Approximate Solutions of the Liouville Equation.
II. Stationary Variational Principles

Eugene P. Gross[1]

Stationary variational functionals for the Laplace transform of the Liouville distribution are constructed. The value of the functional is the autocorrelation function that one wishes to compute. It is shown that the functionals may be transformed to a renormalized form. Trial functions not involving the potential explicitly give rise to time-dependent autocorrelation functions determined only by equilibrium spatial correlation functions. Another class of functionals is constructed by independently varying the parity symmetric and antisymmetric parts of the distribution function. Trial functions need only be assumed for one of these—the optimum value of the other one is given exactly. This procedure is used to improve the simplest known theories for velocity and density autocorrelation functions.

1. INTRODUCTION

In an earlier paper[1] (hereafter denoted as I) we studied time-dependent solutions of the Liouville equation in the linear response domain.[2] This is the domain near the exact equilibrium distribution Φ, where the amplitude

---

[2] See I for a discussion of related work.

of a disturbance is small. However, one is interested in a theory that deals with arbitrarily rapid spatial and temporal processes.

The approach in I was based on assumed forms for the N-body symmetric distribution function $f_N(t)$. In the lowest approximation f_N is assumed to be of the form $\Phi[1 + \sum_{\alpha=1}^{N} \psi(\mathbf{p}_\alpha \mathbf{q}_\alpha t)]$. The deviation from equilibrium is assumed to be one-body additive for all time. The assumed form for f_N determines the reduced singlet, doublet, etc., distributions. It yields a truncation scheme for the time-dependent BBGKY equations. The result of the first approximation is a modified Vlasov equation with the bare interparticle potential replaced by the Ornstein–Zernike direct correlation function. The singlet distribution function has the correct short-time behavior. For example, one satisfies the sum rule $\int \omega^2 S(k, \omega)\, d\omega$ for the Fourier–Laplace transform of the density autocorrelation function. In the second approximation f_N is permitted to contain two-body additive terms for all t. This restricted form determines the time-dependent triplet distribution function in terms of the singlet and doublet. Again one has a truncation of the hierarchy—the approximate theory consists of coupled equations for the singlet and doublet distributions.

It was shown in I that the scheme is renormalized in the following sense. By using the exact equilibrium hierarchy, the time-dependent distributions can be shown to satisfy equations where the bare potential is absent. The equations contain only equilibrium spatial correlation functions. For example, in the first approximation it is the direct correlation function that replaces the bare potential.

In the present paper we continue the strategy of making direct assumptions on the approximate functional form of $f_N(t)$. We take advantage of the linearity of the Liouville equation

$$f_N = \Phi(1 + F_N), \quad \frac{\partial F_N}{\partial t} + L F_N = 0, \quad L = \sum_{\alpha=1}^{N} \left(\frac{\mathbf{p}_\alpha}{m} \frac{\partial}{\partial \mathbf{q}_\alpha} - \frac{\partial V}{\partial \mathbf{q}_\alpha} \frac{\partial}{\partial \mathbf{p}_\alpha} \right) \quad (1)$$

and work with the Laplace transform

$$(\sigma + L)\bar{F}_N(\sigma) = F_0 \quad (2)$$

Here

$$F(\sigma) = \int_0^\infty e^{-\sigma t} F_N(t)\, dt, \qquad F_N(t) = (1/2\pi i) \int_{c-i\infty}^{c+i\infty} \bar{F}(\sigma)\, e^{\sigma t}\, d\sigma \quad (3)$$

and F_0 is the initial value $F_N(t = 0)$. Our starting point is a stationary variational principle for the Liouville equation.

We define the momentum-reversed distribution $\bar{F}_-(\mathbf{p}_1 \cdots \mathbf{q}_N/\sigma)$ as

$$\bar{F}_-(\mathbf{p}_1 \cdots \mathbf{q}_N/\sigma) = \bar{F}(\mathbf{p}_1 \cdots \mathbf{q}_N/\sigma) \quad (4)$$

(an underscore beneath a number denotes the negative of the number). It obeys the equation

$$(\sigma - L)\,\bar{F}_-(\sigma) = F_{0-} \tag{5}$$

We construct the functional

$$J(\sigma) = \int \Phi\bar{F}_-[(\sigma + L)\bar{F} - F_0]\,d\Gamma - \int \Phi\bar{F}F_{0-}\,d\Gamma \tag{6}$$

and examine its variation with respect to $\bar{F}$. We make use of the facts that $L\Phi = 0$, Φ is invariant under momentum reversal, and L changes sign under momentum reversal. It is then clear that the condition of stationarity of J yields the Liouville equations for $\bar{F}$ and $\bar{F}_-$.

When $\bar{F}$ satisfies the Liouville equation the stationary value of J is

$$[J(\sigma)] = -\int \Phi F_N F_{0-}\,d\Gamma \tag{7}$$

(for ease of notation we will drop the bar indicating the Laplace transform). For example, if $F_0 = \sum_{\alpha=1} \delta(\mathbf{q}_\alpha - \mathbf{x})$, we have $F_{0-} = F_0$ and $[J]$ is the negative of the Laplace transform of the density autocorrelation function. The variational principle permits an accurate computation of the latter quantity in the following sense. If F is near the correct solution of the Liouville equation and is in error of order ϵ, the density autocorrelation function is only in error of order ϵ^2.

The approach to the solutions of the Liouville equation using stationary variational principles enables us to direct the approximations toward the goal of accurately computing quantities of particular interest. We also gain a great deal of freedom in the approximations that can be made. For example, one can work with nonorthogonal functions in a controlled way. One can insist on approximations that are compatible with the microscopic conservation laws by employing Lagrange multipliers to handle constraints. In addition, general symmetry and invariance properties can be exploited maximally.

An example of the utility of the variational approach is found in Section 2. There we use elementary integration by parts to transform the functional to a manifestly renormalized form. This replaces the somewhat cumbersome use of the exact equilibrium hierarchy in I. Furthermore, we obtain renormalized results for approximation schemes that lie outside the framework of I. In Section 2 we derive a further normalization-independent form of the stationary variational principle whose utility was demonstrated by Schwinger in other contexts. In Section 3 we rederive the equations of I and exhibit some of the additional flexibility of the variational approach.

In the present classical, nonrelativistic theory all equilibrium correlation functions are well defined, including averages of functionals of the potential

energy. One is therefore not compelled to use the renormalized form of the theory. In Section 4 we note that the distribution $\bar{F}(\mathbf{p}_1 - - \mathbf{q}_N/\sigma)$ is the sum of a part F^A that reverses sign under the operation $\mathbf{p}_i \rightarrow -\mathbf{p}_i$ and of a part F^S that is unchanged. The functional J may be varied independently with respect to the two parts. Given an approximate F^S, the optimum F^A may be computed exactly. When this is inserted into J we obtain a new functional in which only F^S is to be varied. The new operator is L^2, which is self-adjoint and invariant to momentum reversal.

In Section 5 we examine the problem of the evolution of a symmetric initial distribution that is spatially homogeneous and of the form

$$F(t = 0) = \sum_{i=1}^{N} f_0(\mathbf{p}_i).$$

The one-body additive assumption $F(\sigma) = \sum_{i=1}^{N} f(\mathbf{p}_i/\sigma)$ yields no change in the initial distribution. The less restrictive assumption that only the symmetric part is one-body additive leads to an exactly soluble result where at least the short-time behavior is reasonable.

In Section 6 we examine the problem of determining the density auto-correlation function. The one-body additivity assumption $F = \sum_{i=1} \psi(\mathbf{p}_i\mathbf{q}_i/\sigma)$ leads to the modified Vlasov equation. However, we may make this assumption only for the symmetric part and use the optimum associated anti-symmetric part. The theory is still exactly soluble. Along with the equilibrium pair correlation function, there now appears the new quantity $\langle \sum_{i=1} \nabla_i^2 V \rangle$.

