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Correlated Motions in Simple Classical Liquids

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This paper reports a method for studying correlation functions for simple classical liquids. One atom of the liquid is considered to be an external agent acting on the others, and Liouville's equation is formally solved to obtain their response. From this solution an equation for the velocity autocorrelation function is derived. The method is also applied to the distinct-particle part of the density-density correlation function, $G_d(\vec{x},t)$. The moment relations for $G_d(\vec{x},t)$ are in this way made to depend on a hierarchy of equations relating the static correlation functions. When the basic equations derived by this method are approximated further, previously given approximations for $G_d(\vec{x},t)$ are obtained.

I. INTRODUCTION

In a recent paper[1] Singwi and Sjölander have given an approximate theory of the velocity autocorrelation function of a classical liquid. The philosophy of their method is to consider one atom of the liquid as an external driving agent on the other atoms and to find the response of the others to this one. In I this response was calculated from a simplified kinetic equation for the one particle distribution function of the other atoms.

This paper extends the method of I and has two purposes. First, we show that within the philosophy of I a formal exact solution for the response can be found from the full Liouville equation of the system. To apply this solution to the velocity autocorrelation function, it is necessary to find the change in the density caused by the passage of the particle considered as the external agent. We find, in analogy with linear response theory, but more generally, that this density change is given by a generalized density-density correlation function. This function can be split into self- and distinct-particle parts, just as for the equilibrium function. The approximate solution of I is obtained if we drop the distinct-particle part. Therefore we find that in I any contribution of collective motions to the velocity autocorrelation function was neglected.

The second purpose is to apply this philosophy to the equilibrium density-density correlation function $G(\vec{x},t)$. This function is of central importance in the theory of radiation scattering by condensed systems.[2] $G(\vec{x},t)$ can be written as the sum of a self-part $G_s(\vec{x},t)$ and a distinct-atom part $G_d(\vec{x},t)$. Since the method of this paper is to treat the response of the other particles to the motion of one, it is naturally suited to calculating the distinct-atom part $G_d(\vec{x},t)$. We can thus assume that $G_s(\vec{x},t)$ is known (along with all static correlation functions) and use it in the theory for $G_d(\vec{x},t)$.

We use the method of the paper to discuss the first four moment relations for $G_d(\vec{x},t)$, and to show how two approximations for $G_d(\vec{x},t)$, previously given in the literature, can be derived. The method emphasizes the importance of conservation laws in determining the properties of $G_d(\vec{x},t)$.

This method seems most suitable for studying the behavior of $G_d(\vec{x},t)$ for small times, and our discussion is mostly confined to this limit. We have not yet been able to demonstrate whether the hydrodynamic limit[3] for $G_d(\vec{x},t)$ can be obtained by this method or not.

The outline of this paper is as follows. Section II contains definitions of the quantities of interest. Section III gives the solution for the response of the other atoms. Section IV discusses the resulting modifications in I. Section V applies the method to calculating the moments of $G_d(\vec{x},t)$. Section VI derives two previously given approximations for $G_d(\vec{x},t)$ by the present formalism. Section VII summarizes the results.

II. DEFINITIONS

We consider a system of $N+1$ atoms, labelled $0,1,\ldots,N$, in a box of volume $\mathcal{V}$. Atom 0 will be called the "blue" atom; it will be treated differently from the others. Atoms $1,\ldots,N$ will be called the "other" atoms. The position and velocity of the ith atom at time t are denoted $\vec{x}_i(t)$ and $\vec{v}_i(t)$, respectively.

The microscopic density of other atoms is

$$\rho^N(\vec{x},t)=\sum_{i=1}^{N}\rho^{(i)}(\vec{x},t)\,, \tag{2.1}$$

where $\rho^{(i)}(\vec{x},t)$ is the density of the ith atom:

$$\rho^{(i)}(\vec{x},t)=\delta(\vec{x}-\vec{x}_i(t)),\quad i=0,1,\ldots,N. \tag{2.2}$$

Similarly, the microscopic current of the other atoms is

$$\vec{j}^{\,N}(\vec{x},t)=\sum_{i=1}^{N}\vec{j}^{\,(i)}(\vec{x},t)\,, \tag{2.3}$$

where

$$\vec{j}^{\,(i)}(\vec{x},t)=\vec{v}_i(t)\delta(\vec{x}-\vec{x}_i(t))\,,\qquad i=0,1,\ldots,N \tag{2.4}$$

is the current of the ith atom.

There are two quantities of interest in this paper. One is the velocity autocorrelation function, defined by

$$\Phi(t)=\langle\vec{v}_0(t)\cdot\vec{v}_0(0)\rangle/\langle v_0^2\rangle\,, \tag{2.5}$$

where $\langle\ldots\rangle$ denotes an average over an ordinary equilibrium ensemble.

To obtain an equation of motion for the velocity autocorrelation function, we first write Newton's second law for the blue atom

$$M d\vec{v}_0(t)/dt=-\nabla_{\vec{x}_0}\int d\vec{x}\,V(\vec{x}_0(t)-\vec{x})\rho^N(\vec{x},t)\,; \tag{2.6}$$

and we then "correlate" this with $\vec{v}_0(0)$, so that

$$M(d/dt)\langle\vec{v}_0(t)\cdot\vec{v}_0(0)\rangle$$

$$=-\int d\vec{x}\,\langle\nabla_{\vec{x}_0}V(\vec{x}_0(t)-\vec{x})\rho^N(\vec{x},t)\cdot\vec{v}_0(0)\rangle\,. \tag{2.7}$$

Here M is the mass of an atom, and $V(\vec{x})$ is the interparticle potential.

The second quantity of interest in this paper is the distinct-particle part of the density-density correlation function. This can be written as

$$G_d(\vec{x},t)=\mathcal{V}\langle\rho^N(\vec{x},t)\rho^{(0)}(0,0)\rangle\,. \tag{2.8}$$

The point of view we take in calculating these correlation functions is as follows. We consider that the trajectory of the "blue" atom is known. The motion of the "blue" atom provides a time-dependent external force which drives the N-particle system of the other particles. We calculate the response of the other particles from a time-dependent Liouville equation. From the solution of the Liouville equation we can calculate the average density $\rho(\vec{x},t)$ and current $\vec{J}(\vec{x},t)$. (The absence of superscripts distinguishes these quantities from the microscopic quantities defined earlier.) These functions $\rho(\vec{x},t)$ and $\vec{J}(\vec{x},t)$ still depend on the microscopic coordinates of the blue atom.

