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Perturbative Theory of Self-Diffusion in Classical Many-Particle Systems. I. Velocity Autocorrelation Function*

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To investigate the diffusive motion of a test particle in a classical many-body system, the projection-operator formalism of Zwanzig has been applied to the calculation of the velocity autocorrelation function. The memory kernel in this formalism is investigated by using a perturbation expansion in a parameter characteristic of the time scale of correlations in the system. General studies of the asymptotic time behavior of the correlation function are given, as well as several explicit calculations for modeled interparticle potentials.

I. INTRODUCTION

Time correlation functions of dynamical variables play an important role in the description of many-body systems such as liquids or plasmas. It is well known[1] that transport parameters which characterize the irreversible behavior of such systems can be expressed in terms of time correlation functions calculated under equilibrium conditions. Moreover, the cross sections for scattering of radiation (neutrons or photons) from an aggregate of particles can be directly related to the time correlation of density fluctuations in the system.[2]

Typically, time correlation functions for dense many-particle systems have been calculated using either phenomenological models of molecular motions[3-6] or perturbative solutions of the many-body problem in either the weak interaction or low-density limits.[7] However, recent developments in nonequilibrium statistical mechanics have suggested yet another type of perturbation scheme suitable for such calculations. This scheme, originally suggested by Fano[8] and later studied by Rice,[9] involves the use of the projection operator techniques of Zwanzig[10] to introduce a perturbation expansion in a parameter which is characteristic of the time during which the many-body system "remembers" correlations among particles. Such an expansion appears to be more appropriate for studying dense systems than do expansions in the interaction strength or density of particles, since in these systems this "coherence time" is expected to be quite small.

This perturbation scheme will be applied to the study of test-particle motions in classical many-body systems, and in particular, will be used to study the velocity autocorrelation function $\langle \vec{v}_1(0) \cdot \vec{v}_1(t) \rangle$ for such systems. This latter function is of interest not only because of the central role it plays in the theory of self-diffusion and Brownian motion, but as well because of its significance in the determination of the incoherent cross section for thermal neutron scattering from molecular systems.[11] It should also be admitted at the outset that the velocity autocorrelation is the quantity most readily accessible to theoretical investigation and hence serves logically as our first application of the perturbation method.

II. AUTOCORRELATION FUNCTION

Consider the autocorrelation function of a classical dynamical variable $u(\Gamma)$ of the particle coordinates $\Gamma = (\vec{q}_1, \ldots, \vec{q}_N, \vec{p}_1, \ldots, \vec{p}_N)$:

$$\Phi(t) \equiv [\int d\Gamma \rho_0(\Gamma) u(\Gamma) u(\Gamma_t)] \times [\int d\Gamma \rho_0(\Gamma) u(\Gamma) u(\Gamma)]^{-1} = \langle u(0)u(t) \rangle \langle u(0)u(0) \rangle^{-1} , \quad (1)$$

where $\rho_0(\Gamma)$ is the equilibrium canonical ensemble distribution for the N-particle system,

$$\rho_0(\Gamma) \equiv (Z_N)^{-1} e^{-\beta H_N}, \quad \beta \equiv 1/k_B T . \quad (2)$$

(Our notation is conventional.) Zwanzig[10] has derived an exact equation for $\Phi(t)$,

$$\frac{d\Phi}{dt} = -\int_0^t d\tau K(\tau) \Phi(t-\tau), \quad \Phi(0) = 1 , \quad (3)$$

and has explicitly evaluated the "memory kernel" $K(t)$ as

$$K(t) = [\int d\Gamma \rho_0(\Gamma) \dot{u}(\Gamma) e^{it(1-P)L} \dot{u}(\Gamma)] [\langle u(0)u(0) \rangle]^{-1} . \quad (4)$$

Here, L is the Liouville operator $L = i\{H, \cdot\}$, and P is a projection operator defined by its action upon an arbitrary phase function $f(\Gamma)$ as

$$Pf(\Gamma) = \langle u(0)u(0)\rangle^{-1} u(\Gamma)\rho_0(\Gamma)\int d\Gamma' u(\Gamma')f(\Gamma') \quad . \tag{5}$$

