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To cite this article: A J Archer 2006 *J. Phys.: Condens. Matter* **18** 5617

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Dynamical density functional theory for dense atomic liquids

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Received 6 April 2006, in final form 25 April 2006

Published 2 June 2006

Online at stacks.iop.org/JPhysCM/18/5617

Abstract

Starting from Newton's equations of motion, we derive a dynamical density functional theory (DDFT) applicable to atomic liquids. The theory has the feature that it requires as input the Helmholtz free energy functional from equilibrium density functional theory. This means that, given a reliable equilibrium free energy functional, the correct equilibrium fluid density profile is guaranteed. We show that when the isothermal compressibility is small, the DDFT generates the correct value for the speed of sound in a dense liquid. We also interpret the theory as a dynamical equation for a coarse grained fluid density and show that the theory can be used (making further approximations) to derive the standard mode coupling theory that is used to describe the glass transition. The present theory should provide a useful starting point for describing the dynamics of inhomogeneous atomic fluids.

1. Introduction

Classical density functional theory (DFT) [1, 2] allows one to determine the equilibrium ensemble average one body density profile of a fluid in the presence of an arbitrary external field $V^{\text{ext}}(\mathbf{r})$. As DFT is based upon a minimization principle for a free energy density functional [1, 2], one can use DFT to calculate thermodynamic quantities such as surface tensions. In practice, DFT is not exact because the exact free energy functional is generally unknown. Nonetheless, the theory has proved to be very powerful; there exist in the literature a large number of rather accurate approximations for the Helmholtz free energy functional [2] and equilibrium DFT is a well developed theoretical framework for describing static fluid phenomena [3]. Given this body of knowledge, constructing a dynamical density functional theory (DDFT), that requires as input the same Helmholtz free energy functional as the equilibrium DFT, for the dynamics of the one body density profile of an inhomogeneous fluid that is out of equilibrium is a very appealing idea. In recent work [4, 5], Marconi and Tarazona derived an equation of motion for the one body density profile of a fluid of particles with stochastic equations of motion (i.e. for colloidal fluids). This theory has been

applied to a number of problems [6–15] and has proved to be rather accurate where comparison with the results of Brownian dynamics simulations has been made. The question that then naturally arises is whether one can construct a DDFT for a fluid of particles with motion governed by Newton's equations. In a recent paper, Chan and Finken [16] proved that the non-equilibrium one body density $\rho(\mathbf{r}, t)$ is uniquely determined for a given time dependent external field $V^{\text{ext}}(\mathbf{r}, t)$, where t is the time. They showed that in general the DDFT requires a non-equilibrium free energy functional that is not the same as the free energy functional entering equilibrium DFT and that the (approximate) theory of Marconi and Tarazona [4, 5] can be obtained by taking the adiabatic limit of the 'exact' DDFT [16]. Given that very little is known about the non-equilibrium free energy functional, this makes practical calculations of the fluid dynamics in the Chan–Finken framework somewhat difficult.

In the present paper, we derive an approximate DDFT for a fluid of particles described by Newton's equations of motion (i.e. an atomic fluid, as opposed to a colloidal fluid). Our DDFT requires as input the equilibrium free energy functional and therefore makes practical calculation of the fluid dynamics much more tractable. The theory is an approximate one, and in the form derived here is most relevant to dense fluids. On applying the theory, in the limit that the ratio of the heat capacities $C_P/C_V \rightarrow 1$ (i.e. when the isothermal compressibility is small), we find that the DDFT reproduces the correct value for the speed of sound waves in a dense liquid, and predicts the length scale over which sound waves are attenuated. We also interpret the theory as one for a coarse grained one body density profile, $\bar{\rho}(\mathbf{r}, t)$, and from these equations we derive (making a number of further approximations) the mode coupling theory (MCT) that is used to describe the glass transition [3, 17]. We believe that the present theory will provide a useful starting point for determining the dynamics of the one body density profile of an atomic fluid.

This paper is laid out as follows. In section 2, starting from Newton's equations of motion, we derive equations of motion for the ensemble average fluid one body density profile $\rho(\mathbf{r}, t)$. In section 3, we introduce a number of approximations in order to close the equations derived in section 2. This closure yields us the DDFT. In section 4 we apply the DDFT in two particular situations: (i) sound waves propagating in a fluid and (ii) dynamic two point correlation functions, where we derive the MCT. Finally, in section 5 we draw some conclusions.

2. Density equations of motion

The (classical) density operator for a system of N identical particles is $\hat{\rho}(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t))$, where $\mathbf{r}^N = \{\mathbf{r}_i(t)\}$ is the set of position coordinates of the particles and the index i labels the different particles. In Fourier space, the density operator is given by

$$\rho_{\mathbf{k}}(t) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \hat{\rho}(\mathbf{r}, t) = \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}. \quad (1)$$

Newton's equations of motion for these particles are

$$\ddot{\mathbf{r}}_i(t) = -\frac{1}{m} \frac{\partial V(\mathbf{r}^N, t)}{\partial \mathbf{r}_i}, \quad (2)$$

where m is the mass of a particle and

$$V(\mathbf{r}^N, t) = \sum_i V^{\text{ext}}(\mathbf{r}_i, t) + \frac{1}{2} \sum_{i,j} v(\mathbf{r}_i(t) - \mathbf{r}_j(t)) \quad (3)$$

is the potential energy of the system. We assume this is composed of one body contributions due to the external potential $V^{\text{ext}}(\mathbf{r}, t)$ and a sum of pair interactions between the particles; $v(r)$

is the pair potential. Following Zaccarelli *et al* [18], we take two derivatives of equation (1) to obtain

$$\ddot{\rho}_{\mathbf{k}}(t) = - \sum_i (\mathbf{k} \cdot \dot{\mathbf{r}}_i(t))^2 e^{i\mathbf{k} \cdot \mathbf{r}_i} + \sum_i i(\mathbf{k} \cdot \ddot{\mathbf{r}}_i(t)) e^{i\mathbf{k} \cdot \mathbf{r}_i}. \quad (4)$$