To calculate the correlation functions we replace $\rho^N(\vec{x},t)$ in Eqs. (2.7) and (2.8) by $\rho(\vec{x},t)$ and complete the remaining average on the coordinates of the blue atom.

The approximation involved in this procedure comes in the last step. The trajectory of the blue particle, described by $\vec{x}_0(t)$ and $\vec{v}_0(t)$, depends on the initial coordinates and momenta of all $N+1$ particles. So when we integrate over the phase space of N particles to get $\rho(\vec{x},t)$ and $\vec{J}(\vec{x},t)$, $\vec{x}_0(t)$ and $\vec{v}_0(t)$ must be involved in the integration. That means, for example, that when we replace $\rho^N(\vec{x},t)$ in Eq. (2.7) with $\rho(\vec{x},t)$, we should also replace $\vec{x}_0(t)$ by an averaged path whose initial position and velocity are specified (because we integrate only over phase space for the other particles). Our approximation then is to continue to treat $\vec{x}_0(t)$ in Eq. (2.7) and in later equations as a deterministic variable. The average path of the blue particle should then be determined in a self-consistent way along the lines given in I.

This point will be discussed again when it arises in our derivations.

III. THE RESPONSE OF THE OTHER PARTICLES

In this section we calculate the response of the other particles from Liouville's equation, considering the blue particle to be a time-dependent external disturbance.

Liouville's equation for the N-particle distribution function (d.f.) is

$$i(\partial/\partial t)f_N(\vec{X},\vec{P},t)-L(t)f_N(\vec{X},\vec{P},t)=0\,. \tag{3.1}$$

Here $\vec{X}=\{\vec{x}_1,\ldots,\vec{x}_N\}$, $\vec{P}=\{\vec{p}_1,\ldots\vec{p}_N\}$ is a shorthand notation for the phase-space variables, the positions and momenta of the other particles. These variables will often be omitted for brevity. $L(t)$ is a time-dependent Liouville operator, given by

$$L(t)=L+L'(t) \tag{3.2}$$

with $$L=-i\sum_{m=1}^{N}\Big[(\vec{p}_m/M)\cdot\nabla_m-\sum_{\substack{n=1\\ n\neq m}}^{N}\nabla_m V(\vec{x}_m-\vec{x}_n)\cdot\frac{\partial}{\partial\vec{p}_m}\Big] \tag{3.3}$$

and $$L'(t)=-i\sum_{m=1}^{N}\nabla_m V(\vec{x}_m-\vec{x}_0(t))\cdot\frac{\partial}{\partial\vec{p}_m}\,. \tag{3.4}$$

If the blue particle were stationary at point $\vec{R}$, then Eq. (3.1) would have a solution corresponding to the N-particle system being at equilibrium in the external field produced by the blue particle. That solution is

$$f_N^{(\mathrm{eq})}(\vec{X},\vec{P})=\Big\{e^{-\beta H_N}\exp\Big[-\beta\sum_{m=1}^{N}V(\vec{x}_m-\vec{R})\Big]\Big\}\Big\{\int d\Gamma_N e^{-\beta H_N}\exp\Big[-\beta\sum_{m=1}^{N}V(\vec{x}_m-\vec{R})\Big]\Big\}^{-1}\,. \tag{3.5}$$

Here β is the inverse temperature in energy units, H_N is the unperturbed Hamiltonian of the N-particle system, and the integral is over the phase space for N particles.

When the blue particle moves it produces a time-dependent external potential on the other particles. We define a time-dependent function $f_N^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))$ by replacing $\vec{R}$ in Eq. (3.5) with $\vec{x}_0(t)$.

$$f_N^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))=\Big\{e^{-\beta H_N}\exp\Big[-\beta\sum_{m=1}^{N}V(\vec{x}_m-\vec{x}_0(t))\Big]\Big\}\Big\{\int d\Gamma_N e^{-\beta H_N}\times\exp\Big[-\beta\sum_{m=1}^{N}V(\vec{x}_m-\vec{x}_0(t))\Big]\Big\}^{-1}\,. \tag{3.6}$$

Note that the denominator of Eq. (3.6) is actually independent of time.

By definition $f_N^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))$ has the property

$$L(t)f_N^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))=0\,, \tag{3.7}$$

but it does not satisfy the full Liouville equation Eq. (3.1).

We write the solution of Eq. (3.1) as the sum of two terms[4]:

$$f_N(\vec{X},\vec{P},t)=f_N^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))+\bar{f}_N(\vec{X},\vec{P},t)\,. \tag{3.8}$$

Using Eq. (3.7), $\bar{f}_N(\vec{X},\vec{P},t)$ is found to satisfy the equation

$$i(\partial/\partial t)\bar{f}_N-L(t)\bar{f}_N=-i(\partial/\partial t)f_N^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))\,. \tag{3.9}$$

The solution of Eq. (3.9) which has the initial condition

$$\bar{f}_N(0)=0 \tag{3.10}$$

is $$\bar{f}_N(t)=-\int_0^t dt'\,U(t,0)U^{-1}(t',0)(\partial/\partial t')f_N^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t'))\,, \tag{3.11}$$

where $U(t,0)$ is the evolution operator for the Liouville operator $L(t)$. The sum of Eqs. (3.6) and (3.11) gives the response of the other particles.

The average density $\rho(\vec{x},t)$ is calculated from the d.f. and can be written as the sum of two terms.

$$\rho(\vec{x},t)=\rho^{(\mathrm{eq})}(\vec{x},t)+\bar{\rho}(\vec{x},t)\,, \tag{3.12}$$

where
$$\rho^{(\mathrm{eq})}(\vec{x},t)=\int d\Gamma_N \sum_{n=1}^{N} \delta(\vec{x}-\vec{x}_n) f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))\,, \tag{3.13}$$

and
$$\bar{\rho}(\vec{x},t)=\int d\Gamma_N \sum_{n=1}^{N} \delta(\vec{x}-\vec{x}_n)\bar{f}_N(\vec{X},\vec{P},t)\,. \tag{3.14}$$

We show in the Appendix that $f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))$ can be written

$$f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))=\upsilon \int d\vec{p}_0\, d\vec{x}_0\, e^{-\beta H_{N+1}}\, \delta(\vec{x}_0-\vec{x}_0(t))\Big/ \int d\Gamma_{N+1}\, e^{-\beta H_{N+1}}\,. \tag{3.15}$$

In Eq. (3.15) $\vec{x}_0$ and $\vec{p}_0$ are general phase-space variables of the blue particle, whereas $\vec{x}_0(t)$ represents the actual path of the blue atom.