If we define the Laplace transform of $\Phi(t)$ in the usual manner as

$$\tilde{\Phi}(z) \equiv \int_0^\infty dt\, e^{-zt}\,\Phi(t) \quad , \tag{6}$$

then we can easily perform a Laplace transformation on Eq. (3) and solve for

$$\tilde{\Phi}(z) = [z + \tilde{K}(z)]^{-1} \quad , \tag{7}$$

where

$$\tilde{K}(z) = \langle \dot{u}(0)[z - i(1-P)L]^{-1}\dot{u}(0)\rangle \quad . \tag{8}$$

Further, if $K(t)$ possesses a Fourier transform $K^*(\omega)$, one can show that

$$\Phi(z) = \left(z + \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{d\omega}{z - i\omega}\, K^*(\omega)\right)^{-1} \quad . \tag{9}$$

This representation appears in theories based upon the idea of "linear response."[12]

Another form of Eq. (7) may be obtained if one makes use of the operator identity $(A+B)^{-1} = A^{-1} - A^{-1}B(A+B)^{-1}$. Equation (8) then becomes

$$\tilde{K}(z) = \frac{\langle \dot{u}(0)(z - iL)^{-1}\dot{u}(0)\rangle / \langle u^2(0)\rangle}{1 - z^{-1}\langle \dot{u}(0)(z - iL)^{-1}\dot{u}(0)\rangle / \langle u^2(0)\rangle} \quad , \tag{10}$$

$$= \frac{\tilde{k}(z)}{1 - (1/z)\tilde{k}(z)} \quad , \tag{11}$$

$$\tilde{\Phi}(z) = (1/z)[1 - (1/z)\tilde{k}(z)] \quad . \tag{12}$$

These results have been noted by others.[3] The kernel $\tilde{k}(z)$ is the Laplace transform of the autocorrelation function for the variable $\dot{u}$. In the particular case of interest here, we have $u = \vec{p}_1$ and $\dot{u} = \vec{F}_1$. One sees from these equations that when, in the thermodynamic limit, the right-hand limit $\tilde{\Phi}(0^+)$ exists (and is proportional to the coefficient of self-diffusion), conclusions may be drawn about $k(t)$. Indeed, since $\tilde{k}(z) = z - z^2\tilde{\Phi}(0^+) + \cdots$, we note that the area under the force autocorrelation curve is zero ("backflow"), and that its first time moment is given by the diffusion coefficient.

In the case $u = \vec{p}_1$, we have

$$K(t) = (\beta/3m)\int d\Gamma \rho_0(\Gamma)\vec{F}_1(\Gamma)\cdot e^{it(1-P)L}\vec{F}_1(\Gamma). \tag{13}$$

When the forces are conservative and pair wise, so that

$$\vec{F}_1(\Gamma) = \sum_{k=2}^{N} \vec{F}(\vec{q}_1 - \vec{q}_k) = -\frac{\partial}{\partial \vec{q}_1}\sum_{k=2}^{N} V(\vec{q}_1 - \vec{q}_k), \tag{14}$$

further simplification is possible. The correlation of forces becomes a correlation of a certain modified density, and we find that

$$K(t) = (\beta/3m)\int d^3r \int d^3r'\, \vec{F}(\vec{r})\cdot \vec{F}(\vec{r}') \times \langle \rho_1(\vec{r}, 0)\rho_1(\vec{r}', t)\rangle \quad , \tag{15}$$

where

$$\rho_1(\vec{r}, t) = e^{it(1-P)L}\sum_{k=2}^{N} \delta(\vec{r} - \vec{q}_1 + \vec{q}_k) \tag{16}$$