While some of the results of the applications illustrated in this paper are of interest in themselves, the assumptions on the distribution functions are still primitive. They do serve to illustrate the techniques we will use in using more realistic approximations.

2. TRANSFORMATIONS OF THE FUNCTIONAL

We have the functional (6) where F and F_- are real when σ is real. We will first transform the functional so that the quantity we want to compute, namely $[J]$, is "renormalized," i.e., is expressible solely in terms of static correlation functions. The bare potential that is contained in L does not appear. That this is possible was shown in paper I, but in a somewhat cumbersome way. The result is almost trivial when the problem is approached via the variational principle.

Consider the expression

$$J_L = \int \Phi F_- LF \, d\Gamma = \int \Phi F_- \left[\sum_{\alpha} \left(\frac{\mathbf{p}_\alpha}{m} \frac{\partial}{\partial \mathbf{q}_\alpha} - \frac{\partial V}{\partial \mathbf{q}_\alpha} \frac{\partial}{\partial \mathbf{q}_\alpha} \right) \right] F \, d\Gamma \qquad (8)$$

It may be rewritten as

$$J_{\mathrm{L}} = -KT \sum_{\alpha} \int F_- \left(\frac{\partial \Phi}{\partial \mathbf{p}_\alpha} \frac{\partial}{\partial \mathbf{p}_\alpha} - \frac{\partial \Phi}{\partial \mathbf{q}_\alpha} \frac{\partial}{\partial \mathbf{p}_\alpha} \right) F \, d\Gamma \tag{9}$$

where K is Boltzmann's constant. Integrating by parts; we find

$$-J_{\mathrm{L}} = KT \int \Phi \{F_- , F\}_{\mathrm{PB}} \, d\Gamma \tag{10}$$

where

$$-\{F_- , F\}_{\mathrm{PB}} = \sum_{\alpha} \left(\frac{\partial F_-}{\partial \mathbf{p}_\alpha} \frac{\partial F}{\partial \mathbf{q}_\alpha} - \frac{\partial F_-}{\partial \mathbf{q}_\alpha} \frac{\partial F}{\partial \mathbf{p}_\alpha} \right)$$

is the Poisson bracket.

This is already a renormalized form. For, suppose F is expressed in terms of a complete set of functions in phase space $F = \sum a_n(\sigma) \, \Phi_n(\mathbf{p}_1 \cdots \mathbf{q}_N)$, where the a_n are coefficients to be determined so as to satisfy the Liouville equation. Then J becomes a quadratic form in the a_n :

$$J = \sum_{n,n'} a_n a_{n'} (\sigma \langle \Phi_{n-} \Phi_{n'} \rangle + \langle \{\Phi_{n-} , \Phi_{n'}\}_{\mathrm{PB}} \rangle) - \sum a_n(\langle \Phi_{n-} F_0 \rangle + \langle \Phi_n F_{0-} \rangle) \tag{11}$$

The stationarity condition leads to a set of linear inhomogeneous equations for the a_n. All coefficients are equilibrium correlation functions. The approach in I was based on a particular ordering of the Φ_n in terms of one-body additive and two-body additive functions, etc.

There are other renormalized forms that are useful. If we reverse the momenta in this second term of the Poisson bracket and note the invariance of Φ under this transformation, we find

$$J_{\mathrm{L}} = 2KT \int \Phi \sum_{\alpha=1}^{N} \frac{\partial F}{\partial \mathbf{p}_\alpha} \frac{\partial F_-}{\partial \mathbf{q}_\alpha} \, d\Gamma \tag{12}$$

Integrating by parts, we find

$$J_{\mathrm{L}} = -2KT \int F_- \sum_{\alpha} \left(\frac{\partial \Phi}{\partial \mathbf{p}_\alpha} \frac{\partial F}{\partial \mathbf{q}_\alpha} + \Phi \frac{\partial^2 F}{\partial \mathbf{p}_\alpha \partial \mathbf{q}_\alpha} \right) d\Gamma$$

$$= 2 \int \Phi F_- \sum_{\alpha} \left(\frac{\mathbf{p}_\alpha}{m} - KT \frac{\partial}{\partial \mathbf{p}_\alpha} \right) \frac{\partial F}{\partial \mathbf{q}_\alpha} \, d\Gamma \tag{13}$$

Introducing the one-body additive operator

$$D \equiv \sum_{\alpha=1}^{N} D_\alpha = \sum_{\alpha=1}^{N} \left(\frac{\mathbf{p}_\alpha}{m} - KT \frac{\partial}{\partial \mathbf{p}_\alpha} \right) \frac{\partial}{\partial \mathbf{q}_\alpha} \tag{14}$$

we have

$$J = \langle F_-, (\sigma + 2D) F \rangle - \langle F_- F_0 \rangle - \langle F F_{0-} \rangle \tag{15}$$

We now introduce variational principles involving complex functions. We want to have the freedom to choose trial functions for $F_N(t)$ that are complex. For example, in the computation of the density autocorrelation function we start with the initial condition $F_0 = \sum_{\alpha=1}^{N} \exp(i\mathbf{k}\mathbf{q}_\alpha)$ and compute $\langle F_0^* F_N(t) \rangle$.

The equation to be satisfied is $(\partial F_N/\partial t) + L F_N = 0$. Because the equation is linear and L is real, we also have $(\partial F_N^*/\partial t) + L F_N^* = 0$. The Laplace transforms of the two equations are

$$(\sigma + L)\bar{F}(\sigma) = F_0, \qquad (\sigma + L)\overline{F^*}(\sigma) = F_0^*$$

where $\overline{F^*}(\sigma) = \int_0^\infty e^{-\sigma t} F^*(t)\, dt$. If we have the solution to the first equation, namely $\bar{F}(\sigma)$, we can find the solution to the second equation by taking the complex conjugate of $\bar{F}(\sigma)$, *treating σ as real*. Furthermore, with an approximate $\bar{F}(\sigma)$ we can always restrict ourselves to trials for $\overline{F^*}(\sigma)$ which are constructed from $\bar{F}(\sigma)$ in the same way. On the other hand, even for real σ, $\bar{F}(\sigma)$ is complex, i.e., contains two independent real functions. Thus we can take an alternative point of view and treat $\bar{F}(\sigma)$ and $\overline{F^*}(\sigma)$ as two independent functions in the variation.

We now understand the * operation to represent complex conjugation with σ left unaltered even when it is complex. (For notational convenience we drop the bars that indicate Laplace transforms.) Let us form the functional

$$J_c = \int \Phi F_-^* \{(\sigma + L) F - F_0\}\, d\Gamma - \int \Phi F_- F_0^*\, d\Gamma. \tag{16}$$

Varying F and F^* independently, we have

$$\delta J_c = \int \Phi\, \delta F_-^* \{(\sigma + L) F - F_0\}\, d\Gamma$$

$$= \int \Phi\, \delta F_- (\sigma - L) F_-^*\, d\Gamma - \int \Phi\, \delta F_- F_0^*\, d\Gamma$$

where we have integrated by parts in the second term. The condition of stationarity yields the desired equations,

$$(\sigma + L) F = F_0, \qquad (\sigma + L) F^* = F_0^*$$

and the stationary value of J_c is

$$[J_c] = -\int \Phi F_- F_0^*\, d\Gamma \tag{17}$$

Thus J_c is a suitable complex functional. A symmetric complex function is

$$J_{cs} = \tfrac{1}{2}\langle F_-{}^*(\sigma + L)F + F_-(\sigma + L)F^*\rangle - \langle F_-F_0{}^* + F_-{}^*F_0\rangle \quad (18)$$

with $[J_{cs}] = -\tfrac{1}{2}\langle F_-F_0{}^* + F_-{}^*F_0\rangle$.