Note that the Hamiltonian in Eq. (3.15) is for a system of $N+1$ particles. This looks formally different from the previous expression for $f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))$, Eq. (3.6), which contained no factors containing the kinetic energy of the blue particle. Actually there is no difference, because in Eq. (3.15) we have just inserted the kinetic-energy terms into both numerator and denominator. The reason that this is possible is, of course, that in classical statistical mechanics the momentum and configuration dependent parts of the equilibrium d. f. are completely factored from each other.

Using Eq. (3.15) we can write

$$\rho^{(\mathrm{eq})}(\vec{x},t)=[\upsilon/(N+1)]\left[(N+1)N\int d\Gamma_{N+1}\delta(\vec{x}-\vec{x}_1)\,\delta(\vec{x}_0-\vec{x}_0(t))\,e^{-\beta H_{N+1}}\Big/\int d\Gamma_{N+1}\,e^{-\beta H_{N+1}}\right]. \tag{3.16}$$

The second factor in Eq. (3.16) is precisely the definition of the equilibrium static two-particle correlation function $n_2(\vec{x},\vec{x}_0(t))$ for an $N+1$ particle system.[5] Therefore

$$\rho^{(\mathrm{eq})}(\vec{x},t)=n_0{}^{-1}n_2(\vec{x},\vec{x}_0(t))=n_0 g(\vec{x}-\vec{x}_0(t))\,, \tag{3.17}$$

where $g(\vec{x})$ is the pair correlation function normalized to unity at large $|\vec{x}|$, and n_0 is the average density $(N+1)/\upsilon$.

We now calculate $\bar{\rho}(x,t)$. From Eq. (3.6) we have

$$\frac{\partial}{\partial t'} f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t'))=\beta f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t'))\int d\vec{x}' \sum_{m=1}^{N} \delta(\vec{x}'-\vec{x}_m)\,\vec{\nabla}V(\vec{x}'-\vec{x}_0(t'))\cdot\vec{v}_0(t')\,. \tag{3.18}$$

Inserting Eq. (3.18) into Eq. (3.11) and using Eq. (3.14) gives

$$\bar{\rho}(\vec{x},t)=-\beta\int_0^t dt'\int d\vec{x}'\left[\int d\Gamma_N \sum_{n=1}^{N}\delta(\vec{x}-\vec{x}_n)\,U(t,0)U^{-1}(t',0)\sum_{m=1}^{N}\delta(\vec{x}'-\vec{x}_m)f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t'))\right]$$
$$\times\vec{\nabla}V(\vec{x}'-\vec{x}_0(t'))\cdot\vec{v}_0(t')\,. \tag{3.19}$$

It is in Eq. (3.19) that we have made the approximation discussed at the end of Sec. II. The $\vec{x}_0(t')$ and $\vec{v}_0(t')$, which appear in the last two factors of Eq. (3.19), depend on the initial coordinates and momenta of all the particles, and they should therefore be included in the integral $\int d\Gamma_N\cdots$. Our justification for this separation is that since we still have to perform an average on the coordinates of the blue particle to get the correlation functions, these latter factors will become essentially functions describing the self-motion of a single atom, and these should be reasonably insensitive to the detailed features of the initial conditions of the other atoms.

We can now identify the correlation function appearing in Eq. (3.19). If the blue particle were not present, and the N particle system were in equilibrium, then

$$U(t,0)U^{-1}(t',0)\to e^{-iL(t-t')} \quad\text{and}\quad f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\mathrm{x}_0(t))\to f_N{}^{(0)}(\vec{X},\vec{P})=e^{-\beta H_N}\Big/\int d\Gamma_N e^{-\beta H_N}.$$

The correlation function in Eq. (3.19) would then be

$$\int d\Gamma_N \sum_{n=1}^{N}\delta(\vec{x}-\vec{x}_n)\,e^{-iL(t-t')}\sum_{m=1}^{N}\delta(\vec{x}'-\vec{x}_m)f_N{}^{(0)}(\vec{X},\vec{P})=n_0 G(\vec{x}-\vec{x}',t-t'),$$

where $G(\vec{x}-\vec{x}',t-t')$ is the equilibrium density-density correlation function. In analogy with the equilibrium case, we define

$$G(\vec{x},t;\ \vec{x}',t'\,|\,\vec{x}_0)=[n_0 g(\vec{x}'-\vec{x}_0(t'))]^{-1}\int d\Gamma_N \sum_{n=1}^{N}\delta(\vec{x}-\vec{x}_n)U(t,0)U^{-1}(t',0)\sum_{m=1}^{N}\delta(\vec{x}'-\vec{x}_m)f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t')). \tag{3.21}$$

This depends on the history of the motion of the blue atom between times t and t'.

The denominator is put into Eq. (3.21) for normalization purposes.

The physical interpretation of $G(\vec{x}, t; \vec{x}', t' | \vec{x}_0)$ is that it gives the probability that if one of the other particles is known to be at $\vec{x}'$ at time t', then any of the other particles will be at $\vec{x}$ at time t, taking into account the motion of the blue particle. It is thus a generalization of the equilibrium density-density correlation function to a specific nonequilibrium situation.