is the density at $\vec{q}_1 - \vec{r}$ at time t when the system undergoes the "motion" generated by $(1-P)L$. On the other hand, one can use the particular relation $\beta\vec{F}_1\rho_0(\Gamma) = (\partial/\partial\vec{q}_1)\rho_0(\Gamma)$ to eliminate one of the $\vec{F}_1$'s and to write

$$K(t) = \frac{-1}{3m}\int d\Gamma\, \rho_0(\Gamma)\frac{\partial}{\partial \vec{q}_1}\cdot [e^{it(1-P)L}\vec{F}_1(\Gamma)] \quad , \tag{17}$$

$$= \frac{-1}{3m}\int d^3r\, F_\beta(\vec{r}) \times \left\langle \frac{\partial}{\partial q_{1\beta}}\sum_{k=2}^{N}\delta(\vec{r} - \vec{q}_1^{\,*}(t) + \vec{q}_k^{\,*}(t))\right\rangle \quad , \tag{18}$$

$$= \frac{-1}{3m}\int d^3r\, F_\beta(\vec{r})\frac{\partial}{\partial r_\alpha}\left\langle \sum_{k=2}^{N}\delta(\vec{r} - \vec{q}_1^{\,*}(t) + \vec{q}_k^{\,*}(t)) \times \frac{\partial}{\partial q_{1\beta}}\,(q_{k\alpha}^*(t) - q_{1\alpha}^*(t))\right\rangle \quad , \tag{19}$$

where $q_k^*(t) = q_k^*(\Gamma, t) = e^{it(1-P)L}q_k$. When $t = 0$, Eq. (19) becomes

$$K(0) = \frac{1}{3m}\int d^3r\, F_\beta(\vec{r})\frac{\partial}{\partial r_\alpha}\,\delta_{\alpha\beta}n_0 g(\vec{r}) \quad , \tag{20}$$

$$= (n_0/3m)\int d^3r\, \nabla^2 V(\vec{r})g(\vec{r}) \quad , \tag{21}$$

where n_0 is the averaged density of particles.

In general, then, one can write

$$K(t) = \frac{1}{3m}\int d^3r\, \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta}\,\Delta_{\alpha\beta}(\vec{r}, t) \quad . \tag{22}$$

The quantity $\Delta_{\alpha\beta}$ is an isotropic tensor of the second rank and may be written

$$\Delta_{\alpha\beta}(\vec{r}, t) = \delta_{\alpha\beta}\Delta_1(r^2, t) + (r_\alpha r_\beta/r^2)\,\Delta_2(r^2, t) \quad , \tag{23}$$

with

$$\Delta_1 = \tfrac{1}{2}(\mathrm{Tr}\,\Delta_{\alpha\beta} - r_\alpha \Delta_{\alpha\beta} r_\beta/r^2) \quad , \qquad \Delta_2 = \tfrac{1}{2}(3\, r_\alpha \Delta_{\alpha\beta} r_\beta/r^2 - \mathrm{Tr}\,\Delta_{\alpha\beta}) \quad . \tag{24}$$

The kernel becomes

$$K(t) = \frac{1}{3m}\int d^3r\,[\nabla^2 V(\vec{r})\Delta_1(r^2, t)] + \frac{1}{3m}\int d^3r \times [(\vec{r}\cdot\nabla)^2 V(\vec{r}) - (\vec{r}\cdot\nabla)V(\vec{r})]r^{-2}\Delta_2(r^2, t) \quad , \tag{25}$$

or

$$K(t) = \frac{4\pi}{3m}\int_0^\infty dr\left[\frac{d}{dr}\left(r^2\frac{dV}{dr}\right)\Delta_1(r^2, t)\right.$$

$$+r^2\frac{d^2V}{dr^2}\Delta_2(r^2,t)\Big] \ , \qquad (26)$$

since the forces are central. In the limit $t\to 0$, the second integral vanishes and $\Delta_1(r^2,t)\to g(r)$.