We can express the potential energy as

$$V(\mathbf{r}^N, t) = \sum_i \int \frac{d\mathbf{k}}{(2\pi)^3} V_{\mathbf{k}}^{\text{ext}}(t) e^{-i\mathbf{k} \cdot \mathbf{r}_i} + \frac{1}{2} \sum_{i,j} \int \frac{d\mathbf{k}}{(2\pi)^3} v_{\mathbf{k}} e^{-i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)}, \quad (5)$$

in an obvious notation. Differentiation gives

$$\frac{\partial V(\mathbf{r}^N, t)}{\partial \mathbf{r}_i} = \int \frac{d\mathbf{k}}{(2\pi)^3} V_{\mathbf{k}}^{\text{ext}}(t) (-i\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{r}_i}) + \sum_j \int \frac{d\mathbf{k}}{(2\pi)^3} v_{\mathbf{k}} (-i\mathbf{k} e^{-i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)}). \quad (6)$$

Combining equations (2), (4) and (6) we obtain the following equation [18]:

$$\begin{aligned} \ddot{\rho}_{\mathbf{k}}(t) = & - \sum_i (\mathbf{k} \cdot \dot{\mathbf{r}}_i(t))^2 e^{i\mathbf{k} \cdot \mathbf{r}_i} - \frac{1}{m} \sum_{i,j} \int \frac{d\mathbf{k}'}{(2\pi)^3} v_{\mathbf{k}'}(\mathbf{k} \cdot \mathbf{k}') e^{-i\mathbf{k}' \cdot (\mathbf{r}_i - \mathbf{r}_j)} e^{i\mathbf{k} \cdot \mathbf{r}_i} \\ & - \frac{1}{m} \sum_i \int \frac{d\mathbf{k}'}{(2\pi)^3} V_{\mathbf{k}'}^{\text{ext}}(t) (\mathbf{k} \cdot \mathbf{k}') e^{-i\mathbf{k}' \cdot \mathbf{r}_i} e^{i\mathbf{k} \cdot \mathbf{r}_i}. \end{aligned} \quad (7)$$

Using equation (1) this can be rewritten as

$$\begin{aligned} \ddot{\rho}_{\mathbf{k}}(t) = & - \sum_i (\mathbf{k} \cdot \dot{\mathbf{r}}_i(t))^2 e^{i\mathbf{k} \cdot \mathbf{r}_i} - \frac{1}{m} \int \frac{d\mathbf{k}'}{(2\pi)^3} v_{\mathbf{k}'}(\mathbf{k} \cdot \mathbf{k}') \rho_{\mathbf{k}-\mathbf{k}'}(t) \rho_{\mathbf{k}'}(t) \\ & - \frac{1}{m} \int \frac{d\mathbf{k}'}{(2\pi)^3} V_{\mathbf{k}'}^{\text{ext}}(t) (\mathbf{k} \cdot \mathbf{k}') \rho_{\mathbf{k}-\mathbf{k}'}(t). \end{aligned} \quad (8)$$

This equation is simply a generalization to the case with an external field of equation (8) in [18].

We transform equation (8) back into real space and obtain the following:

$$\begin{aligned} \ddot{\rho}(\mathbf{r}, t) = & - \sum_i \int \frac{d\mathbf{k}}{(2\pi)^3} (\mathbf{k} \cdot \dot{\mathbf{r}}_i(t))^2 e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r})} + \frac{1}{m} \nabla \cdot \int d\mathbf{r}' \hat{\rho}(\mathbf{r}, t) \hat{\rho}(\mathbf{r}', t) \nabla v(\mathbf{r} - \mathbf{r}') \\ & + \frac{1}{m} \nabla \cdot [\hat{\rho}(\mathbf{r}, t) \nabla V^{\text{ext}}(\mathbf{r}, t)]. \end{aligned} \quad (9)$$

Our interest is in ensemble average quantities. We therefore average in equation (9) over the ensemble of initial momenta and positions to obtain an equation of motion for the ensemble average one body density, $\rho(\mathbf{r}, t) = \langle \hat{\rho}(\mathbf{r}, t) \rangle$:

$$\begin{aligned} \ddot{\rho}(\mathbf{r}, t) = & - \left\langle \sum_i \int \frac{d\mathbf{k}}{(2\pi)^3} (\mathbf{k} \cdot \dot{\mathbf{r}}_i(t))^2 e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r})} \right\rangle + \frac{1}{m} \nabla \cdot \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}', t) \nabla v(\mathbf{r} - \mathbf{r}') \\ & + \frac{1}{m} \nabla \cdot [\rho(\mathbf{r}, t) \nabla V^{\text{ext}}(\mathbf{r}, t)], \end{aligned} \quad (10)$$

where $\langle \dots \rangle$ denotes the ensemble average and where $\rho^{(2)}(\mathbf{r}, \mathbf{r}', t) = \langle \hat{\rho}(\mathbf{r}, t) \hat{\rho}(\mathbf{r}', t) \rangle$ is the ensemble average, time dependent, two body distribution function. We now consider the first term on the right-hand side of equation (10). This contains the expression $\mathbf{k} \cdot \dot{\mathbf{r}}_i(t) = k \dot{r}_{i,\text{par}}(t)$, where $\dot{r}_{i,\text{par}}(t)$ is the component of the velocity of the i th particle in the direction of \mathbf{k} . We write $\dot{r}_{i,\text{par}}^2(t) = \langle \dot{r}_{i,\text{par}}^2 \rangle + \alpha_i(t)$, where $\alpha_i(t)$ is just the fluctuation of $\dot{r}_{i,\text{par}}^2(t)$ about its mean equilibrium value. Note also that the equilibrium quantity $\langle \dot{r}_{i,\text{par}}^2 \rangle = k_B T / m$, from equipartition. We may therefore re-write the first term on the right-hand side of equation (10) as follows:

$$\begin{aligned} \left\langle \sum_i \int \frac{d\mathbf{k}}{(2\pi)^3} (\mathbf{k} \cdot \dot{\mathbf{r}}_i(t))^2 e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r})} \right\rangle = & \int \frac{d\mathbf{k}}{(2\pi)^3} k^2 \left\langle \sum_i \alpha_i(t) e^{i\mathbf{k} \cdot \mathbf{r}_i} \right\rangle e^{-i\mathbf{k} \cdot \mathbf{r}} \\ & + \frac{k_B T}{m} \int \frac{d\mathbf{k}}{(2\pi)^3} k^2 \left\langle \sum_i e^{i\mathbf{k} \cdot \mathbf{r}_i} \right\rangle e^{-i\mathbf{k} \cdot \mathbf{r}} = B(\mathbf{r}, t) - \frac{k_B T}{m} \nabla^2 \rho(\mathbf{r}, t). \end{aligned} \quad (11)$$