Putting Eq. (3.21) into Eq. (3.19) and combining with Eq. (3.17) gives our final result for the density of other particles.

$$\rho(\vec{x}, t) = n_0 g(\vec{x} - \vec{x}_0(t)) - n_0 \beta \int_0^t dt' \int d\vec{x}' \, G(\vec{x}, t; \vec{x}.,'t' | \vec{x}_0) \, g(\vec{x}' - \vec{x}_0(t')) \vec{\nabla} V(\vec{x}' - \vec{x}_0(t')) \cdot \vec{v}_0(t') . \tag{3.22}$$

IV. EQUATION OF MOTION FOR $\Phi(t)$

Newton's second law for the blue atom is obtained by putting Eq. (3.22) into Eq. (2.7). Symmetry arguments show that $\rho^{(\mathrm{eq})}(\vec{x}, t)$ makes no contribution, so that

$$M d\vec{v}_0(t)/dt = - n_0 \beta \int_0^t dt' \int d\vec{x} d\vec{x}' \, \vec{\nabla}_{\vec{x}_0} V(\vec{x}_0(t) - \vec{x}') G(\vec{x}, t; \vec{x}', t' | \vec{x}_0) \, g(\vec{x}' - \vec{x}_0(t')) \vec{\nabla} V(\vec{x}' - \vec{x}_0(t')) \cdot \vec{v}_0(t') . \tag{4.1}$$

Comparing this equation with Eq. (13) of I shows two changes:

(1) Instead of a generalization of the full density-density correlation function, the result of I had a generalization of the self-part only.

(2) Instead of the combination of functions $- \beta g(\vec{x}' - \vec{x}_0(t')) \vec{\nabla} V(\vec{x}' - \vec{x}_0(t'))$, the result of I had $\vec{\nabla} g(\vec{x}' - \vec{x}_0(t'))$.

The result of I was obtained by solving a simplified equation for the single-particle distribution function, in which the term describing the interaction between the particles was replaced by a single relaxation-time approximation. By making this approximation the effects of collective motions were lost. This loss shows up in the equations by the replacement of $G(\vec{x}, t; \vec{x}', t' | \vec{x}_0)$ by its self-part. Also in I the approach towards thermal equilibrium was for simplicity assumed to be exponential in time.

The second difference can be understood in the same way. Ignoring collective effects, the single relaxation-time approximation may be considered most valid for a dilute gas. But the static pair correlation function of a dilute gas is given by $\exp(- \beta V(\vec{x}))$ so that $\vec{\nabla} g(\vec{x})$ and $- \beta g(\vec{x}) \vec{\nabla} V(\vec{x})$ are equal. Even in a liquid $\vec{\nabla} g(\vec{x})$ and $- \beta g(\vec{x}) \vec{\nabla} V(\vec{x})$ are qualitatively similar so that the general features of the results of I are not expected to be significantly altered by this change.

A discussion of the effects of collective motions on the velocity autocorrelation function is more difficult. The purpose of I was to derive an approximate result for the memory function $\Gamma(t)$ of $\Phi(t)$ in the equation

$$(d/dt)\Phi(t) + \int_0^t dt' \, \Gamma(t - t')\Phi(t') = 0 , \tag{4.2}$$

and to see if the main features of $\Gamma(t)$ could be explained in terms of the interparticle potential and static pair correlation function. It was shown there that the hard core of the interparticle potential is very important in producing the initial sharp decrease in $\Gamma(t)$. This feature is not expected to be changed by including collective effects.

V. THE DENSITY-DENSITY CORRELATION FUNCTION

Our equation for $G_d(\vec{x}, t)$ is obtained by putting Eq. (3.22) into Eq. (2.8). The result is

$$G_d(\vec{x}, t) = G_d^{(\mathrm{eq})}(\vec{x}, t) + \overline{G}_d(\vec{x}, t) , \tag{5.1}$$

where $$G^{(\mathrm{eq})}(\vec{x}, t) = n_0 \mathcal{V} \langle g(\vec{x} - \vec{x}_0(t)) \, \rho^{(0)}(0, 0) \rangle \tag{5.2}$$

and $$\overline{G}_d(\vec{x}, t) = - n_0 \beta \mathcal{V} \int_0^t dt' \int d\vec{x}' \langle G(\vec{x}, t; \vec{x}', t' | \vec{x}_0) \, g(\vec{x}' - \vec{x}_0(t')) \vec{\nabla} V(\vec{x}' - \vec{x}_0(t')) \cdot \vec{v}_0(t') \rho^{(0)}(0, 0) \rangle . \tag{5.3}$$

Important quantities associated with $G_d(\vec{x}, t)$ are the values of its time derivatives at $t = 0$. These are closely related to the frequency moments of the Fourier transform of $G_d(\vec{x}, t)$; hence they are often called moment relations.[6] Classically, $G_d(\vec{x}, t)$ is an even function of time, so all the odd moments vanish. The second moment of $G_d(\vec{x}, t)$ also vanishes, and the fourth[7] and sixth[8] moments are known exactly.

The low-order moment relations are closely related to the microscopic conservation laws of the system.[9] The microscopic derivation of the moment relations can be summarized as follows. The microscopic particle conservation equations for the other particles and for the blue particle are

$$(\partial/\partial t)\rho^N(\vec{x}, t) + \vec{\nabla} \cdot \vec{J}^N(\vec{x}, t) = 0, \tag{5.4}$$

$$(\partial/\partial t)\rho^{(0)}(\vec{x}, t) + \vec{\nabla} \cdot \vec{j}^{(0)}(\vec{x}, t) = 0 . \tag{5.5}$$

Using the stationarity property of equilibrium correlation functions, i.e.,

$$\langle \dot{A}(t)B(0)\rangle = -\langle A(t)\dot{B}(0)\rangle \,, \tag{5.6}$$

the translational invariance of the liquid, and these conservation laws, we get from Eq. (2.8)

$$\ddot{G}_d(\vec{x},t) = \mathcal{V}\nabla_\alpha\nabla_\gamma\langle J_\alpha{}^N(\vec{x},t)j_\gamma{}^{(0)}(0,0)\rangle \,, \tag{5.7}$$

for the second time derivative, and

$$G_d{}^{(\mathrm{iv})}(\vec{x},t) = \mathcal{V}\nabla_\alpha\nabla_\gamma\langle \ddot{J}_\alpha{}^N(\vec{x},t)j_\gamma{}^{(0)}(0,0)\rangle \tag{5.8}$$

for the fourth time derivative. In Eqs. (5.7) and (5.8) the Greek subscripts indicate Cartesian components of the vectors, and repeated subscripts are to be summed over the three components; also $\nabla_\alpha = \partial/\partial x_\alpha$.

In particular $\ddot{G}_d(\vec{x},0)$ vanishes because the velocities of different particles are uncorrelated at equal times. $G_d{}^{(\mathrm{iv})}(\vec{x},0)$ is found from the equations of motion for the particles.