III. PERTURBATION EXPANSION

We turn now to the approximate solution. It is convenient to decompose the Liouville operator as

$$L = L_1 + L_B + L_C \ , \qquad (27)$$

where $L_1 = -\frac{i}{m}\vec{p}_1\cdot\frac{\partial}{\partial\vec{q}_1}$,

$$L_B = -\frac{i}{m}\sum_{k=2}^{N}\vec{p}_k\cdot\frac{\partial}{\partial\vec{q}_k} - \frac{i}{2}\sum_{k,l=2}^{N}\vec{F}_{kl}\cdot\left(\frac{\partial}{\partial\vec{p}_k}-\frac{\partial}{\partial\vec{p}_l}\right),$$

$$L_C = -i\sum_{k=2}^{N}\vec{F}_{1k}\cdot\left(\frac{\partial}{\partial\vec{p}_1}-\frac{\partial}{\partial\vec{p}_k}\right) .$$

Thus, we decompose L into a one-particle operator L_1, an N-1 particle operator $L_B[=L^{(N-1)}]$, and an operator L_C representing the coupling between "1" and the other N-1 particles. Physically speaking, we separate a "test particle," from an N-1 particle "bath" and follow the motion of the test particle as it moves through the bath, interacting via L_C.

Since $PL_1 = PL_B = 0$ (if we demand that surface integrals in phase space vanish), we write

$$[z-i(1-P)L]^{-1} = [z-i(L_1+L_B)-i(1-P)L_C]^{-1}, \qquad (28)$$

$$= [z-i(L_1+L_B)]^{-1} + [z-i(L_1+L_B)]^{-1} \times i(1-P)L_C[z-i(L_1+L_B)]^{-1} + \cdots , \qquad (29)$$

and our approximation consists of keeping only the first term. The formula which we obtain for the approximate function $K_0(t)$ is

$$K_0(t) = (1/3m)\int d^3r\,\nabla^2 V(\vec{r}) \times\left\langle\sum_{j=2}^{N}\delta(\vec{r}-(\vec{q}_1+\frac{t}{m}\vec{p}_1)+q_j^B(t))\right\rangle , \qquad (30)$$

with $q_j^B(t) = e^{itL_B}q_j$. Equation (30) may be obtained directly from (19) through the assumption that the test-particle motion is unaffected by the bath, and vice-versa. Δ_2, the off-diagonal part of $\Delta_{\alpha\beta}$, is proportional to the coupling and vanishes.

The k-space version of (30) is instructive. It is

$$K_0(t) = \frac{-1}{3m}\int\frac{d^3k}{(2\pi)^3}\,k^2\tilde{V}(\vec{k})\tilde{\mathcal{G}}_d(\vec{k},t)\,e^{-k^2t^2/2m\beta} \ , \qquad (31)$$

with

$$\tilde{\mathcal{G}}_d = \sum_{k=2}^{N}\langle e^{-i\vec{k}\cdot\vec{q}_1}e^{itL_B}e^{i\vec{k}\cdot\vec{q}_k}\rangle \ , \qquad (32)$$

$$V(\vec{r}) = (2\pi)^{-3}\int d^3k\,e^{i\vec{k}\cdot\vec{r}}\tilde{V}(\vec{k}) \ . \qquad (33)$$

The function $\tilde{\mathcal{G}}_d$ resembles the "distinct" density correlation function of Van Hove,[2]

$$\tilde{G}_d(\vec{k},t) = \sum_{j=2}^{N}\langle e^{-i\vec{k}\cdot\vec{q}_1}e^{itL}e^{i\vec{k}\cdot\vec{q}_j}\rangle \ . \qquad (34)$$

If the particle-bath coupling $\to 0$, we find that $\tilde{G}_d\to\tilde{\mathcal{G}}_d$. The expression (30), our approximate Δ_1, whose Fourier transform is

$$\exp(-k^2t^2/2m\beta)\tilde{\mathcal{G}}_d(\vec{k},t) \ ,$$

refers correlation to a moving census point. That is, we seek the average density of bath particles in the neighborhood of a free-streaming test particle, subject to a certain ensemble of initial conditions. The G_d function refers to the same initial ensemble but takes account of the influence of the test particle upon the bath. The "decoupling" expressed by (30) permits test and bath particles to approach each other arbitrarily closely. Thus, $K_0(t)$ will not exist for singular potentials. We might remedy this difficulty by an *ad hoc* procedure, but that is precisely what we wish to avoid.