The complex functionals may also be transformed to renormalized form. We have

$$\langle F_-{}^*LF\rangle = -KT \int \Phi\{F_-{}^*, F\}_{\text{PB}}\, d\Gamma = \langle F_-{}^*DF\rangle + \langle F_-DF^*\rangle$$

$$J_c = \sigma\langle F_-{}^*F\rangle + \langle F_-{}^*DF\rangle + \langle F_-DF^*\rangle - \langle F_-{}^*F_0 + F_-F_0{}^*\rangle \quad (19)$$

In the next section we give some examples of the use of the variational principles.

Under certain circumstances it may be useful to remove an overall normalization factor. This is the Schwinger variant of the stationary variational principle.[2] We set $F = A(\sigma)\,G$, where A is a parameter. Varying A and A^* in J_c, we find

$$A = \langle G_-{}^*F_0\rangle / (\sigma\langle G_-{}^*G\rangle + \langle G_-{}^*LG\rangle) \quad (20)$$

and

$$[J_c] = -\langle G_-F_0{}^*\rangle\langle G_-{}^*F_0\rangle / (\sigma\langle G_-{}^*G\rangle + \langle G_-{}^*LG\rangle) \quad (21)$$

Hence

$$J_c = -\langle F_-F_0{}^*\rangle\langle F_-{}^*F_0\rangle / (\sigma\langle F_-{}^*F\rangle + \langle F_-{}^*LF\rangle) \quad (22)$$

is a new form of the variational principle.

The Schwinger form is sometimes surprisingly powerful. For example, the crudest choice of a trial function is $F = [1/(\sigma + L_0)]\,F_0$, where

$$F = \sum_{\alpha=1} \exp(i\mathbf{k}\mathbf{q}_\alpha)$$

This is a free-particle estimate of the evolution of the distribution function. Nonetheless, the value of J_c is exactly that given by the Zwanzig modification of the Vlasov equation.[3] With the usual variation principle one is required to vary the functional form of a one-body additive trial function.

3. USE OF THE RENORMALIZED FORM

In the present section we rederive the results of *I*. The variational form of the theory is more flexible, however. It allows us to make both extensions and also restrictions at any stage of the basic theory.

We start with the real form of the functional and assume the one-body additive form

$$F_N = \sum_{\alpha=1}^{N} \psi(\mathbf{p}_\alpha \mathbf{q}_\alpha/\sigma) = \hat{N}(\bar{1})\,\psi(\bar{1}) \tag{23}$$

The only part of the functional that requires special consideration is J_L. We use the form

$$J_L = 2KT \int \Phi \sum_\alpha \frac{\partial F_-}{\partial \mathbf{p}_\alpha} \frac{\partial F}{\partial \mathbf{q}_\alpha}\, d\Gamma$$

$$= 2KT \int \Phi \sum_\alpha \frac{\partial \psi}{\partial \mathbf{p}_\alpha}(\underline{\mathbf{p}}_\alpha,\mathbf{q}_\alpha) \frac{\partial \psi}{\partial \mathbf{q}_\alpha}(\mathbf{p}_\alpha,\mathbf{q}_\alpha)\, d\Gamma \tag{24}$$

Introducing one delta function, this is

$$J_L = 2KT \sum_{\alpha=1}^{N} \int \Phi \frac{\partial \psi}{\partial \mathbf{p}_\alpha}(\mathbf{p}_\alpha) \frac{\partial \psi}{\partial x}(\mathbf{p}_\alpha x)\,\delta(\mathbf{q}_\alpha - \mathbf{x})\, d^3x\, d\Gamma$$

$$\tag{25}$$

$$= -2KT \sum_{\alpha=1}^{N} \int \Phi \frac{\partial \psi}{\partial \mathbf{p}_\alpha}(\mathbf{p}_\alpha x) \frac{\partial \psi}{\partial x}(\mathbf{p}_\alpha x)\,\delta(\mathbf{q}_\alpha - \mathbf{x})\, d^3x\, d\Gamma$$

Introducing another delta function, we have

$$J_L = -2KT \sum_{\alpha=1}^{N} \delta(\mathbf{p}_\alpha - \mathbf{p}) \frac{\partial \psi}{\partial \mathbf{p}}(\mathbf{px}) \frac{\partial \psi}{\partial \mathbf{x}}(\underline{\mathbf{p}}\mathbf{x})\,\delta(\mathbf{q}_\alpha - \mathbf{x})\, d^3x\, d\Gamma$$

$$\tag{26}$$

$$= -2KT \int \int \hat{N}(\mathbf{px}) \frac{\partial \psi}{\partial \mathbf{p}}(\mathbf{px}) \frac{\partial \psi}{\partial \mathbf{x}}(\underline{\mathbf{p}}\mathbf{x})\, d^3p\, d^3x\, d\Gamma$$

Hence the total functional is

$$J = \sigma\langle \hat{N}(\bar{1})\,\hat{N}(\bar{2})\rangle\,\psi(\bar{1})\,\psi(\bar{2}) - 2\langle N(\bar{1})\,N(\bar{2})\rangle\,\psi(\bar{1})\,\psi_0(\bar{2})$$

$$-2KT\langle N(\bar{1})\rangle\,\frac{\partial \psi(\bar{1})}{\partial p_1}\,\frac{\partial \psi(\bar{1})}{\partial x_1} \tag{27}$$

The variation with respect to $\psi(\mathbf{p}_1\mathbf{x}_1)$ yields

$$\sigma\langle N(1)\,N(\bar{2})\rangle\,\psi(\bar{2}) - KT\frac{\partial\langle N(1)\rangle}{\partial p_1}\frac{\partial \psi(1)}{\partial x_1} = \langle N(1)\,N(\bar{2})\rangle\,\psi_0(\bar{2}) \tag{28}$$

This is the modified Vlasov equation discussed in I and obtained earlier by Nelkin, Zwanzig, and others.[3]

The only new point is that the stationary value of J, using the correct solution of the above equation, is

$$[J] = -\langle N(\bar{1})\,N(\bar{2})\rangle\,\psi(\bar{1})\,\psi_0(\bar{2}) \tag{29}$$

The complex form of the functional is

$$J_c = \sigma \langle N(\bar{1}) \, N(\bar{2}) \rangle \, \psi^*(\bar{1}) \, \psi(\bar{2}) - \langle N(\bar{1}) \, N(\bar{2}) \rangle \{ \psi^*(\bar{1}) \, \psi_0(\bar{2}) + \psi(\bar{1}) \, \psi_0^*(\bar{2}) \}$$

$$- KT \langle N(\bar{1}) \rangle 1 \Big\{ \frac{\partial \psi^*(\bar{1})}{\partial \mathbf{p}_1} \frac{\partial \psi(\bar{1})}{\partial \mathbf{x}_1} + \frac{\partial \psi(\bar{1})}{\partial \mathbf{p}_1} \frac{\partial \psi^*(\bar{1})}{\partial \mathbf{x}_1} \Big\} \tag{30}$$

Variation with respect to $\psi^*(1)$ again yields Eq. (28). The stationary value is $[J] = -\langle N(\bar{1}) \, N(\bar{2}) \rangle \, \psi(\bar{1}) \, \psi_0^*(\bar{2})$. The complex form is particularly convenient. For example, in the study of the density autocorrelation function $\psi_0(\mathbf{px}) = \exp(i\mathbf{kx})$ and we may assume $\psi(1) = \tilde{\psi}(\mathbf{p}_1/\mathbf{k}) \exp(i\mathbf{kx}_1)$. The transition to the Fourier transform then can be made at the level of J_c. We then obtain the functional J_{11} of Eq. (35).