We shall show how the moment relations come out when $\rho^N(\vec{x},t)$ and $\vec{J}^N(\vec{x},t)$ are replaced by $\rho(\vec{x},t)$ and $\vec{J}(\vec{x},t)$ calculated from the d.f. of Eq. (3.8).

First we introduce some new notations. We define

$$\{\rho^N(\vec{x},t)\rho^N(\vec{x}',t')\}_0 = \int d\Gamma_N \sum_{n=1}^{N}\delta(\vec{x}-\vec{x}_n)\;U(t,0)U^{-1}(t',0)\sum_{m=1}^{N}\delta(\vec{x}'-\vec{x}_m)f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t'))\,. \tag{5.9}$$

Then
$$\rho(\vec{x},t) = n_0 g(\vec{x}-\vec{x}_0(t)) - \beta\int_0^t dt'\int d\vec{x}'\{\rho^N(\vec{x},t)\rho^N(\vec{x}',t')\}_0\vec{\nabla}V(\vec{x}'-\vec{x}_0(t'))\cdot\vec{v}_0(t')\,. \tag{5.10}$$

Using Eq. (3.15), we find that the equal time value is

$$\{\rho^N(\vec{x},t)\rho^N(\vec{x}',t)\}_0 = \delta(\vec{x}-\vec{x}')n_0 g(\vec{x}'-\vec{x}_0(t)) + n_0{}^{-1}n_3(\vec{x},\vec{x}',\vec{x}_0(t))\,, \tag{5.11}$$

where $n_3(\vec{x},\vec{x}',\vec{x}'')$ is the equilibrium static three-particle correlation function.

In calculating $\vec{J}(\vec{x},t)$ from our solution of Liouville's equation, we find that $f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t))$ makes no contribution to the current, so that

$$\vec{J}(\vec{x},t) = -\beta\int_0^t dt'\int d\vec{x}'\{\vec{J}^N(\vec{x},t)\rho^N(\vec{x}',t')\}_0\vec{\nabla}V(\vec{x}'-\vec{x}_0(t'))\cdot\vec{v}_0(t')\,, \tag{5.12}$$

where
$$\{\vec{J}^N(\vec{x},t)\rho^N(\vec{x}',t')\}_0 = \int d\Gamma_N\sum_{n=1}^{N}\vec{v}_n\delta(\vec{x}-\vec{x}_n)\,U(t,0)U^{-1}(t',0)\sum_{m=1}^{N}\delta(\vec{x}'-\vec{x}_m)f_N{}^{(\mathrm{eq})}(\vec{X},\vec{P}\,|\,\vec{x}_0(t'))\,. \tag{5.13}$$

This has the properties

$$\{J^N(\vec{x},t)\rho^N(\vec{x}',t)\}_0 = 0, \tag{5.14}$$

and
$$(\partial/\partial t)\{\rho^N(\vec{x},t)\rho^N(\vec{x}',t')\}_0 + \vec{\nabla}\cdot\{\vec{J}^N(\vec{x},t)\rho^N(\vec{x}',t')\}_0 = 0. \tag{5.15}$$

When we calculate $(\partial/\partial t)\rho(\vec{x},t)$ from Eq. (5.10), we get three terms; the first comes from $\rho^{(\mathrm{eq})}(\vec{x},t)$, the second and third come from the fact that the time variable appears both in the upper limit and in the integrand of the integral defining $\overline{\rho}(\vec{x},t)$. The third contribution is related to $\vec{\nabla}\cdot\vec{J}(\vec{x},t)$ through Eq. (5.15). The second contribution can be evaluated using Eq. (5.11). The result is

$$\begin{aligned}(\partial/\partial t)\rho(\vec{x},t) + \vec{\nabla}\cdot\vec{J}(\vec{x},t) = -n_0[\nabla g(\vec{x}-\vec{x}_0(t)) + \beta g(\vec{x}-\vec{x}_0(t))\vec{\nabla}V(\vec{x}-\vec{x}_0(t))\\ + \beta n_0{}^{-2}\int d\vec{x}'n_3(\vec{x},\vec{x}',\vec{x}_0(t))\vec{\nabla}V(\vec{x}'-\vec{x}_0(t))]\cdot\vec{v}_0(t)\,.\end{aligned} \tag{5.16}$$

There is a hierarchy of equations, derived by Green,[10] relating the equilibrium static s and $s+1$ particle correlation functions. The first equation of the hierarchy, relating $n_2(\vec{x},\vec{x}')$ and $n_3(\vec{x},\vec{x}',\vec{x}'')$, is

$$\nabla g(\vec{x}-\vec{x}') + \beta g(\vec{x}-\vec{x}')\nabla V(\vec{x}-\vec{x}') + \beta n_0{}^{-2}\int d\vec{x}''n_3(\vec{x},\vec{x}',\vec{x}'')\vec{\nabla}V(\vec{x}-\vec{x}'') = 0. \tag{5.17}$$

This is precisely the quantity in the square brackets on the right-hand side of Eq. (5.16) [identify $\vec{x}$ as $\vec{x}_0(t)$, $\vec{x}'$ as $\vec{x}$, and $\vec{x}''$ as $\vec{x}'$]. So we get the conservation law

$$(\partial/\partial t)\rho(\vec{x},t) + \vec{\nabla}\cdot\vec{J}(\vec{x},t) = 0 \tag{5.18}$$

properly, and $G_d(\vec{x},t)$ calculated by this method has the correct second moment. The fact that the second moment and Eq. (5.17) are related was first stated by Schofield.[9] In the method used here, the second moment depends directly on Eq. (5.17).