In order to obtain the second line we have used equation (1) and defined

$$B(\mathbf{r}, t) \equiv \int \frac{d\mathbf{k}}{(2\pi)^3} k^2 \left\langle \sum_i \alpha_i(t) e^{i\mathbf{k} \cdot \mathbf{r}_i} \right\rangle e^{-i\mathbf{k} \cdot \mathbf{r}}. \quad (12)$$

Substituting equation (11) into (10) we obtain

$$\begin{aligned} \ddot{\rho}(\mathbf{r}, t) + B(\mathbf{r}, t) &= \frac{k_B T}{m} \nabla^2 \rho(\mathbf{r}, t) + \frac{1}{m} \nabla \cdot \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}', t) \nabla v(\mathbf{r} - \mathbf{r}') \\ &+ \frac{1}{m} \nabla \cdot [\rho(\mathbf{r}, t) \nabla V^{\text{ext}}(\mathbf{r}, t)]. \end{aligned} \quad (13)$$

This equation, taken together with equation (12), is still formally exact. We note that the right-hand side of this equation is simply the derivative of the first equation of the YBG hierarchy [3]. This means that at equilibrium the right-hand side of equation (13) is equal to zero and therefore at equilibrium $B(\mathbf{r}, t) = 0$. In the appendix we present an alternative derivation of equation (13), starting from the first equation of the BBGKY hierarchy [3]. The derivation gives us an alternative expression for $B(\mathbf{r}, t)$, that may provide further insight into the nature of this term.

3. The DDFT

Equation (13) is the starting point for our derivation of the DDFT. We make two approximations in equation (13) in order to render a closed and tractable DDFT. Our first assumption is the same as that used to derive the colloidal DDFT [4, 5, 7, 8]: we assume that the two particle correlations in the non-equilibrium fluid are the same as in an equilibrium fluid with the same one body density profile, i.e. we assume that we can apply the following sum rule, which is exact for an equilibrium fluid [7]:

$$-k_B T \rho(\mathbf{r}) \nabla c^{(1)}(\mathbf{r}) = \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') \nabla v(\mathbf{r}, \mathbf{r}'), \quad (14)$$

where $c^{(1)}(\mathbf{r})$ is the one body direct correlation function and is equal to the functional derivative of the excess (over ideal) part of the Helmholtz free energy functional [1, 2]:

$$c^{(1)}(\mathbf{r}) = -\beta \frac{\delta F_{\text{ex}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \quad (15)$$

We must also make an approximation for the term $B(\mathbf{r}, t)$ in equation (13). Since at equilibrium $B(\mathbf{r}, t) = 0$, the simplest approximation we can make is to assume $B(\mathbf{r}, t) \propto \dot{\rho}(\mathbf{r}, t)$. Making these two approximations we obtain our main result:

$$\frac{\partial^2 \rho(\mathbf{r}, t)}{\partial t^2} + \nu \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \frac{1}{m} \nabla \cdot \left[\rho(\mathbf{r}, t) \nabla \frac{\delta F[\rho(\mathbf{r}, t)]}{\delta \rho(\mathbf{r}, t)} \right], \quad (16)$$

where ν is an undetermined (collision) frequency. In general, we expect ν to be a (non-local) functional of the density $\rho(\mathbf{r}, t)$. We show below that when density modulations are small, then the collision frequency $\nu = k_B T / mD$, where D is the self-diffusion coefficient. F is the Helmholtz free energy functional:

$$F[\rho(\mathbf{r}, t)] = F_{\text{id}}[\rho(\mathbf{r}, t)] + F_{\text{ex}}[\rho(\mathbf{r}, t)] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}, t) \rho(\mathbf{r}, t), \quad (17)$$

where

$$F_{\text{id}}[\rho(\mathbf{r}, t)] = k_B T \int d\mathbf{r} \rho(\mathbf{r}, t) [\ln(\rho(\mathbf{r}, t) \Lambda^3) - 1] \quad (18)$$

is the ideal gas contribution to the free energy, and where Λ is the thermal de Broglie wavelength. We must emphasize that strictly speaking F is defined as a functional of the equilibrium ensemble average density profile $\rho(\mathbf{r})$. We are effectively assuming that we may use F as an approximation for the unknown dynamical free energy functional. It is important to note that at equilibrium, given a reliable approximation for F , equation (16) guarantees the exact equilibrium fluid density profile [7]. For the case when the potential energy $V(\mathbf{r}^N, t)$ also contains three body and higher body interactions, as we show in the appendix, one still obtains equation (16), making approximations equivalent to those made above. The argument used is somewhat similar to the approach used in [7] to generalize the DDFT of Marconi and Tarazona [4, 5] to the case with multi-body interactions.