We now illustrate how the variational approach can be used to conserve the gains of a given approximation when one proceeds to improve the approximation. Let

$$F = \sum_{\alpha=1}^{N} \tilde{\psi}(\mathbf{p}_\alpha/\mathbf{k}) \exp(i\mathbf{kq}_\alpha) + G(\mathbf{p}_1 \cdots \mathbf{p}_N, \mathbf{q}_1 \cdot \mathbf{q}_N/\mathbf{k}) \tag{31}$$

We have added a function G, which is to represent a limited extension of the one-body theory. Let us choose G to be orthogonal to the one-body part in function space in the sense

$$\int \Phi \sum_{\alpha=1}^{N} \tilde{\psi}^*(\mathbf{p}_\alpha/\mathbf{k})[\exp(-i\mathbf{kq}_\alpha)] \, G \, d\Gamma = 0$$

$$\int \Phi G_-^* \sum \tilde{\psi}(\mathbf{p}_\alpha/\mathbf{k}) \exp(i\mathbf{kq}_\alpha) \, d\Gamma = 0 \tag{32}$$

We will take account of these constraints by means of two Lagrange multipliers λ and λ^*. The new functional has the form

$$J = J_{11} + J_{22} + \int \psi^*(\underline{\mathbf{p}}/\mathbf{k}) \, \phi(p) \, R(\mathbf{p}/\mathbf{k}) \, d^3p + \int \psi(\mathbf{p}/\mathbf{k}) \, \phi R^*(\underline{\mathbf{p}}/\mathbf{k}) \, d^3p \tag{33}$$

$$\phi(p) \, R(\mathbf{p}/\mathbf{k}) \equiv \int \Phi \sum \delta(\mathbf{p}_\alpha - \mathbf{p})[\exp(i\mathbf{kq}_\alpha)]\{(\sigma - \lambda) + L\} \, G \, d\Gamma \tag{34}$$

J_{22} is the part of the functional involving G alone, i.e., is Eq. (15) with F replaced by G. J_{11} is simply

$$J_{11} = N \int \phi(p) \, \psi^*(\underline{\mathbf{p}}/\mathbf{k})\{\sigma + (i\mathbf{kp}/m)\} \, \psi(\mathbf{p}/\mathbf{k}) \, d^3p + \sigma P_2(k) \, \Lambda^* \Lambda(k)$$

$$- N \int \phi \psi^*(\underline{\mathbf{p}})\{\psi_0 + (P_2/N) \, \Lambda_0\} - N \int \phi\{\psi_0^*(\mathbf{p}) + (P_2/N) \, G_0^*\} \tag{35}$$

where

$$\Lambda = \int \Phi(p)\psi(\mathbf{p}/\mathbf{k}) \, d^3p.$$

We can now vary $\psi^*(\mathbf{p}/\mathbf{k})$ and G_-^* independently. In the variation of ψ^* the mixed term adds an additional term to the inhomogeneous part of the modified Vlasov equation. We then find the optimum ψ for given G as

$$\psi(\mathbf{p}) = \int T(\mathbf{p}/\mathbf{p^1}) \, R(\mathbf{p^1}) \, d^3p^1 + \int T(\mathbf{p}/\mathbf{p^1})\{\psi^0(\mathbf{p^1}) + (P_2/N) \Lambda_0\} \, d^3p^1 \quad (36)$$

with

$$T(\mathbf{p}/\mathbf{p^1}) = \frac{\delta(\mathbf{p}-\mathbf{p^1})}{\sigma + (i\mathbf{k}\mathbf{p}/m)} - \sigma \frac{P_2(k)}{N} \frac{1}{\sigma + (i\mathbf{k}\mathbf{p}/m)}$$

$$\times \frac{\phi(p^1)}{\sigma + (i\mathbf{k}\mathbf{p^1}/m)} \cdot \frac{1}{1 + (\sigma P_2/N) \, I(k\sigma)} \quad (37)$$

$$I(k\sigma) = \int \frac{\phi \, d^3p}{\sigma + (i\mathbf{k}\mathbf{p}/m)}$$

As a result, ψ can be eliminated from the functional. We find a new functional involving G alone. There is an effective interaction as a result of this elimination.[3] To simplify things, we consider the study of the density autocorrelation function where $\psi_0 = \Lambda_0 = 1$. We then find

$$J = -N \left(1 + \frac{P_2}{N}\right) \frac{I}{1 + \sigma(P_2 I/N)} + J_{22} + \int R^*(\mathbf{p}) \, T(\mathbf{p}/\mathbf{p^1}) \, R(\mathbf{p^1}) \, d^3p \, d^3p^1 \quad (38)$$

$$+ \left(1 + \frac{P_2}{N}\right) \frac{1}{1 + \sigma(P_2 I/N)} \int \frac{R^*(\mathbf{p}) \, \phi(p) \, d^3p}{\sigma + (i\mathbf{k}\mathbf{p}/m)}$$

There are also the modified constraint conditions to determine λ and λ^* that are the result of inserting the solution for ψ in Eqs. (32). The first term in J is a constant and is the result of the one-body theory, i.e., $G \equiv 0$. Now, however, a limited choice for G, for example, a linear combination of a finite number of many-body modes, allows us to immediately improve the estimate of the density autocorrelation function.

Finally, we exhibit the variational analog of the two-body additive approximation using the complex function. We assume

$$F_N = \hat{N}(\bar{1}) \, \psi(\bar{1}) + \tfrac{1}{2}\hat{N}(\overline{12}) \, \psi(\overline{12}) \quad (39)$$

together with the orthogonality condition

$$\langle \hat{N}(\bar{1}) \, \hat{N}(\overline{23}) \, \psi^*(\bar{1}) \, \psi(\overline{23}) \rangle = 0 \quad (40)$$

---

[3] The same elimination of one-body additive functions has been carried out by Akcasu and Duderstadt[5] in the framework of a different formalism.

Using Lagrange multipliers to handle this and the complex conjugate condition, we have

$$J = J_{11} + J_{12} + J_{21} + J_{22} \tag{41}$$

$$
\begin{aligned}
J_{22} = {} & \tfrac{1}{8}\langle N(\overline{12})\,N(\overline{34})\rangle\,\psi^*(\overline{12})\{\sigma\psi(\overline{34}) - \psi_0(\overline{34})\} + \text{c.c.} \\
& + \tfrac{1}{4}\psi^*(\overline{12})\{\langle N(\overline{12})\rangle[D(\overline{1}) + D(\overline{2})]\,\psi(\overline{12}) \\
& + \langle N(\overline{123})\rangle[D(\overline{1})\,\psi(\overline{13}) + D(\overline{2})\,\psi(\overline{23})]\}
\end{aligned}
\tag{42}
$$

$$
\begin{aligned}
J_{12} + J_{21} = {} & \tfrac{1}{4}\psi^*(\overline{12})\{\langle N(\overline{12})\rangle[D(\overline{1})\,\psi(\overline{1}) + D(\overline{2})\,\psi(\overline{2})] \\
& + \langle N(\overline{123})\rangle\,D(\overline{3})\,\psi(\overline{3})\} \\
& + \tfrac{1}{2}\psi^*(\overline{12})\langle N(\overline{12})\,N(\overline{3})\rangle[(\sigma - \lambda)\,\psi(\overline{3}) - \psi_0(\overline{3})] + \text{c.c.}
\end{aligned}
\tag{43}
$$

$$
\begin{aligned}
J_{11} = {} & \psi^*(\overline{1})\langle N(\overline{1})\,N(\overline{2})\rangle[\sigma\psi(\overline{2}) - \psi_0(\overline{2})] + \langle N(\overline{1})\rangle \\
& (\mathbf{p}_1/m)[\partial\psi(\overline{1})/\partial\mathbf{x}_1] - \psi_0{}^*(\overline{1})\langle N(\overline{1})\,N(\overline{2})\rangle\,\psi(\overline{2})
\end{aligned}
\tag{44}
$$