To calculate $G_d^{(\mathrm{iv})}(\vec{x}, 0)$ we need $\ddot{\vec{J}}(\vec{x}, 0)$. This is a more tedious calculation, so we shall only outline the steps. Using Eq. (5.14), we find from Eq. (5.12) that

$$\dot{\vec{J}}(\vec{x}, t) = -\beta \int_0^t dt' \int d\vec{x}' (\partial/\partial t)\{\vec{J}^N(\vec{x}, t)\rho^N(\vec{x}', t')\}_0 \vec{\nabla} V(\vec{x}' - \vec{x}_0(t')) \cdot \vec{v}_0(t'), \tag{5.19}$$

and also

$$\ddot{\vec{J}}(\vec{x}, 0) = -\beta \int d\vec{x}' [(\partial/\partial t)\{\vec{J}^N(\vec{x}, t)\rho^N(\vec{x}', t')\}_0]_{t'=t=0} \vec{\nabla} V(\vec{x}' - \vec{x}_0(0)) \cdot \vec{v}_0(0). \tag{5.20}$$

Using the equations of motion for the particles, the quantity $[(\partial/\partial t)\{\vec{J}^N(\vec{x}, t)\rho^N(\vec{x}', t')\}_0]_{t'=t=0}$ can be expressed in terms of the equilibrium static correlation functions for two, three, and four particles. By using Eq. (5.17), which relates the two- and three-particle correlation functions, and the second equation of the hierarchy

$$\vec{\nabla} n_3(\vec{x}, \vec{x}', \vec{x}'') + \beta n_3(\vec{x}, \vec{x}', \vec{x}'')\vec{\nabla} V(\vec{x} - \vec{x}') + \beta n_3(\vec{x}, \vec{x}', \vec{x}'')\vec{\nabla} V(\vec{x} - \vec{x}'') + \beta \int d\vec{x}''' \, n_4(\vec{x}, \vec{x}', \vec{x}'', \vec{x}''')\vec{\nabla} V(\vec{x} - \vec{x}''') = 0, \tag{5.21}$$

which relates the three- and four-particle correlation functions, one obtains

$$[(\partial/\partial t)\{\vec{J}^N(\vec{x}, t)\rho^N(\vec{x}', t')\}_0]_{t'=t=0} = (n_0\beta M)^{-1}\{-[\vec{\nabla}\delta(\vec{x} - \vec{x}')]n_2(\vec{x}', \vec{x}_0(0)) + \delta(\vec{x} - \vec{x}')\vec{\nabla} n_2(\vec{x}, \vec{x}_0(0))\}. \tag{5.22}$$

Equation (5.20) then becomes

$$\ddot{\vec{J}}(\vec{x}, 0) = (n_0/M)\, g(\vec{x} - \vec{x}_0(0))\vec{\nabla}[\vec{\nabla} V(\vec{x} - \vec{x}_0(0)) \cdot \vec{v}_0(0)]. \tag{5.23}$$

From this we get

$$\begin{aligned} \mathcal{V}\langle \ddot{J}_\alpha(\vec{x}, 0) j_\gamma^{(0)}(0, 0)\rangle &= (n_0/\beta M^2)\mathcal{V}\langle g(\vec{x} - \vec{x}_0(0))[\nabla_\alpha \nabla_\gamma V(\vec{x} - \vec{x}_0(0))]\,\delta(\vec{x}_0(0))\rangle \\ &= (n_0/\beta M^2) \int d\vec{x}' g(\vec{x} - \vec{x}')\nabla_\alpha \nabla_\gamma V(\vec{x} - \vec{x}')\mathcal{V}\langle\delta(\vec{x}' - \vec{x}_0(0))\delta(\vec{x}_0(0))\rangle. \end{aligned} \tag{5.24}$$

But $\mathcal{V}\langle\delta(\vec{x}' - \vec{x}_0(0))\delta(\vec{x}_0(0))\rangle = \delta(\vec{x}')$, $\qquad$ (5.25)

so $\mathcal{V}\langle \ddot{J}_\alpha(\vec{x}, 0) j_\gamma^{(0)}(0, 0)\rangle = (n_0/\beta M^2)\, g(\vec{x})\nabla_\alpha \nabla_\gamma V(\vec{x})$. $\qquad$ (5.26)

This gives $G_d^{(\mathrm{iv})}(\vec{x}, 0) = (n_0/\beta M^2)\nabla_\alpha \nabla_\gamma[g(\vec{x})\nabla_\alpha \nabla_\gamma V(\vec{x})]$, $\qquad$ (5.27)

which is the correct fourth moment.

In analogy to the derivation of the second moment, the fourth moment depends on the first two members of the hierarchy of Green's equations.

VI. DERIVATION OF OTHER APPROXIMATIONS FOR $G_d(\vec{x},t)$

In this section we shall show how some previously given approximations for $G_d(\vec{x}, t)$ can be derived from the present method.

From Eq. (5.2) we can write

$$G_d^{(\mathrm{eq})}(\vec{x}, t) = n_0 \int d\vec{x}' g(\vec{x} - \vec{x}')\mathcal{V}\langle\rho^{(0)}(\vec{x}', t)\rho^{(0)}(0, 0)\rangle. \tag{6.1}$$

The definition of the Van Hove self-correlation function is

$$G_s(\vec{x}, t) = \mathcal{V}\langle\rho^{(0)}(\vec{x}, t)\rho^{(0)}(0, 0)\rangle, \tag{6.2}$$

so that $G_d^{(\mathrm{eq})}(\vec{x}, t) = n_0 \int d\vec{x}' g(\vec{x} - \vec{x}')G_s(\vec{x}', t)$. $\qquad$ (6.3)

Equation (6.3) was proposed as an approximation for $G_d(\vec{x}, t)$ by Vineyard and is known as the convolution approximation.[11] It has often been discussed in the literature. We note here that this approximation results from keeping only the $f_N^{(\mathrm{eq})}(\vec{X}, \vec{P} \,|\, \vec{x}_0(t))$ part of our solution for $f_N(\vec{X}, \vec{P}, t)$. The work of Sec. V shows that approximating f_N in this way gives large time variation in the density of other particles in the vicinity of the blue particle, but that there is no current, i.e., this approximation violates particle conservation.