In order to show that when density modulations are small the coefficient $\nu = k_B T / mD$, we consider a fluid in which a (small) number, n , of the particles are labelled in such a way that we can think of them as a different species of particles, without changing any of the interaction potentials between the particles. If at time $t = 0$ the n labelled particles are confined to a small volume near the origin ($\mathbf{r} = 0$), then in the limit $t \rightarrow \infty$ the density profile of these particles will be $\rho_l(r, t) = nG_s(r, t)$, where l denotes the labelled particles and $G_s(r, t)$ is the van Hove self-correlation function [3]. In this limit the one body density of the remaining particles $\rho(r, t) \simeq \rho_b$, where ρ_b is the bulk fluid density. It is known that in the limit $t \rightarrow \infty$ that [3]

$$G_s(r, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(\frac{-r^2}{4Dt}\right). \quad (19)$$

Using this result, together with equation (16) generalized to a two component fluid, we obtain the following after making a Taylor expansion of the excess Helmholtz free energy functional:

$$\frac{\partial^2 \rho_l(\mathbf{r}, t)}{\partial t^2} + \nu \frac{\partial \rho_l(\mathbf{r}, t)}{\partial t} = \frac{k_B T}{m} \nabla^2 \rho_l(\mathbf{r}, t) + \dots, \quad (20)$$

where \dots denotes terms of order ρ_l^2 , $\rho_l(\rho - \rho_b)$ and higher order terms. Furthermore, in the limit $t \rightarrow \infty$, $\dot{\rho}_l \gg \ddot{\rho}_l$, so we may neglect the $\ddot{\rho}_l$ term. Substituting equation (19) into equation (20) we obtain the result that $\nu = k_B T / mD$.

At this point, we note that in cases where the collision frequency ν is large, then $\nu \dot{\rho} \gg \ddot{\rho}$ and we may, in certain circumstances, approximate equation (16) by

$$\nu \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \frac{1}{m} \nabla \cdot \left[\rho(\mathbf{r}, t) \nabla \frac{\delta F[\rho(\mathbf{r}, t)]}{\delta \rho(\mathbf{r}, t)} \right]. \quad (21)$$

This is equivalent to the DDFT of Marconi and Tarazona [4, 5], which was derived for colloidal fluids (fluids of Brownian particles)—see also the discussion in [19].

4. Applications of the DDFT

Having argued for considering equation (16) as an approximation to the equation governing the dynamics of the particles, we now examine some of the consequences. The first case we consider is that of sound waves propagating in a dense fluid.

4.1. Sound waves in a dense liquid

We Taylor expand the excess Helmholtz free energy functional in terms of density modulations $\delta\rho(\mathbf{r}, t)$ about a uniform bulk density ρ_b (i.e. we write $\rho(\mathbf{r}, t) = \rho_b + \delta\rho(\mathbf{r}, t)$). Omitting terms

beyond $\mathcal{O}(\delta\rho^2)$ we obtain [2, 7]

$$F_{\text{ex}}[\rho(\mathbf{r}, t)] = F_{\text{ex}}[\rho_b] - c^{(1)}(\infty) \int d\mathbf{r} \delta\rho(\mathbf{r}, t) - \frac{k_B T}{2} \int d\mathbf{r} \int d\mathbf{r}' \delta\rho(\mathbf{r}, t) \delta\rho(\mathbf{r}', t) c^{(2)}(\mathbf{r} - \mathbf{r}'), \quad (22)$$

where $c^{(2)}(r)$ is the Ornstein–Zernike pair direct correlation function. Combining equation (22) with (16) we obtain [7]

$$\frac{\partial^2 \delta\rho(\mathbf{r}, t)}{\partial t^2} + v \frac{\partial \delta\rho(\mathbf{r}, t)}{\partial t} = \frac{k_B T}{m} \nabla^2 \delta\rho(\mathbf{r}, t) - \frac{k_B T \rho_b}{m} \nabla^2 \int d\mathbf{r}' \delta\rho(\mathbf{r}', t) \nabla c^{(2)}(\mathbf{r} - \mathbf{r}'), \quad (23)$$

where we have omitted terms of order $\delta\rho^2$ and higher. Sound waves correspond to the following fluid one body density profile:

$$\begin{aligned} \rho(\mathbf{r}, t) &= \rho_b + \delta\rho(\mathbf{r}, t) \\ &= \rho_b + \epsilon \exp[i(\mathbf{q} \cdot \mathbf{r} - \omega t)], \end{aligned} \quad (24)$$

where ϵ is the amplitude, which is assumed to be small compared to the bulk fluid density ρ_b and $|\mathbf{q}| = k + i\lambda^{-1}$. The speed of sound in the liquid $c_s = \omega/k$, and λ is the distance over which the amplitude of the sound is attenuated by a factor $1/e$. Substituting equation (24) into equation (23) we obtain

$$(-\omega^2 - i\omega v) \delta\rho = \left(-\frac{q^2 k_B T}{m} + \frac{q^2 \rho_b k_B T \hat{c}(q)}{m} \right) \delta\rho, \quad (25)$$

where $\hat{c}(q)$ is the Fourier transform of $c^{(2)}(r)$. Equating the real and imaginary parts on the left- and right-hand sides of equation (25) we obtain the dispersion relation

$$\omega^2(k) = \frac{k^2 k_B T}{m S(k)}, \quad (26)$$

and the following expression for the attenuation length:

$$\lambda(k) = \frac{2\omega}{vk}, \quad (27)$$

where we have used the fact that the fluid static structure factor $S(k) = (1 - \rho_b \hat{c}(k))^{-1}$ and we have assumed that $k \gg \lambda^{-1}$.

Sound waves correspond to the long wavelength limit. In this limit, $S(k) \simeq S(0) = \rho_b k_B T \chi_T$, i.e. proportional to the isothermal compressibility χ_T , yielding

$$c_s^2 = \frac{1}{\rho_b m \chi_T}. \quad (28)$$

The adiabatic speed of sound in liquids is known to be [3]

$$c_s^2 = \frac{\gamma}{\rho_b m \chi_T}, \quad (29)$$

where $\gamma = C_P/C_V$ is the ratio of the heat capacities. The reason that our expression (28) for c_s differs from the true value, given by equation (29), can be traced back to the approximation $B(\mathbf{r}, t) \simeq v \dot{\rho}(\mathbf{r}, t)$, used to obtain equation (16) from (13). In making this approximation we are effectively neglecting temperature fluctuations. However, the density fluctuations corresponding to sound waves occur on timescales too fast to reach isothermal conditions; sound wave fluctuations are an adiabatic processes. Using the fact that $C_P = C_V + T \chi_T \beta_V^2 / \rho_b$ [3], where β_V is the thermal pressure coefficient, we see that it is only at low temperatures and high densities, when χ_T is small, that $C_P \simeq C_V$, and equation (28) yields the correct value for c_s , in agreement with equation (29).