Using integration by parts on the complex conjugate terms, we find

$$
\begin{aligned}
J_{22} = {} & \tfrac{1}{4}\langle N(\overline{12})\,N(\overline{34})\rangle\,\psi^*(\overline{12})[\sigma\psi(\overline{34}) - \psi_0(\overline{34})] \\
& + \tfrac{1}{4}\psi^*(\overline{12})\{\langle N(\overline{12})\rangle[L(\overline{12}) + L(\overline{21})]\,\psi(\overline{12}) \\
& + \langle N(\overline{123})\rangle\,M(\overline{12/3})[\psi(\overline{13}) + \psi(\overline{23})]\}
\end{aligned}
\tag{45}
$$

$$
\begin{aligned}
J_{12} + J_{21} = {} & \psi^*(\overline{12})\langle N(\overline{12})\,N(\overline{3})\rangle[(\sigma - \lambda)\,\psi(\overline{3}) - \psi_0(\overline{3})] + \text{c.c.} \\
& + \psi^*(\overline{12})\langle N(\overline{12})\rangle\{L(\overline{12}) + L(\overline{21})\}\{\psi(\overline{1}) + \psi(\overline{2})\} + \text{c.c.}
\end{aligned}
\tag{46}
$$

In this form the variation with respect to $\psi^*(\underline{12})$ is easy to carry out. The desired equation for $\psi(12)$ is just the expression multiplying $\psi^*(\underline{12})$. The above functional yields Eq. (40) of I, apart from the constraint term and the different normalization of F_N.

4. PARITY CONSIDERATIONS AND THE LIOUVILLE OPERATOR

In the preceding sections we have stressed theories based on the renormalized form of the functional. It may, however, be advantageous to use trial functions which explicitly contain the bare potential. In particular, the trials may contain powers of the Liouville operator. This is of course suggested by the formal exact solution $F = (\sigma + L)^{-1} F_0$. With trials that contain L explicitly[4] the variational parameters involve equilibrium averages of functions of the potential energy. These are well defined for both short-range forces and for Coulomb forces.

As a simple example, we take a trial function of the form

$$F = \sum_{m=0}^{M} A_m L^m F \tag{47}$$

for some finite M. The formal short-time expansion of the exact solution is

$$F = (1/\sigma)\{1 - (L/\sigma) + (L^2/\sigma^2) + - \cdots\} F_0$$

We expect the coefficients A_m, as determined from the variational principle, to have the correct behavior as $\sigma \to 0$. Thus the theory, whatever else its inadequacies, should have correct short-time behavior to any desired approximation. We use the real variational principle, and for simplicity take $F_{0-} = F_0$. Then

$$J = \sum_{n,m}^{M} A_n A_m \{\sigma K_{n+m} + K_{n+m+1}\} - 2 \sum_{n=0}^{M} A_n K_n \tag{48}$$

where

$$K_n = \int \Phi F_0 L^n F_0 \, d\Gamma \tag{49}$$

We have used the fact that

$$\langle L_-^m F_0 L^n F_0 \rangle = \langle F_0 L^{m+n} F_0 \rangle$$

The variation yields the linear equations

$$\sum_{m=0}^{M} A_n \{\sigma K_{n+m} + K_{n+m+1}\} = K_n, \qquad n = 0, 1, \dots, M \tag{50}$$

In particular, for $M = 1$ we find

$$A_1 = -A_0/\sigma, \qquad A_0 = \sigma[\sigma^2 - (K_2/K_0)]^{-1}, \qquad [J] = -A_0 K_0 \tag{51}$$

$[J]$ has poles at $\sigma = \pm i(|K_2/K_0|)^{1/2}$. Since $K_0 > 0$ and $K_2 < 0$, the distribution function is the sum of two oscillating terms. As a special example, consider the velocity relaxation problem. Let

$$F_0 = \sum_{\alpha=1}^{N} f_0(\mathbf{p}_\alpha) \qquad \text{with} \qquad \int f_0(\mathbf{p}) \, \phi(p) \, d^3p = 0 \tag{52}$$

Then

$$K_0 = N \int f_0(\mathbf{p}) f_0(\mathbf{p}) \, \phi(p) \, d^3p$$

$$K_2 = \frac{-KT}{3} \left\langle \sum_{\alpha=1}^{N} \nabla_\alpha^2 V \right\rangle \int \frac{\partial f_0}{\partial \mathbf{p}} (\mathbf{p}) \frac{\partial f_0}{\partial \mathbf{p}} (\mathbf{p}) \, d^3p \tag{53}$$

For the case $M = 3$ there are two pairs of imaginary roots. We are not interested in the case where there are an odd number of roots, although the variational method permits one to do so. In such cases there is always an isolated $\sigma = 0$ root. For example, for $M = 2$ the roots are $\sigma = 0$, $\sigma^2 = K_4/K_2$. The reason for preferring an even number of parameters is linked to a deeper consideration which we now discuss.

The Liouville operator is antisymmetric under the operation of momentum reversal $\mathbf{p}_\alpha \rightarrow -\mathbf{p}_\alpha$. It is also antisymmetric under coordinate reversal $\mathbf{q}_\alpha \rightarrow -\mathbf{q}_\alpha$, and is symmetric under the combined operations. If F_0 is a symmetric function under the "p" parity operation, the odd powers $L^n F_0$ are antisymmetric. In fact, one can always write

$$F = F^S + F^A, \qquad F_{-}^A = -F^A, \qquad F_{-}^S = F^S \tag{54}$$

$$\sigma F^S + L F^A = F_0{}^S, \qquad \sigma F^A + L F^S = F_0{}^A \tag{55}$$

We can now eliminate F^A by writing $F^A = (F_0{}^A/\sigma) - (LF^S/\sigma)$, and find

$$(\sigma^2 - L^2) F^S = \sigma F_0{}^S - L F_0{}^A \tag{56}$$

These considerations also hold for approximate trial functions. In the variational functional the symmetric and antisymmetric functions may be varied independently. For any approximate F^S the optimal choice of F^A is the one written above. We can therefore eliminate it from the functional and find (for $F_0{}^A = 0$)

$$J = \langle F^{S*}[\sigma - (L^2/\sigma)] F^S \rangle - \langle F^{S*}F_0 + F^S F_0{}^* \rangle \tag{57}$$

Of course, we can also eliminate F^S and find a functional for F^A. The normalization-independent principle is

$$J = -\sigma \langle F^S F_0{}^* \rangle \langle F^{S*}F_0 \rangle / \langle F^{S*}(\sigma^2 - L^2) F^S \rangle \tag{58}$$

The operator L^2 is invariant under the separate parity operations. Let us investigate the Liouville series approach for the case $M = 4$. We need only two terms in F^S,

$$F^S = (A_0 + A_2 L^2) F_0 \tag{59}$$

$$J_c = \sum A_m{}^* A_n [\sigma K_{n+m} - (1/\sigma) K_{n+m+2}] - \sum (A_n{}^* K_n + A_n K_n) \tag{60}$$

The roots of the associated determinantal equation are given by

$$(K_0 \sigma^2 - K_2)(K_4 \sigma^2 - K_6) - (K_2 \sigma^2 - K_4)^2 = 0 \tag{61}$$

The integrals K_4 and K_6 are straightforward but tedious to evaluate. For the density autocorrelation function we have

$$K_0 = \langle \rho(k)\,\rho(-k)\rangle = N + P_2(k), \qquad K_2 = k^2(KT/m) \qquad (62)$$

It is possible to improve the theory so that one obtains correct behavior for all times in the noninteracting particle limit. We take a trial function

$$F^S = (\sigma^2 - L_0{}^2)^{-1}\,\sigma F_0 , \qquad L_0 = \sum (\mathbf{p}_\alpha/m)\,\partial/\partial\mathbf{q}_\alpha \qquad (63)$$