IV. CRITIQUE OF APPROXIMATION

It is clear that Eq. (29) describes a modified short-time expansion for the memory kernel. Such an expansion, containing "secular" terms, is of little use for time larger than a collision time.[13] However, in our analysis, the expansion appears in the denominator of the expression for $\tilde{\Phi}(z)$. Thus, the approximate $\Phi_0(t)$ is bounded at long times and is correct at very short times. One might view the approximation as the summation of a class of diagrams in the perturbation expansion of $\Phi(t)$.

One can obtain a somewhat better view of the approximation by the following argument: Let the action of the "coupling" in Eq. (8) be expressed by a relaxation time $\tau_C = \lambda_C^{-1}$, and the "natural" relaxation time of the bath by $\tau_B = \lambda_B^{-1}$. Then, we find that

$$\tilde{\Phi}(z) = [z + K(0)/(z+\lambda_B+\lambda_C)]^{-1} \ . \qquad (35)$$

This mathematical model has appeared in several papers.[14] In any case, the expansion (29) performed upon (35) generates a series τ_B/τ_C, the short-memory approximation.[8,9] One sees easily that in lowest approximation the area under $\Phi(t)$ and the asymptotic behavior (i.e., the values of the decay times) have errors of order (τ_B/τ_C), while the short-time behavior is correct through the t^2 term.

An improved analysis would make use of the likelihood that the various L's have a continuous spectrum of relaxation times. Then, one obtains

$$\Phi(z)=\left[z+\int_0^\infty d\lambda\, C(\lambda)/(z+\lambda)\right]^{-1} , \tag{36}$$

and we must deal with an expansion of $C(\lambda)$. The accuracy of our approximate formulas will then depend upon the uniformity of convergence of the series. One should also note that obtaining Eq. (36) from Eq. (9) involves the analytic continuation of $\tilde{K}(z)$ into the left half-plane. Further, the physically appealing form (36) suggests that $z=0$ is a branch point for $\tilde{K}(z)$ in the thermodynamic limit. We shall find this feature in the approximation of lowest order

V. ASYMPTOTIC BEHAVIOR

Since $K_0(t)=K_0(-t)$, a formal expansion of Eq. (30) in powers of t produces only even powers. The leading term is correct; the others are not. One obtains

$$\Phi_0(t)=1-(1/3m)\langle\nabla^2 V\rangle t^2/2!+O(t^4) \tag{37}$$

for the velocity autocorrelation. Here, the first two terms are correct. Error enters into the t^4 term where three-body correlations appear.[13]

The large-time behavior of $K_0(t)$ depends upon the large-time large-space (small-k) behavior of $\tilde{\mathcal{G}}_d(\vec{k},t)$ or, in lowest order $\tilde{G}_d(\vec{k},t)$. In this limit, the behavior of the density correlations is described by the equations of hydrodynamics,[15,16] and the correlations are those of diffusive modes and damped sound-wave modes. More precisely, we have, in the limit in question ($k^2\to 0$, $t\to\infty$),

$$\begin{aligned}\chi(k^2,t)&\equiv\int d^3r\, e^{-i\vec{k}\cdot\vec{r}}[G(\vec{r},t)-n_0]\\ &=\chi(k^2,0)[(C_v/C_p)\,e^{-\Gamma k^2 t}\cos C_0 kt\\ &\quad+(1-C_v/C_p)\,e^{-D_T k^2 t}] ,\end{aligned} \tag{38}$$

where C_v and C_p are the specific heats, D_T is the coefficient of thermal diffusion, C_0 is the sound speed as $k\to 0$, and Γ is the damping coefficient. If we wish to normalize this asymptotic formula to the correct value at $t=0$, we take $\chi(k^2,0)=1+n_0(g(\vec{r})-1)_k$. We shall also need

$$\lim_{k^2\to 0}\chi(k^2,0)=k_B T\left(\frac{\partial n_0}{\partial p}\right)_T>0 , \tag{39}$$

which is proportional to the isothermal compressibility of the fluid.