4.2. DDFT and MCT

Using DDFT (in various formulations) to describe the slow dynamics of fluids at state points near to the glass transition has been suggested by Kawasaki and co-workers [20–24]. In this section we show how the standard mode coupling theory (MCT) can be obtained from a temporally coarse grained DDFT, as opposed to the spatially coarse grained DDFT, described in [20]. Our approach, in principle, allows us to include the effects of external potentials in the MCT. The arguments in this section are to some extent equivalent to those made in [18].

Equation (16), as derived above, is an equation for the ensemble average fluid one body density profile, $\rho(\mathbf{r}, t)$. However, we may also interpret it as an equation for the time evolution of a coarse grained density profile, $\bar{\rho}(\mathbf{r}, t)$. For example, we define a temporally coarse grained density [8]:

$$\bar{\rho}(\mathbf{r}, t) = \int_{-\infty}^{\infty} dt' K(t - t') \hat{\rho}(\mathbf{r}, t'), \quad (30)$$

where $K(t)$ is a normalized function of finite width in time. Multiplying equation (9) by $K(t - t')$ and then integrating over t , we obtain an equation of the same form as equation (10) for the coarse grained density $\bar{\rho}(\mathbf{r}, t)$. This equation involves the coarse grained two body density distribution function:

$$\bar{\rho}^{(2)}(\mathbf{r}, \mathbf{r}', t) = \int_{-\infty}^{\infty} dt' K(t - t') \hat{\rho}(\mathbf{r}, t') \hat{\rho}(\mathbf{r}', t'). \quad (31)$$

If we assume further that we have coarse grained sufficiently that we can approximate the term involving $\bar{\rho}^{(2)}(\mathbf{r}, \mathbf{r}', t)$ using the sum rule (14), and that the coarse grained equivalent of $B(\mathbf{r}, t)$, $\bar{B} \simeq \nu \bar{\rho}$, then we obtain equation (16) as our equation of motion for the coarse grained density $\bar{\rho}(\mathbf{r}, t)$. We are effectively assuming that we can approximate the coarse grained free energy functional by the Helmholtz free energy functional entering equilibrium DFT—i.e. the free energy F in equation (17) is now a functional of the coarse grained density $\bar{\rho}(\mathbf{r}, t)$.

We now proceed to obtain the MCT, using a particular approximation for F , namely the Taylor expansion in equation (22). We will also assume for the time being that the external potential $V_{\text{ext}} = 0$. What follows is to some extent the argument of Kawasaki in [25]. Using equation (22) in equation (16) we find [7]

$$\begin{aligned} \frac{\partial^2 \bar{\rho}(\mathbf{r}, t)}{\partial t^2} + \nu \frac{\partial \bar{\rho}(\mathbf{r}, t)}{\partial t} - \frac{k_B T}{m} \nabla^2 \bar{\rho}(\mathbf{r}, t) \\ + \frac{k_B T}{m} \nabla \cdot \left[(\rho_b + \delta \bar{\rho}(\mathbf{r}, t)) \int d\mathbf{r}' \delta \bar{\rho}(\mathbf{r}', t) \nabla c^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b) \right] = 0. \end{aligned} \quad (32)$$

Fourier transforming equation (32) we obtain [7]

$$\ddot{\rho}_{\mathbf{k}}(t) + \nu \dot{\rho}_{\mathbf{k}}(t) = -\frac{k^2}{\beta m} \rho_{\mathbf{k}}(t) + \frac{\rho_b k^2}{\beta m} c_{\mathbf{k}} \rho_{\mathbf{k}}(t) + \frac{1}{\beta m} \frac{1}{(2\pi)^3} \int d\mathbf{k}' \mathbf{k} \cdot \mathbf{k}' \rho_{\mathbf{k}'}(t) c_{\mathbf{k}'} \rho_{\mathbf{k}-\mathbf{k}'}(t), \quad (33)$$

where $c_{\mathbf{k}}$ is the Fourier transform of the pair direct correlation function $c^{(2)}(r)$, obtained by taking two functional derivatives of $F[\bar{\rho}(\mathbf{r}, t)]$, and $\rho_{\mathbf{k}}(t)$ denotes the Fourier transform of $\delta \bar{\rho}(\mathbf{r}, t)$. We rewrite equation (33), in the form

$$\ddot{\rho}_{\mathbf{k}}(t) + \nu \dot{\rho}_{\mathbf{k}}(t) + \Omega_{\mathbf{k}}^2 \rho_{\mathbf{k}}(t) = \hat{R}_{\mathbf{k}}(t), \quad (34)$$

where $\Omega_{\mathbf{k}}^2 = k^2 / \beta m S_{\mathbf{k}}$ (we have defined the static structure factor $S_{\mathbf{k}} = [1 - \rho_b c_{\mathbf{k}}]^{-1}$) and where we have defined

$$\hat{R}_{\mathbf{k}}(t) = \frac{1}{\beta m (2\pi)^3} \int d\mathbf{k}' \mathbf{k} \cdot \mathbf{k}' \rho_{\mathbf{k}'}(t) c_{\mathbf{k}'} \rho_{\mathbf{k}-\mathbf{k}'}(t). \quad (35)$$

Equation (34) is suggestive, since it is known that one can always write formally the equation of motion for a dynamical variable such as $\rho_{\mathbf{k}}(t)$ in the following form [25, 26]:

$$\ddot{\rho}_{\mathbf{k}}(t) + \nu \dot{\rho}_{\mathbf{k}}(t) + \Omega_{\mathbf{k}}^2 \rho_{\mathbf{k}}(t) = - \int_0^t dt' m_{\mathbf{k}}(t') \dot{\rho}_{\mathbf{k}}(t - t') + R_{\mathbf{k}}(t), \quad (36)$$

where $R_{\mathbf{k}}(t)$ is a noise term and the memory function is given formally by

$$m_{\mathbf{k}}(t) = \frac{\langle R_{\mathbf{k}}(t) R_{-\mathbf{k}}(0) \rangle}{\langle |\dot{\rho}_{\mathbf{k}}(t)|^2 \rangle}, \quad (37)$$