For the density autocorrelation function

$$F^S = \sum [\exp(i k \mathbf{q}_\alpha)]\{\sigma^2 + [(\mathbf{k}\cdot\mathbf{p}_\alpha)^2/m^2]\}^{-1} \qquad (64)$$

Skipping the detailed calculations, we find, using the norm-independent functional

$$[J] = -\sigma(N + P_2)^2\,T_0{}^2/\Delta$$
$$\Delta = NT_0 + P_2\sigma^2 T_0{}^2 + \tfrac{4}{3}KT\,(k^2/m^2)\Big\langle \sum_\alpha \nabla_\alpha{}^2 V\Big\rangle Z \qquad (65)$$

Here

$$P_2(k) = \Big\langle \sum_{\alpha\neq\beta} \exp[i k(\mathbf{q}_\alpha - \mathbf{q}_\beta)]\Big\rangle \qquad (66)$$

$$T_0 = \int \phi\,d^3p\{\sigma^2 + [(\mathbf{k}\cdot\mathbf{p})^2/m^2]\}^{-1} \qquad (67)$$

$$Z = \int [(\mathbf{k}\cdot\mathbf{p})^2/m^2]\,\phi\,d^3p\{\sigma^2 + [(\mathbf{k}\cdot\mathbf{p})^2/m^2]\}^{-4} \qquad (68)$$

The term containing $\langle\sum_{\alpha=1}^{N}\nabla_\alpha{}^2 V\rangle$ corrects the modified Vlasov equation. There are obvious extensions of this type of theory, which has the advantage that the autocorrelation function is directly given in terms of quadratures. However, instead of pursuing this line of thought, we turn to simple extensions which involve functional variations.

5. VELOCITY RELAXATION PROBLEM

We now study the problem of the evolution of a spatially homogeneous initial perturbation of the form

$$F_0 = \sum_{\alpha=1}^{N} \psi_0(\mathbf{p}_\alpha)$$

First we take the initial distribution to be even under momentum reversal. The crudest assumption is $F = \sum_{\alpha=1}^{N} \psi(\mathbf{p}_\alpha/\sigma)$. This however, gives nothing

since $J_L = KT\langle\{F_-{}^*, F\}\rangle = 0$. Hence the initial distribution persists indefinitely.

The one-body assumption $F^S = \sum_{\alpha=1}^{N} \psi(\mathbf{p}_\alpha \mid \sigma)$, $\psi(\mathbf{p}_\alpha) = \psi(\mathbf{p}_\alpha)$, made only on the symmetric part yields nontrivial results. For, then,

$$ F^A = -\frac{LF^S}{\sigma} = -\frac{1}{\sigma}\sum \frac{\partial V}{\sigma \mathbf{q}_\alpha} \frac{\partial \psi}{\partial \mathbf{p}_\alpha} (\mathbf{p}_\alpha \mid \sigma) \tag{69} $$

The antisymmetric part describes effects of forces between the particles. In the functional (57) we need

$$ \langle LF^{*S}LF^S \rangle = NV_0 \int \phi(p) \frac{\partial \psi^*}{\partial \mathbf{p}} (\mathbf{p}) \frac{\partial \psi}{\partial \mathbf{p}} (\mathbf{p}) \, d^3p $$

where

$$ NV_0 = \frac{1}{3} \left\langle \sum_\alpha \frac{\partial V}{\partial \mathbf{q}_\alpha} \frac{\partial V}{\partial \mathbf{q}_\alpha} \right\rangle = \frac{KT}{3} \left\langle \sum_\alpha \nabla_\alpha{}^2 V \right\rangle \tag{70} $$

The complete functional is

$$ J = N\sigma \int \phi\psi^*(\mathbf{p}) \, \psi(\mathbf{p}) \, d^3p + N(N-1) \sigma\Lambda^*\Lambda + \frac{N}{\sigma} V_0 \int \phi \frac{\partial \psi^*}{\partial \mathbf{p}} \frac{\partial \psi}{\partial \mathbf{p}} \, d^3p $$

$$ - N \int \phi\psi^*(\mathbf{p}) \, \psi_0(\mathbf{p}) \, d^3p - N \int \phi\psi_0{}^*(\mathbf{p}) \, \psi(\mathbf{p}) \, d^3p $$

$$ - N(N-1)(\Lambda^*\Lambda_0 + \Lambda_0{}^*\Lambda) \tag{71} $$

where $\Lambda = \int \phi\psi(\mathbf{p}) \, d^3p$.

The variation with respect to $\psi^*(\mathbf{p})$ yields

$$ \sigma\phi(\mathbf{p}) \, \psi(\mathbf{p}) - \frac{V_0}{\sigma} \frac{\partial}{\partial \mathbf{p}} \left(\phi \frac{\partial \psi}{\partial \mathbf{p}} \right) + (N-1) \sigma\phi\Lambda = \phi\psi_0 + \phi(N-1) \Lambda_0 \tag{72} $$

Integrating over momenta, we find $\Lambda = \Lambda_0$. It suffices to take $\Lambda_0 = 0$.

The stationary value of the functional is

$$ [J] = -\langle F_0{}^*F^S \rangle $$

and is the Laplace transform of the evolved distribution. If we satisfy the equation for $\psi(\mathbf{p})$, we have

$$ [J] = -N \int \phi(p) \, \psi_0{}^*(\mathbf{p}) \, \psi(\mathbf{p}) \, d^3p \tag{73} $$

The short-time behavior is given by solving Eq. (72) in inverse powers of σ,

$$ \psi(p) = \frac{\psi_0}{\sigma} (\mathbf{p}) - \frac{V_0}{\sigma^2} \frac{1}{\phi} \frac{\partial}{\partial \mathbf{p}} \left(\phi \frac{\partial}{\partial \mathbf{p}} \frac{\psi_0}{\sigma} \right) + \cdots \tag{74} $$

Thus

$$[J] \rightarrow -\frac{N}{\sigma} \int \phi \psi_0{}^* \psi_0 \, d^3p + \frac{NV_0}{\sigma^3} \int \phi \frac{\partial \psi_0{}^*}{\partial \mathbf{p}} \frac{\partial \psi^0}{\partial \mathbf{p}} (p) + \cdots \qquad (75)$$

This agrees with the exact solution based on

$$F = \frac{F_0}{\sigma} - \frac{LF_0}{\sigma^2} + \frac{1}{\sigma^3} L^2 F + \cdots$$

We now turn to the exact solution of Eq. (72). Introducing $g = \phi^{1/2}\psi$, we find

$$-\frac{1}{2} \frac{\partial^2 g}{\partial \mathbf{p}^2} + \frac{1}{2} \frac{p^2}{(2mKT)^2} g + \frac{1}{2} \left(\frac{\sigma^2 - 3}{V_0 2mKT} \right) g = \frac{\phi^{1/2}}{V_0} \psi^0(\mathbf{p}) \qquad (76)$$

This is the Schrödinger equation for the three-dimensional harmonic oscillator with an inhomogeneous part. We reduce it to unit frequency by introducing $\mathbf{p} = \mathbf{r}(2mKT)^{1/2}$,

$$-\frac{1}{2} \frac{\partial^2 g}{\partial \mathbf{r}^2} + \frac{1}{2} r^2 g + Eg = \frac{\phi^{1/2} 2mKT}{2V_0} \qquad (77)$$

where $E = \frac{1}{2}[\sigma^2(2mKT/V_0) - 3]$ and $\phi = (2\pi mKT)^{-3/2} \exp(-\frac{1}{2}r^2)$.