Another approximation for $G(\vec{x}, t)$ has recently been given by Nelkin and Ranganathan[12] by solving the linearized Vlasov equation. We can derive their result in the following way: We imagine that in calculating the response of the other particles to the motion of the blue particle, the initial perturbation is treated exactly but that the subsequent propagation is treated only to linear order in the coupling between the other particles and the blue particle. In that case $\rho^{(\mathrm{eq})}(\vec{x}, t)$ remains exactly as we have found it in Eq. (3.17). Since $\bar{\rho}(\vec{x}, t)$ is explicitly proportional to $V(\vec{x}' - \vec{x}_0(t'))$, we neglect the influence from the blue particle elsewhere and make the replacement

$$\{\rho^N(\vec{x}, t)\rho^N(\vec{x}', t')\}_0 \rightarrow n_0 G(\vec{x} - \vec{x}', t - t') . \tag{6.4}$$

However, linear response theory is not appropriate for potentials with hard cores. To treat such potentials, an effective potential must be found which can then be used in formulas derived from linear response theory. It has been shown by Percus[13] that a first approximation to such an effective potential is

$$V_{\mathrm{eff}}(\vec{x}) = -\beta^{-1} c(\vec{x}), \tag{6.5}$$

where $c(\vec{x})$ is the Ornstein-Zernike direct correlation function.

The replacement of $V(\vec{x})$ by $-\beta^{-1}c(\vec{x})$ is also indicated by another consideration. If we apply the philosophy of Eq. (6.4) to calculating the current, we must make the replacement

$$\{\vec{J}^N(\vec{x}, t)\rho^N(\vec{x}', t')\}_0 \rightarrow \langle \vec{J}^N(\vec{x}, t)\rho^N(\vec{x}', t')\rangle , \tag{6.6}$$

where the quantity on the right-hand side of Eq. (6.6) is the equilibrium current-density correlation function. If we now attempt to verify particle conservation, we find, because $G(\vec{x} - \vec{x}', t - t')$ has the property

$$G(\vec{x} - \vec{x}', 0) = \delta(\vec{x} - \vec{x}') + n_0 g(\vec{x} - \vec{x}') , \tag{6.7}$$

instead of the property in Eq. (5.10), that particle conservation has been violated. The contribution of $\rho^{(\mathrm{eq})}(\vec{x}, t)$ to $(\partial/\partial t)\rho(\vec{x}, t)$ is no longer cancelled by the contribution coming from differentiating the time dependence in the upper limit of the integral defining $\bar{\rho}(\vec{x}, t)$. However, if $V(\vec{x})$ is replaced by $-\beta^{-1}c(\vec{x})$, we see by using the equation relating $g(\vec{x})$ and $c(\vec{x})$,

$$g(\vec{x}) - 1 = c(\vec{x}) + n_0 \int d\vec{x}'\, c(\vec{x} - \vec{x}')[g(\vec{x}') - 1)] , \tag{6.8}$$

that this cancellation again occurs. The conclusion is that $V(\vec{x})$ must be replaced by $-\beta^{-1}c(\vec{x})$ to maintain particle conservation.

NR also replace the potential by the direct correlation function in the linearized Vlasov equation. Their argument for doing so is based on getting the second moment correctly. Since the second moment is equivalent to particle conservation, our argument and theirs must have essentially the same content.

If we make the replacements of Eqs. (6.4) and (6.5) in Eq. (5.3), we get the following equation for $G_d(\vec{x}, t)$.

$$G_d(\vec{x}, t) = n_0 \int d\vec{x}'\, g(\vec{x} - \vec{x}') G_s(\vec{x}', t) - n_0 \int_0^t dt' \int d\vec{x}'\, d\vec{x}''\, G(\vec{x} - \vec{x}', t - t') c(\vec{x}' - \vec{x}'')(\partial/\partial t') G_s(\vec{x}'', t') . \tag{6.9}$$

To get the last term we have introduced $\vec{j}^{(0)}(\vec{x}, t)$ using Eq. (2.4); done an integration by parts; and used the conservation law for the blue particle, Eq. (5.5), and the definition of $G_s(\vec{x}, t)$, Eq. (6.2).

Since we consider that we know $G_s(\vec{x}, t)$, we separate $G(\vec{x}, t)$ in the integral in Eq. (6.9) into its self and distinct parts. We then find the following integral equation for $G_d(\vec{x}, t)$:

$$\begin{aligned} G_d(\vec{x}, t) &+ n_0 \int_0^t dt' \int dx'\, d\vec{x}''\, G_d(\vec{x} - \vec{x}', t - t') c(\vec{x}' - \vec{x}'')(\partial/\partial t') G_s(\vec{x}'', t') \\ &= n_0 \int d\vec{x}'\, g(\vec{x} - \vec{x}') G_s(\vec{x}', t) - n_0 \int_0^t dt' \int d\vec{x}'\, d\vec{x}''\, G_s(\vec{x} - \vec{x}', t - t') c(\vec{x}' - \vec{x}'')(\partial/\partial t') G_s(\vec{x}'', t') . \end{aligned} \tag{6.10}$$

Equation (6.10) can be solved by Fourier transforming with respect to the spatial variables and Laplace transforming with respect to time. We define $F_s(\vec{k}, t)$, $F_d(\vec{k}, t)$, $F(\vec{k}, t)$, $c(\vec{k})$, $\gamma(\vec{k})$ to be the spatial Fourier transforms of $G_s(\vec{x}, t)$, $G_d(\vec{x}, t)$, $G(\vec{x}, t)$, $c(\vec{x})$, $n_0(g(\vec{x}) - 1)$, respectively, and $\hat{F}_s(\vec{k}, p)$, $\hat{F}_d(\vec{k}, p)$, $\hat{F}(\vec{k}, p)$ to be the Laplace transforms with respect to time of $F_s(\vec{k}, t)$, $F_d(\vec{k}, t)$, $F(\vec{k}, t)$, respectively.

The solution of Eq. (6.10) is then

$$\hat{F}_d(\vec{k}, p) = \{(2\pi)^3 n_0 \delta(\vec{k}) p^{-1} + \gamma(\vec{k}) \hat{F}_s(\vec{k}, p) - n_0 c(\vec{k}) \hat{F}_s(\vec{k}, p)[p\hat{F}_s(\vec{k}, p) - 1]\} / \{1 + n_0 c(\vec{k})[p\hat{F}_s(\vec{k}, p) - 1]\} . \tag{6.11}$$

Now adding $\hat{F}_s(\vec{k}, p)$ gives

$$\hat{F}(\vec{k}, p) = (2\pi)^3 n_0 \delta(\vec{k})/p + [1 + \gamma(\vec{k})] \hat{F}_s(\vec{k}, p)/\{1 + n_0 c(\vec{k})[p\hat{F}_s(\vec{k}, p) - 1]\} . \tag{6.12}$$

[The term proportional to $\delta(\vec{k})$ comes from the $t \to \infty$ limit of $G(\vec{x}, t)$. It can be separated from the other term by using $\hat{F}_s(0, p) = p^{-1}$, which follows from the normalization of $G_s(\vec{x}, t)$.] If in this equation we replace $\hat{F}_s(\vec{k}, p)$ by its limit for free particles, then we have the result obtained by NR by solving the linearized Vlasov equation [also with the replacement of Eq. (6.5)].