where $\langle \dots \rangle$ denotes the average over the ensemble of initial configurations of the density. Since $\dot{\rho}_{\mathbf{k}}(t) = i\mathbf{k} \cdot \mathbf{j}_{\mathbf{k}}(t) = i\mathbf{k} j_{\mathbf{k}}^L(t)$, where $j_{\mathbf{k}}^L(t)$ is the longitudinal current, the denominator in (37) is simply equal to $k^2 N k_B T / m$. One finds that $\rho_{-\mathbf{k}}(0)$ and $R_{\mathbf{k}}(t)$ are statistically independent [25], so on multiplying equation (36) by $\rho_{-\mathbf{k}}(0)$, and then averaging, one obtains the following dynamical equation:

$$\ddot{\phi}_{\mathbf{k}}(t) + \nu \dot{\phi}_{\mathbf{k}}(t) + \Omega_{\mathbf{k}}^2 \phi_{\mathbf{k}}(t) = - \int_0^t dt' m_{\mathbf{k}}(t') \dot{\phi}_{\mathbf{k}}(t - t'), \quad (38)$$

where the normalized correlator

$$\phi_{\mathbf{k}}(t) = \frac{\langle \rho_{\mathbf{k}}(t) \rho_{-\mathbf{k}}(0) \rangle}{\langle \rho_{\mathbf{k}}(0) \rho_{-\mathbf{k}}(0) \rangle}. \quad (39)$$

Equation (38) is formally exact. However, one does not have a tractable form for the memory function $m_{\mathbf{k}}(t')$. It is at this point that we return to the DDFT equations (34) and (35) and we make the following *assumption* [25]:

$$\langle R_{\mathbf{k}}(t) R_{-\mathbf{k}}(0) \rangle \simeq \langle \hat{R}_{\mathbf{k}}(t) \hat{R}_{-\mathbf{k}}(0) \rangle, \quad (40)$$

i.e. we will assume that the time correlations in $\hat{R}_{\mathbf{k}}(t)$ and $R_{\mathbf{k}}(t)$ are the same [25]. We also assume the usual MCT factorization of four-point correlation functions into products of two-point correlation functions [3, 17]: $\langle \rho_{\mathbf{k}'}(t) \rho_{\mathbf{k}-\mathbf{k}'}(t) \rho_{\mathbf{k}''}(0) \rho_{-\mathbf{k}-\mathbf{k}'}(0) \rangle \simeq \langle \rho_{\mathbf{k}'}(t) \rho_{\mathbf{k}''}(0) \rangle \langle \rho_{\mathbf{k}-\mathbf{k}'}(t) \rho_{-\mathbf{k}-\mathbf{k}'}(0) \rangle + \langle \rho_{\mathbf{k}'}(t) \rho_{-\mathbf{k}-\mathbf{k}'}(0) \rangle \langle \rho_{\mathbf{k}-\mathbf{k}'}(t) \rho_{\mathbf{k}''}(0) \rangle$ and we obtain the standard MCT expression for the memory function [17, 25]:

$$m_{\mathbf{k}}(t) = \frac{k_B T \rho_b}{2(2\pi)^3 k^2 m} \int d\mathbf{k}' [\mathbf{k} \cdot \mathbf{k}' c_{\mathbf{k}'} + \mathbf{k} \cdot (\mathbf{k} - \mathbf{k}') c_{\mathbf{k}-\mathbf{k}'}]^2 S_{\mathbf{k}'} S_{\mathbf{k}-\mathbf{k}'} \phi_{\mathbf{k}'}(t) \phi_{\mathbf{k}-\mathbf{k}'}(t). \quad (41)$$

In this analysis we have derived equations for determining the correlator (39), where $\rho_{\mathbf{k}}(t)$ is defined as the Fourier transform of the coarse grained density. However, the standard MCT is a theory for the correlator (39), with $\rho_{\mathbf{k}}(t)$ given by equation (1). Strictly speaking, we have derived a theory with exactly the same structure, but for a different correlator. However, given that much of the physics of dense fluids near to the glass transition concerns the behaviour of collective density fluctuations, it is not too surprising that a description in terms of a coarse grained density is not that different from a description in terms of the density field itself.

Returning to the case when there is an external field, we find there is the following additional term on the right-hand side of equation (34):

$$E_{\mathbf{k}}(t) = i\mathbf{k} \cdot \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \bar{\rho}(\mathbf{r}, t) \nabla V_{\text{ext}}(\mathbf{r}, t). \quad (42)$$

This results in additional terms in equation (36) as well as modifying the memory function $m_{\mathbf{k}}(t)$. Consider an external potential $V_{\text{ext}}(\mathbf{r}) \sim \exp(i\mathbf{q} \cdot \mathbf{r})$, i.e. a periodic field such as that generated by a laser with wavelength $2\pi/q$. In this case we find

$$E_{\mathbf{k}}(t) \simeq -\epsilon \mathbf{k} \cdot \mathbf{q} \rho_{\mathbf{k}+\mathbf{q}}(t), \quad (43)$$

where ϵ is proportional to the amplitude of the external field. This term in equation (34) couples density fluctuations with wavelength \mathbf{k} to fluctuations with wavelength $\mathbf{k} + \mathbf{q}$. Note also that the coupling is strongest when \mathbf{k} is parallel to \mathbf{q} . Including such a contribution in equation (36), multiplying through by $\rho_{-\mathbf{k}}(0)$ and then averaging would result in an equation relating the dynamics of $\phi_{\mathbf{k}}(t)$ to the correlator $\langle \rho_{\mathbf{k}+\mathbf{q}}(t) \rho_{-\mathbf{k}}(0) \rangle$. For an equilibrium homogeneous fluid this correlator would be zero for $\mathbf{q} \neq 0$. However, for the inhomogeneous fluid this is not the case. This makes including the influence of an external field in the MCT a difficult problem!