Let us consider initial distributions $\psi_0(r)$ that are spherically symmetric. It then suffices to expand g in Laguerre functions. Let

$$\psi_k = (\exp -\tfrac{1}{2}r^2) L_k^{1/2}(r^2) C_k, \qquad k = 0, 1, 2,\ldots \qquad (78)$$

The normalization $\int_0^\infty \psi_k{}^2 4\pi r^2 \, dr = 1$ yields

$$C_k = \frac{1}{(2\pi)^{1/2}} \left(\frac{\Gamma(k+1)}{\Gamma^3(k+\frac{3}{2})} \right)^{1/2} \qquad (79)$$

The expansion $g = \sum_{k=0}^\infty A_k \psi_k$ then yields

$$A_n\{\sigma^2(mKT/V_0) + 2n\} = (mKT/V_0) \, \sigma \int_0^\infty \psi_n \phi^{1/2} \psi_0 4\pi r^2 \, dr \qquad (80)$$

This solves the problem. The value of the functional is

$$[J] = -N \int \phi \psi_0{}^*(p) \, \psi(p) \, d^3p$$

$$= -N(2mKT)^{3/2} \sum_{n=0} A_n \int \phi^{1/2} \psi_0{}^*(r) \, \psi_n 4\pi r^2 \, dr$$

$$[J] = -N(2mKT)^{3/2} \left(\frac{mKT}{V_0} \right) \sigma \sum_{n=0}^\infty \frac{B_n{}^2}{\sigma^2(mKT/V_0) + 2n} \qquad (81)$$

where

$$B = \int \phi^{1/2} \psi_0^*(r) \, \psi_n 4\pi r^2 \, dr.$$

The expression for $[J]$ has poles when $\sigma_n = \pm i(2V_0/mKT)^{1/2} \, n^{1/2}$, $n = 0, 1, 2, \ldots$. If the initial distribution is an eigenfunction of the oscillator the behavior is oscillatory. However, the frequencies of different eigenfunctions are incommensurable. Thus for a general initial distribution there is a phase mixing of the different components. The singlet distribution is given as

$$\tilde{N}(p/\sigma) = \left\langle \sum \delta(\mathbf{p}_\alpha - \mathbf{p}) \, F \right\rangle = N\phi(p) \, \psi(\mathbf{p}/\sigma)$$

The nonradial parity-even initial distributions may be analyzed in the same way. The case where the initial distribution is antisymmetric under reversal of momenta may be handled by eliminating F^S by writing $F^S = -1/\sigma) \, LF^A$ and assuming $F^A = \sum \psi(\mathbf{p}_\alpha/\sigma)$, $\psi(\mathbf{p}_\alpha/\sigma) = -\psi(\mathbf{p}_\alpha/\sigma)$. One finds that the quantity $\mathbf{\Gamma} = \int \mathbf{p}\phi(p) \, \psi(\mathbf{p}/\sigma) \, d^3p$ is constant in time. This is a consequence of momentum conservation. If $\mathbf{\Gamma} = 0$, the equation for $g(p) = \psi\phi^{1/2}$ is the same as Eq. (77). The singlet distribution is again $\tilde{N}(\mathbf{p}/\sigma) = N\phi(p) \, \psi(\mathbf{p}/\sigma)$.

6. DENSITY AUTOCORRELATION FUNCTION

In this section we continue the strategy of allowing successively wider classes of functions as trial functions in the variational principle. We obtain an improvement of the modified Vlasov theory for the density autocorrelation function.

Let us assume one-body additivity for only the symmetric part. The trial function is

$$F^S = \sum_{\alpha=1}^{N} \psi(\mathbf{p}_\alpha/\mathbf{k}) \exp i\mathbf{k}\mathbf{q}_\alpha, \qquad \psi(\mathbf{p}_\alpha/\mathbf{k}) = \psi(\underline{\mathbf{p}}_\alpha/k) = \psi(\mathbf{p}_\alpha/\underline{\mathbf{k}})$$

$$F^A = -(1/\sigma) \, LF^S \tag{82}$$

The complex functional is

$$J = N \int \phi\psi^* \left[\sigma + \frac{k^2}{m^2} \, \overline{\frac{p_3{}^2}{\sigma}} \right] \psi \, d^3p + P_2[\sigma \Lambda^*\Lambda - \Lambda^*\Lambda_0 - \Lambda_0^*\Lambda]$$

$$+ N \frac{V_0}{\sigma} \int \phi \, \frac{\partial \psi^*}{\partial \mathbf{p}} \, \frac{\partial \psi}{\partial \mathbf{p}} \, d^3p - N \int (\psi^*\psi_0 + \psi_0^*\psi) \, \phi \, d^3p \tag{83}$$

where $\Lambda(\mathbf{k}) = \int \psi(\mathbf{p}/\mathbf{k}) \, \phi \, d^3p$. Functional variation with respect to $\psi^*(\mathbf{p}/\mathbf{k})$ yields

$$\left(\sigma^2 + \frac{k^2\overline{p_3^2}}{m^2}\right) \phi\psi(\mathbf{p}/\mathbf{k}) - V_0 \frac{\partial}{\partial \mathbf{p}} \left(\phi \, \frac{\partial \psi}{\partial \mathbf{p}}\right) + \phi \frac{P_2}{N} \sigma^2 \Lambda = \sigma\phi \left[\psi_0 + \frac{P_2}{N} \Lambda_0\right] \tag{84}$$

Put $\psi = g/\phi^{1/2}$. Then

$$-V_0 \frac{\partial^2 g}{\partial \mathbf{p}^2} + \left[\frac{V_0 p^2}{(2mKT)^2} + \frac{k^2 p_3^2}{3m^2}\right] g + \left(\sigma^2 - \frac{3V_0}{2mKT}\right) g + \phi^{1/2} \frac{P^2}{N} \sigma^2 \Lambda$$

$$= \sigma\phi^{1/2} \left(\psi_0 + \frac{P^2}{N} \Lambda_0\right) \tag{85}$$

This checks with our result on velocity relaxation when $k \to 0$, with V_0 finite. The limit $V_0 \to 0$ is somewhat singular, since the coefficient of the second derivative vanishes. If $V_0 = 0$, we find

$$\left(\sigma^2 + \frac{k^2 p^2}{m^2}\right) g(p) + \phi^{1/2} \frac{P^2}{N} \sigma^2 \Lambda = \sigma^2 \left(\psi_0 + \frac{P^2}{N} \Lambda_0\right) \phi^{1/2} \tag{86}$$

The initial condition for the density correlation function is $\psi_0 = 1$. We then find

$$\Lambda(V_0 = 0) = \sigma \left(1 + \frac{P^2}{N}\right) T_0 \Big/ \left(1 + \sigma^2 \frac{P_2}{N} T_0\right)$$

$$T_0 = \int d^3p \, \frac{\phi}{\sigma^2 + (k^2 p_3^2/m^2)} \tag{87}$$

The stationary value of the functional is

$$[J] = -\{N + P_2(k)\} \Lambda(k) \tag{88}$$

The expression for Λ has a branch cut on the imaginary axis in the σ plane. This is the modified Vlasov theory.

Before studying the exact solution of Eq. (85) let us examine some general features that can be obtained directly. We study the short-time behavior of the density autocorrelation function. Let us look for an asymptotic solution of the differential equation by expanding in inverse powers of σ. Write

$$\psi = (1/\sigma) + (1/\sigma^3) \, A(\mathbf{p}/\mathbf{k}) + (1/\sigma^5) \, B(\mathbf{p}/\mathbf{k}) + \cdots$$

$$\Lambda = (1/\sigma) + (1/\sigma^3) \int A(\mathbf{p}/\mathbf{k}) \, \phi \, d^3p + (1/\sigma^5) \int B(\mathbf{p}/\mathbf{k}) \, \phi \, d^3p + \cdots \tag{89}$$

This yields the results

$$\int A\phi \, d^3p = -(k^2KT/m) \, [1 + (P_2/N)]$$

$$A = -(k^2p^2/3m^2) - (P_2/N) \int A\phi \, d^3p \qquad (90)$$

$$\int B\phi \, d^3p = -\int [(\mathbf{k} \cdot \mathbf{p})^2/m^2] \, A\phi \, d^3p[1 + (P_2/N)]^{-1}$$

The term $(1/\sigma^5) \int B\phi \, d^3p$ disagrees with the exact asymptotic solution of the Liouville equation. In this approximation V_0 does not enter into the asymptotic expansion.