The long-time behavior of $K_0(t)$, associated as it is with small k^2, is then seen to be

$$K_0(t)\to-\frac{1}{3m\pi}\,\tilde{V}(0)\int_0^\infty\frac{dk}{2\pi}\,k^4 e^{-k^2t^2/2m\beta}F(k^2,t), \tag{40}$$

$$F(k^2,t)=\chi(k^2,t)-e^{-D_s k^2 t} . \tag{41}$$

We are calculating $K_0(t)$ to lowest order in the coupling when $\mathcal{G}_d\approx G_d$. The second term in (41) is the transform of the long-time behavior of the function $G_s(\vec{r},t)$, and D_s is the coefficient of self-diffusion. The three integrals which make up (40) are special cases of

$$f(t;\delta,C_0)=\int_0^\infty dk\,k^4 e^{-\alpha k^2t^2-\delta k^2 t}\cos C_0 kt . \tag{42}$$

We note first that the asymptotic behavior is proportional to t^{-5} and independent of δ (diffusion coefficient or damping). Then, evaluation of (42) shows it to be an exponentially small function of $\eta=(2m/k_BT)C_0^2$, the squared ratio of sound speed to thermal speed. Since $C_0\approx 8.5\times 10^4$ cm/sec in liquid argon at[17] 85°K is considerably larger than $(2k_BT/m)^{1/2}$, the sound waves make negligible contribution to (40). There remains

$$K_0(t)\to\frac{1}{t^5}\,\frac{2\pi}{m}\left(\frac{m\beta}{2\pi}\right)^{5/2}\tilde{V}(0)\left[1-\chi(0,0)\left(\frac{C_p-C_v}{C_p}\right)\right] . \tag{43}$$

The factor in brackets is positive and close to unity for the thermodynamic states (of liquid argon) we might consider. The sign of $K_0(t)$ at long times is determined by the sign of the integrated potential. For a stable fluid, this will be positive. An approach to zero through positive values occurs in the computer experiments and in the results of most other theoretical investigations. With some rearranging, (43) becomes

$$t^2K_0(t)\to\frac{\overline{V}}{k_BT}\left(\frac{\tau}{t}\right)^3\frac{1}{\pi^{3/2}}\left[1-\chi(0,0)\left(\frac{C_p-C_v}{C_p}\right)\right], \tag{44}$$

where the average potential energy $\overline{V}$ and range of potential r_0 satisfy $\overline{V}r_0^3=\tilde{V}(0)$, $\tau=r_0/v_T$, and $\frac{1}{2}mv_T^2=k_BT$. τ may be thought of as a collision time. We have not been able to determine whether $K_0(t)$, Eq. (31), exhibits the oscillatory behavior which Rahman has found. It does not, in the simple model we have worked through in Sec. VI.

The power-law behavior of $K_0(t)$ implies power-law behavior for $\Phi_0(t)$ and, in passing, some interesting properties for the Laplace transforms of these functions. For example, write

$$\tilde{K}_0(z)=\int_0^{t^*}dt\,e^{-zt}K_0(t)+\int_{t^*}^\infty dt\,e^{-zt}K_0(t) , \tag{45}$$

$$\tilde{K}_0(z)=\tilde{K}_1(z)+\tilde{K}_2(z) , \tag{46}$$

where t^* is chosen large enough so that the asymptotic behavior of $K_0(t)$ prevails for $t>t^*$. The most singular part of $\tilde{K}_2(z)$ is then given by

$$\tilde{K}_2(z)\sim\text{const}\int_{t^*}^\infty\frac{dt}{t^5}\,e^{-zt}=\frac{\text{const}}{(t^*)^4}\,E_5(zt^*) , \tag{47}$$

where $E_n(x)$ is one of the exponential integrals.