The moment relations satisfied by this approximation (expressed now in Fourier space instead of real space) are found from the coefficients of the expansion of $\hat{F}(\vec{k}, p)$ in powers of p^{-1}, using the known asymptotic expansion of $\hat{F}_s(\vec{k}, p)$ and the relation between $\gamma(\vec{k})$ and $c(\vec{k})$. The second moment is exact, and the fourth moment is

$$F^{(\text{iv})}(\vec{k}, 0) = 3k^4/(\beta M)^2 + (n_0 k^4/3\beta M^2) \int d\vec{x}\, g(\vec{x}) \vec{\nabla}^2 V(\vec{x}) - n_0 c(\vec{k}) k^4/(\beta M)^2 . \tag{6.13}$$

The first two terms of Eq. (6.13) are the exact fourth moment of $F_s(\vec{k}, t)$. The fourth moment in the approximation of NR does not contain the second term of Eq. (6.13) because their result has the free-particle limit of the self-function instead of the exact self-function. The last term of Eq. (6.13) is the fourth moment of the distinct particle function in this approximation; it bears little resemblance to the Fourier transform of the exact result in Eq. (5.24).

The result of NR has been stated[14] to give poor quantitative agreement with the machine calculations of Rahman.[15] Because of this and because the result of Eq. (6.12) gives such a poor representation of the fourth moment, we have not done a quantitative evaluation of it.

Our procedure treats one aspect of the problem better than the linearized Vlasov equation does. NR state that their solution treats properly the initial disturbance of the other particles by the blue particle, but does not treat properly its subsequent propagation. We see from our procedure that in fact this subsequent propagation is treated as if the particle were free. We remedy this defect by assuming that the self-correlation function is known; on that basis we construct an approximation for the distinct-particle function. The inadequacies of Eq. (6.12) then result from these approximations and not on inadequate approximation for the self-motion.

Our result in Eqs. (5.2) and (5.3) is amenable to other approximations. Further work is in progress on this problem.

Note added in proof. The use of the direct correlation function as the effective potential has also been suggested by R. Zwanzig [Phys. Rev. 144, 170 (1966)].

VII. SUMMARY

The main results of this report can be summarized as follows:

(1) Within the philosophy of approach used, an exact derivation has been given of an equation for the velocity autocorrelation function of a liquid. The new equation shows that a similar equation derived earlier neglected the effects of collective modes.

(2) The approach has been extended to discuss the density-density correlation function. A previously discussed relation between the second moment of this function and the hierarchy of equations relating the static s and $s+1$ particle correlation functions has been extended to the fourth moment.

(3) Previously known approximations for $G_d(\vec{x}, t)$ have been shown to be derivable from this approach. In doing this, it has been shown that the replacement of the interparticle potential by an effective potential proportional to the direct correlation function serves the purpose of maintaining particle conservation in a linear response context. It has also been suggested that it may be better to consider the self and distinct parts of $G(\vec{x}, t)$ separately, and assume the former is known when making an approximate theory of the latter.

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APPENDIX

The definition of $f_N^{(\text{eq})}(\vec{X}, \vec{P} | \vec{x}_0(t))$ is

$$f_N^{(\text{eq})}(\vec{X}, \vec{P} | \vec{x}_0(t)) = \left\{ e^{-\beta H_N} \exp\left[-\beta \sum_{i=1}^{N} V(\vec{x}_i - \vec{x}_0(t)) \right] \right\} \left\{ \int d\Gamma_N e^{-\beta H_N} \exp\left[-\beta \sum_{i=1}^{N} V(\vec{x}_i - \vec{x}_0(t)) \right] \right\}^{-1} . \tag{A.1}$$

A factor $\int d\vec{p}_0 \exp(-\beta p_0^2/2M)$ is put into both numerator and denominator. Also write

$$\exp\left[-\beta \sum_{i=1}^{N} V(\vec{x}_i - \vec{x}_0(t)) \right] = \int d\vec{x}_0 \exp\left[-\beta \sum_{i=1}^{N} V(\vec{x}_i - \vec{x}_0) \right] \delta(\vec{x}_0 - \vec{x}_0(t)) . \tag{A.2}$$

Then $$f_N^{(\mathrm{eq})}(\vec{X}, \vec{P} \,|\, \vec{x}_0(t)) = \int d\vec{p}_0 \, d\vec{x}_0 \, \delta(\vec{x}_0 - \vec{x}_0(t)) \, e^{-\beta H_{N+1}} \Big/ \int d\Gamma_{N+1} \, e^{-\beta H_{N+1}} \delta(\vec{x}_0 - \vec{x}_0(t)) \, . \tag{A.3}$$

The density of a uniform system of $N+1$ particles is

$$(N+1)/\upsilon = (N+1) \int d\Gamma_{N+1} \, e^{-\beta H_{N+1}} \delta(\vec{x}_0 - \vec{x}_0(t)) \Big/ \int d\Gamma_{N+1} \, e^{-\beta H_{N+1}} \, . \tag{A.4}$$

Using Eq. (A.4) the denominator of Eq. (A.3) can be replaced by

$$\int d\Gamma_{N+1} \, e^{-\beta H_{N+1}} \delta(\vec{x}_0 - \vec{x}_0(t)) = \upsilon^{-1} \int d\Gamma_{N+1} \, e^{-\beta H_{N+1}} \, . \tag{A.5}$$

Therefore

$$f_N^{(\mathrm{eq})}(\vec{X}, \vec{P} \,|\, \vec{x}_0(t)) = \upsilon \int d\vec{p}_0 \, d\vec{x}_0 \, e^{-\beta H_{N+1}} \, \delta(\vec{x}_0 - \vec{x}_0(t)) \Big/ \int d\Gamma_{N+1} \, e^{-\beta H_{N+1}} \, . \tag{A.6}$$

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