It is easy to find a formal series in powers of V_0 for the quantity $\varLambda(k)$. A closely related series is somewhat more compact. Let

$$W(\mathbf{p}) = \left[\sigma^2 - \frac{3V_0}{2mKT} + \left(\frac{k^2p_3{}^2}{3m^2} + \frac{V_0p^2}{(2mKT)^2}\right)\right]^{-1} \qquad (91)$$

We rewrite Eq. (85) as

$$g(\mathbf{p}) = V_0W(\mathbf{p})(\partial^2g/\partial\mathbf{p}^2) + [1 + (p_2/N)(1 - \sigma\varLambda)] \, \sigma\phi^{1/2}W(\mathbf{p}) \qquad (92)$$

The iteration solution for $g(\mathbf{p})$ is

$$g(\mathbf{p}) = [1 + (P_2/N)(1 - \sigma\varLambda)] \, \sigma \sum_{n=0}^{\infty} V_0{}^n(W \, \partial^2/\partial\mathbf{p}^2)^n \, \phi^{1/2}W(\mathbf{p}) \qquad (93)$$

We then find $\varLambda(k)$ in the same form as Eq. (87),

$$\varLambda = [1 + (P_2/N)] \, \sigma Y[1 + \sigma^2(P_2/N) \, Y]^{-1} \qquad (94)$$

Here

$$Y = \sum_{n=0}^{\infty} V_0{}^nY_n, \qquad Y_n = \int \phi^{1/2}(W \, \partial^2/\partial\mathbf{p}^2)^n \, \phi^{1/2}W \, d^3p \qquad (95)$$

The terms with $n \geqslant 1$ represent corrections to the modified Vlasov formula. They give branch cuts in the σ plane.

Let us now turn to the exact solution of Eq. (85). To reduce the problem to unit frequency, introduce

$$\omega^2 = \frac{1}{(2mKT)^2} + \frac{k^2}{3m^2V_0}, \qquad \omega_0 = (2mKT)^{-1}$$

$$\epsilon = \frac{1}{2}\left(\frac{\sigma^2}{V_0} - \frac{1}{2mKT}\right), \qquad g = (\phi_1\phi_2)^{1/2} \, g_3(p_3) \qquad (96)$$

$$r = \omega^{1/2}p_3, \qquad \phi_3 = \omega_0{}^{1/2}\pi^{-1/2} \exp(-\omega_0p_3{}^2)$$

Then Eq. (85) becomes

$$-\frac{1}{2}\frac{\partial^2 g_3}{\partial r^2} + \frac{1}{2}r^2 g + \frac{\phi_3^{1/2}}{2\omega}\frac{P_2(k)}{NV_0}\sigma^2\Lambda = \frac{\sigma\phi^{1/2}}{2V}\left(1 + \frac{P_2}{N}\right) - \frac{\epsilon}{\omega}q_3 \quad (97)$$

With

$$g = \sum_{n=0}^{\infty} A_n\psi_n \quad (98)$$

where the $\psi_n(r)$ are normalized one-dimensional oscillator eigenfunctions, we find

$$A_n\left(n + \frac{1}{2} + \frac{\epsilon}{\omega}\right) + \frac{\sigma^2\Lambda}{NV_0}\frac{P_2}{2\omega}B_n = \frac{\sigma}{2V_0\omega}\left(1 + \frac{P_2}{N}\right)B_n \quad (99)$$

where $B_n = \int \phi^{1/2}\psi_n\,dr$. The B_n are explicitly

$$B_{2m} = \omega_0^{1/4}2^{-m}[(2m)!]^{1/2}(\alpha^{-1/2}/m!)[(1/\alpha) - 1]^m$$
$$\alpha = \tfrac{1}{2} + (1/4mKT)(1/\omega) \quad (100)$$

Noting that

$$\Lambda = \int \phi^{1/2}g\,dp = \sum_{n=0}^{\infty} A_nB_n\omega^{-1/2} \quad (101)$$

we find the solution for Λ in the form

$$\Lambda[1 + (\sigma^2 P_2/N)\,Y] = \sigma[1 + (P_2/N)]\,Y \quad (102)$$

Here

$$Y = \frac{1}{2V_0\omega^{3/2}}\sum_{n=0}^{\infty}\frac{B_n^2}{(\epsilon/\omega) + \tfrac{1}{2} + n} \quad (103)$$

For finite V_0 the poles of Λ lie at the zeros $\sigma^2 = -S_n^2$ of the expression $1 - \sigma^2(P_2/N)\,Y = 0$. Y has poles when $(\epsilon/\omega) + \tfrac{1}{2} + n = 0$, or when

$$S_n^2 = (1 + 2n)\,V_0\left[\frac{1}{(2mKT)^2} + \frac{k^2}{m^2V_0}\right]^{1/2} - \frac{V_0}{2mKT} \quad (104)$$

For every n there is a pair of real roots S_n^2 giving the positions of the poles. They correspond to a pair of conjugate poles on the imaginary σ axis. Between two poles corresponding to n and $n + 1$, $Y(\sigma)$ and $Y^{-1}(\sigma)$ take on all values between $-\infty$ and $+\infty$. There is therefore one zero of $1 - \sigma^2(P_2/N)\,Y(\sigma)$ between n and $n + 1$. In the limit $V_0 \rightarrow 0$ the infinite series of poles of $\Lambda(k)$ becomes a branch line and yields the one-body additive limit.

7. SUMMARY

In this paper the problem of finding solutions of the Liouville equation in the linear response domain has been attacked from the variational point of view. We have worked with the Laplace transform of the distribution function and set up variational functionals whose stationary value is the quantity we wish to estimate. With the normalization-independent form (22) or (58) the singularities of the functional are the zeros of the denominators. Thus one can develop a perturbation theory which corresponds to a perturbation theory for the mass operator in standard Green's function formulations. Since the averages are taken with the exact Gibbs equilibrium distribution, no unlinked diagram problems arise.

We have exhibited forms for the functional that are renormalized in the sense of paper I. This makes it possible to study a wide class of theories where functional forms in the postulated Liouville distribution are varied. Some of these will be studied in future papers. We have also exhibited forms where the parity symmetric and antisymmetric parts of the distribution are independently varied and one or the other is eliminated exactly. In Sections 5 and 6 we have shown how this can be used to improve theories that involve the simplest trial functions. In the next paper in this series we show that it is possible to find functionals where all the differential conservation laws are automatically satisfied for any trial function. It is important to have these more powerful formulations of the basic problem. Calculations with realistic trial functions inevitably involve three- and four-body equilibrium spatial correlation functions. The labor that must be expended can be justified only if the underlying theory is manifestly sound.

REFERENCES

1. Eugene P. Gross, *Ann. Phys.* **69**(1):42 (1972).
2. R. G. Newton, *Scattering Theory of Particles and Waves*, McGraw-Hill, New York (1966), p. 317.
3. R. Zwanzig, *Phys. Rev.* **144**:170 (1966). M. Nelkin and S. Ranganathan, *Phys. Rev.* **164**:222 (1967).
4. R. Zwanzig, *Phys. Rev.* **156**:190 (1967); R. Nossal and R. Zwanzig, *Phys. Rev.* **157**:120 (1967); R. Nossal, *Phys. Rev.* **166**:81 (1968).
5. A. Z. Akcasu and J. J. Duderstadt, *Phys. Rev.* **188**:1, 479 (1969).