$E_n(x)$ has a singular part

$$E_n(x) = -\frac{(-x)^{n-1}\ln x}{(n-1)!} + \text{analytic function}, \qquad (48)$$

which is logarithmic. Since $\tilde{K}_1(z)$ is an entire function of z, we may conclude that $\tilde{K}_0(z)$ is *analytic in the z plane, cut along the negative real axis.* $\tilde{\Phi}_0(z) = [z + K_0(z)]^{-1}$ is also analytic in the cut plane, with the exception of points at which $z + \tilde{K}_0(z)$ vanishes.

Unless $\Phi(t)$ oscillates in an undamped manner as $t \to \infty$, the poles in $\tilde{\Phi}_0(z)$ will lie in the left half-plane. The latter being the case, we may extract the asymptotic behavior of $\Phi_0(t)$ by defining the inversion contour so that it encircles the negative real axis. Then, for t large, we find that

$$\Phi_0(t) = \frac{1}{2\pi i}\int_{Br} dz\, \frac{e^{zt}}{z + \tilde{K}_0(z)} \sim \int_0^\infty \frac{d\zeta}{2\pi i}\, \frac{K_+(-\zeta) - K_-(-\zeta)}{[\zeta - K_+(-\zeta)][\zeta - K_-(-\zeta)]}\, e^{-\zeta t}, \qquad (49)$$

and examination of the integrand near $\zeta = 0$ gives, for the asymptotic behavior,

$$\frac{\Phi_0(t)}{K_0(t)} \to \left[\int_0^\infty dt\, \Phi_0(t)\right]^2 = \left(\frac{m}{k_B T} D_s\right)^2 . \qquad (50)$$

Thus, $\Phi_0(t)$ mimics the t^{-5} behavior of $K_0(t)$ at long times, though there is little similarity in the behaviors at intermediate times (see Figs. 1 and 2). In Eq. (49), $K \pm (-\zeta)$ are the limiting values, $\tilde{K}_0(-\zeta \pm i\epsilon)$.

While we have been able to extract some interesting information from our model, we do not yet know how close to being true the results are. The Doppler factor $\exp[-k^2t^2/2m\beta]$ associated with the free streaming motion of the test particle plays an important role in the analysis. When the streaming is replaced by the true motion with its weaker time dependence, the t^{-5} relaxation may be slowed. In any case, the computer experiments are not yet precise enough to resolve the point.

We turn now to the computation of $\Phi_0(t)$ and $K_0(t)$ for all times and to a comparison of our work with that of others. Here we shall have to make some further approximations (in $\mathcal{G}_d$), so our results can be regarded only as schematic.

VI. SOME SPECIFIC CALCULATIONS

A. Linear Trajectory Approximation

The reader may have noted a similarity between some of the formulas presented here and formulas for the friction tensor – in the linear trajectory approximation – derived by Helfand.[18] Indeed, in the latter analysis, *all* particles stream during the "dynamical event," whose duration is τ. A closely related approximation for us is

$$\tilde{\mathcal{G}}_d(\vec{k}, t) \approx G_d(\vec{k}, t) \approx n_0 \tilde{g}(\vec{k})\, e^{-k^2t^2/2m\beta}, \qquad (51)$$

which is accurate at very short times. Then, we find that

$$\tilde{K}_0(z) = -\int_0^\infty dk\, a(k) \int_{-i\infty}^{i\infty} \frac{d\omega}{2\pi i}\, \frac{e^{\omega^2/2v_T^2k^2}}{z - \omega}, \quad \mathrm{Re}\, z > 0, \qquad (52)$$

with $a(k) = \frac{(2\pi)^{1/2}}{v_T}\, \frac{n_0}{6m\pi^2}\, k^3 \tilde{V}(k)[g(\vec{r}) - 1]_k$.

