in the path of the particle, they become in quantum mechanics relations between corresponding expectation values. Similarly our equations (19) and (26) are, in the context of static equilibrium, the expectation-value analogues of the corresponding classical equations.

For thin films an equation $\int dz zG(z)$ has been shown to apply, where $G(z)$ includes an external (wall) potential term. Our equations, while clearly less useful in practice than a relation $G(z) = 0$, can in principle be used in determining the variation of the wavefunction, and hence the number density $n(z)$, with the normal coordinate z . Thus they might be used to determine a parameter in any suggested wavefunction. Alternatively, they relate the normal component $t_z(z_1)$ of the kinetic energy density to the variation of the pair distribution function $n^{(2)}(z_1, \mathbf{r}_{12})$ through the surface layers. However, as in the classical case, the pair distribution function $n(\mathbf{r}_1, \mathbf{r}_2)$ in inhomogeneous regions, appearing in $G(z)$, needs to be specified as a prerequisite to use of the equations. Thus approximation schemes such as those appearing in the theories of Shih and Woo (1973) and Chang and Cohen (1973) might be employed, or the wavefunction might be written in the modulated Jastrow form (for bosons):

$$\psi = \prod_{i>j=1}^N f(r_{ij}) \prod_{k=1}^N h(z_k)$$

with $f(r_{ij})$ a known function, and $h(z)$ to be determined from the above equations.

In any case, the validity of our equations is not confined to ${}^3\text{He}/{}^4\text{He}$ systems, but extends to any system with Hamiltonian of the form (2), or any mixed system with the Hamiltonian (28).

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Appendix

We consider the equation (18) with $G(z)$ containing the extra term $n(z) dw/dz = mgn(z)$ arising from a gravitational-type potential, $w(z) = mgz$. For such a potential it is clear that $G(z)$ may be written as a function $G(t)$ of a new variable t , where $t = 0$ is a plane fixed relative to the surface regions, eg such that $n(t = 0) = \frac{1}{2}n_L$ where n_L is the liquid number density. Further, all quantities in $G(z)$ will be independent of N for a sufficiently large system, ie independent of the thickness of the half-slab if we choose to vary this with N .

Writing $t = z - c$ and $G(z) = G(t)$, (18) becomes

$$h(c) = \int_0^{\infty} dz z G(z - c) = 0$$

which is true for all c , assuming only that c is sufficiently large for essentially 'bulk' conditions to prevail at $z = 0$. Hence

$$\frac{dh}{dc} = 0 = - \int_0^{\infty} dz z \frac{dG}{dz} = \int_0^{\infty} dz G(z)$$

by partial integration, and (19) is obtained by putting $w(z) = 0$.

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