5. Conclusions

In this paper we have presented a DDFT for systems of particles whose dynamics is governed by Newton's equations. In section 2, we derived equation (13), an exact equation, which is the starting point for our DDFT. In section 3 we suggested two approximations in order to close equation (13), yielding the DDFT, equation (16). Then, in section 4 we analysed the consequences of assuming equation (16), for the description of sound waves and for describing two point correlation functions. We have shown that the DDFT incorporates the physics described by the MCT, and the present analysis adds to the work of Kawasaki and co-workers [20–25] in suggesting that the DDFT provides a useful framework for studying the glass transition.

We believe that equation (13) needs further study. In particular, we believe that there may be better ways to approximate the term $B(\mathbf{r}, t)$, given by equations (12) or (56). We made the very simple approximation $B(\mathbf{r}, t) \simeq \nu \dot{\rho}(\mathbf{r}, t)$. However, when the modulations in the density profile become large we expect this approximation to break down. Whether this can be remedied by replacing the coefficient ν by a function(al) of the density remains to be investigated. Having said this, the simple approximation suggested in section 3 for the term $B(\mathbf{r}, t)$ in equation (13) results in a dynamical theory that proves to be rather interesting, given that it can be used as a starting point for deriving MCT.

Very recently, a DDFT (modified Cahn–Hilliard theory) of a similar form to that in equation (16) was suggested in [27]. These authors considered a system of particles with stochastic equations of motion with correlations in the stochastic noise. If one considers a system of Brownian particles with Langevin equations of motion of the form

$$\dot{\mathbf{r}}_i(t) = -\Gamma \nabla_i V(\mathbf{r}^N, t) + \Gamma \mathbf{X}_i(t), \quad (44)$$

where Γ^{-1} is a friction constant characterizing the one body drag of the solvent on the colloidal particles and $\mathbf{X}_i(t) = (\xi_i^x(t), \xi_i^y(t), \xi_i^z(t))$ is a white noise term with the property $\langle \xi_i^\alpha(t) \rangle = 0$ and $\langle \xi_i^\alpha(t) \xi_j^\nu(t') \rangle = 2k_B T \delta_{ij} \delta^{\alpha\nu} \delta(t-t')$ (where $\alpha, \nu = x, y, z$ label the Cartesian coordinates), then one can derive a DDFT of the following form [4, 7]:

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \Gamma \nabla \cdot \left[\rho(\mathbf{r}, t) \nabla \frac{\delta F[\rho(\mathbf{r}, t)]}{\delta \rho(\mathbf{r}, t)} \right]. \quad (45)$$

However, if the noise term has memory—i.e. if the noise has the property $\langle \xi_i^\alpha(t) \rangle = 0$ and $\langle \xi_i^\alpha(t) \xi_j^\nu(t') \rangle = 2k_B T \delta_{ij} \delta^{\alpha\nu} W(t-t')$, where $W(t-t') = \exp(-|t-t'|/\gamma)/\gamma$, then arguing along the lines suggested in [27], one arrives at the following (approximate) DDFT equation:

$$\gamma \frac{\partial^2 \rho(\mathbf{r}, t)}{\partial t^2} + \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \Gamma \nabla \cdot \left[\rho(\mathbf{r}, t) \nabla \frac{\delta F[\rho(\mathbf{r}, t)]}{\delta \rho(\mathbf{r}, t)} \right]. \quad (46)$$

The authors of [27] applied a linearized form of equation (46), together with a Ginzburg–Landau free energy functional for F , to study spinodal decomposition. These authors were motivated by the need for a causality constraint in the description of phase transitions expected to occur in excited states of matter produced in heavy ion collisions [27]. They found that

the memory term can have a significant effect in delaying the growth of density fluctuation in the initial stages of spinodal decomposition. Equation (46) has the same formal structure as equation (16). We believe that it is worthwhile to pursue further investigations of these equations. In this sense, the present paper is a starting point for further developing a DDFT framework for tackling the microscopic dynamics of fluids.

Acknowledgments

I am indebted to Bob Evans, Markus Rauscher, Andrea Gambassi, Matthias Fuchs and Joe Brader for useful discussions and to Bob Evans for proof reading this manuscript. I am grateful to EPSRC for support under grant number GR/S28631/01.

Appendix

Here we present an alternative derivation of equation (13). The state of a system of N identical particles is specified by the set of particle position coordinates $\mathbf{r}^N = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ and momenta $\mathbf{p}^N = \{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N\}$. There exists a phase space probability density function, $f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t)$, which gives the probability that the system is in a particular configuration $(\mathbf{r}^N, \mathbf{p}^N)$ at time t . The time evolution of $f^{(N)}$ is governed by the Liouville equation [3]:

$$\frac{\partial f^{(N)}}{\partial t} = \{\mathcal{H}, f^{(N)}\}, \quad (47)$$

where $\{\cdot, \cdot\}$ denotes a Poisson bracket, and the Hamiltonian

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N, t) = \frac{1}{2m} \sum_{i=1}^N |\mathbf{p}_i|^2 + V(\mathbf{r}^N, t), \quad (48)$$

where $V(\mathbf{r}^N, t)$, the potential energy of the system, is given by equation (3). Integrating over the Liouville equation, we obtain equations of motion for reduced phase space distribution functions $f^{(n)}$, where $n < N$. One finds that in order to describe the dynamics of $f^{(n)}$ one must know member $f^{(n+1)}$ of the BBGKY hierarchy [3]. The first member is the following:

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}_1} + \mathbf{X}_1 \cdot \nabla_{\mathbf{p}_1} \right) f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) \\ &= - \int d\mathbf{r}_2 \int d\mathbf{p}_2 \mathbf{F}_{12} \cdot \nabla_{\mathbf{p}_1} f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t), \end{aligned} \quad (49)$$

where $\mathbf{X}_1 = -\nabla_{\mathbf{r}_1} V^{\text{ext}}(\mathbf{r}_1, t)$ is the external force on each particle 1 and $\mathbf{F}_{12} = -\nabla_{\mathbf{r}_1} v(\mathbf{r}_1 - \mathbf{r}_2)$ is the pair force on particle 1 due to particle 2. If we integrate equation (49) with respect to the momentum \mathbf{p}_1 , then we obtain the continuity equation [28]:

$$\frac{\partial \rho(\mathbf{r}_1, t)}{\partial t} + \nabla_{\mathbf{r}_1} \cdot \mathbf{j} = 0, \quad (50)$$

where

$$\rho(\mathbf{r}_1, t) = \int d\mathbf{p}_1 f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) \quad (51)$$

is the average one body density and

$$\mathbf{j}(\mathbf{r}_1, t) = \int d\mathbf{p}_1 \frac{\mathbf{p}_1}{m} f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) \quad (52)$$

is the current. If we now multiply equation (49) through by \mathbf{p}_1/m and then integrate with respect to the momentum \mathbf{p}_1 , then we obtain the following momentum balance equation [28]:

$$\begin{aligned} \frac{\partial \mathbf{j}(\mathbf{r}_1, t)}{\partial t} + \nabla_{\mathbf{r}_1} \cdot \int d\mathbf{p}_1 \frac{\mathbf{p}_1 \mathbf{p}_1}{m^2} f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) - \frac{1}{m} \rho(\mathbf{r}_1, t) \mathbf{X}_1 \\ - \frac{1}{m} \int d\mathbf{r}_2 \mathbf{F}_{12} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) = 0, \end{aligned} \quad (53)$$

where

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) = \int d\mathbf{p}_1 \int d\mathbf{p}_2 f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) \quad (54)$$

is the two body density distribution function. Note that $\mathbf{p}_1 \mathbf{p}_1$ is a tensor product (dyadic) [28]. Taking a time derivative of equation (50) and then using equation (53) to eliminate the term involving $\partial \mathbf{j} / \partial t$ we obtain the following equation:

$$\begin{aligned} \frac{\partial^2 \rho(\mathbf{r}_1, t)}{\partial t^2} = \nabla_{\mathbf{r}_1} \cdot \nabla_{\mathbf{r}_1} \cdot \int d\mathbf{p}_1 \frac{\mathbf{p}_1 \mathbf{p}_1}{m^2} f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) \\ - \frac{1}{m} \nabla_{\mathbf{r}_1} \cdot \int d\mathbf{r}_2 \mathbf{F}_{12} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) - \frac{1}{m} \nabla_{\mathbf{r}_1} \cdot [\rho(\mathbf{r}_1, t) \mathbf{X}_1]. \end{aligned} \quad (55)$$

At equilibrium, from equipartition we find that the integral $\int d\mathbf{p}_1 (\mathbf{p}_1 \mathbf{p}_1) f^{(1)} = mk_B T \rho(\mathbf{r}_1, t) \mathbf{1}$, where $\mathbf{1}$ denotes the 3×3 unit matrix. Using this result in equation (55), we obtain equation (13), together with the following expression for $B(\mathbf{r}, t)$:

$$B(\mathbf{r}, t) = -\nabla \cdot \nabla \cdot \int d\mathbf{p} \left(\frac{\mathbf{p} \mathbf{p}}{m^2} - \frac{k_B T}{m} \mathbf{1} \right) f^{(1)}(\mathbf{r}, \mathbf{p}, t). \quad (56)$$

It is clear from this expression that at equilibrium $B(\mathbf{r}, t) = 0$. This analysis shows that $B(\mathbf{r}, t)$ is essentially the gradient of the off-diagonal elements of the kinetic part of the pressure tensor [28].

We also note here that if the potential energy $V(\mathbf{r}^N, t)$ contains not just one and two body contributions, as given by equation (3), but also contains three body and higher body contributions,

$$\begin{aligned} V(\mathbf{r}^N, t) = \sum_i V^{\text{ext}}(\mathbf{r}_i, t) + \frac{1}{2} \sum_{i,j} v_2(\mathbf{r}_i(t), \mathbf{r}_j(t)) \\ + \frac{1}{6} \sum_{i,j,k} v_3(\mathbf{r}_i(t), \mathbf{r}_j(t), \mathbf{r}_k(t)) + \dots, \end{aligned} \quad (57)$$

then equation (55) becomes

$$\begin{aligned} \frac{\partial^2 \rho(\mathbf{r}_1, t)}{\partial t^2} = \nabla_{\mathbf{r}_1} \cdot \nabla_{\mathbf{r}_1} \cdot \int d\mathbf{p}_1 \frac{\mathbf{p}_1 \mathbf{p}_1}{m^2} f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) - \frac{1}{m} \nabla_{\mathbf{r}_1} \cdot [\rho(\mathbf{r}_1, t) \mathbf{X}_1] \\ - \frac{1}{m} \nabla_{\mathbf{r}_1} \cdot \int d\mathbf{r}_2 \mathbf{F}_{12} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) \\ - \frac{1}{m} \nabla_{\mathbf{r}_1} \cdot \int d\mathbf{r}_2 \int d\mathbf{r}_3 \mathbf{F}_{123} \rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t) + \dots, \end{aligned} \quad (58)$$

where $\mathbf{F}_{123} = -\nabla_{\mathbf{r}_1} v_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is the three body force on particle 1 due to particles 2 and 3 and where

$$\rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t) = \int d\mathbf{p}_1 \int d\mathbf{p}_2 \int d\mathbf{p}_3 f^{(3)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \mathbf{r}_3, \mathbf{p}_3, t) \quad (59)$$

is the three body density distribution function. In the case of many body interactions, the sum rule (14) becomes

$$\begin{aligned}
 -k_B T \rho(\mathbf{r}_1) \nabla c^{(1)}(\mathbf{r}_1) &= \int d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \nabla_{\mathbf{r}_1} v_2(\mathbf{r}_1, \mathbf{r}_2) \\
 &+ \int d\mathbf{r}_2 \int d\mathbf{r}_3 \rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \nabla_{\mathbf{r}_1} v_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \cdots \\
 &= \sum_{n=2}^{\infty} \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_n \rho^{(n)}(\mathbf{r}^n) \nabla_{\mathbf{r}_1} v_n(\mathbf{r}^n).
 \end{aligned} \tag{60}$$

Applying this sum rule as an approximation for terms on the right-hand side of equation (58), together with the approximation $B(\mathbf{r}, t) \simeq v\dot{\rho}(\mathbf{r}, t)$, we obtain equation (16).

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