Equation (52) defines an analytic function for $\mathrm{Re}\, z > 0$ and another for $\mathrm{Re}\, z < 0$. The latter is not the analytic continuation of the former, and it is the continuation which we require for Laplace inversion.

We may continue $\tilde{K}_0(z)$ into $|\arg z| < \frac{3}{4}\pi$ by deforming the contour in the ω integration. The continuation $\tilde{K}_C(z)$ can be written as

$$\tilde{K}_C(z) = \tilde{K}_0(z) - \int_0^\infty dk\, a(k)\, e^{z^2/2v_T^2k^2}, \quad \tfrac{3}{4}\pi > |\arg z| > \tfrac{1}{2}\pi \qquad (53)$$

where $\tilde{K}_0(z)$ is given by Eq. (52).

Any singularities which $\tilde{K}_C$ may possess in $\mathrm{Re}\, z < 0$ will stem from the second term of (53). If $\int_0^\infty dk\, a(k)$ exists, we may proceed further and associate the singularities with the behavior of $a(k)$ near $k = 0$. Indeed, if $a(k) = k^3(a_0 + a_1k^2 + a_2k^4 + \cdots)$, we may express the singular part of (53) in terms of E_n functions and find

$$\tilde{K}_0 = A(z) - \tfrac{1}{2}k_0^4[a_0 E_3(-\gamma z^2) + a_1 k_0^2 E_4(-\gamma z^2) + \cdots], \qquad (54)$$

where

$$A(z) = \tilde{K}(z) - \int_{k_0}^\infty dk\, a(k)\, e^{z^2/2v_T^2k^2}$$

and

$$1/\gamma = 2v_T^2 k_0^2, \qquad (55)$$

and $A(z)$ is analytic in the left half-plane.

Equations (54) and (55) complete the analytic continuation, since we know how to "continue" the E_n functions. Indeed [see Eq. (48)], the sole singularity is a logarithmic branch point at $z = 0$. The function $\tilde{K}_C(z)$ may now be used to study the poles of $\tilde{\Phi}_0(z)$ and the amplitudes of the continuous modes of relaxation as discussed above. Of course, $\tilde{K}_C(z)$ generates the t^{-5} relaxation which we expect, but with a different "coefficient."

B. Detailed Calculations for Simple Potential

We wish to present some numerical results to

suggest that our principal approximation [Eq. (30)] is not entirely frivolous and that its refinement might be a worth-while undertaking. Let us take the simple system

$$V(\vec{r}) = \epsilon e^{-\alpha r}, \quad g(\vec{r}) = 1 - \beta V(\vec{r}) \quad . \tag{56}$$

The exponential potential can be adjusted to describe the equilibrium properties of simple fluids tolerably well, and the approximate form for $g(\vec{r})$ is correct at low densities. Further, we shall improve our estimate equation (51) for G_d by adopting the convolution-Gaussian approximation of Vineyard,[19]

$$\tilde{G}_d(\vec{k}, t) = n_0 \tilde{g}(\vec{k})\, e^{-k^2 w^2(t)} \quad . \tag{57}$$

With these forms, our expression for the memory kernel becomes

$$K_0(t) = (32 n_0 \epsilon^2 \beta / 3m) \int_0^\infty dk\, [k^4/(k^2+\alpha^2)^4] \times \exp\{-k^2[t^2/2m\beta + w^2(t)]\} \quad . \tag{58}$$

For purposes of orientation, we have chosen ϵ such that we retain the proper $t = 0$ limit

$$K_0(0) = (1/3m)\langle \nabla^2 V \rangle = 52 \times 10^{24}\ \text{sec}^{-2} \quad , \tag{59}$$

which is reasonable for argon at 94.4 °K. The range of the potential was chosen as $\alpha = 3.16\ \text{Å}^{-1}$.

Explicit calculations of $K(t)$ are given in Fig. 1 for three different width functions:

$$w^2(t) = t^2/2m\beta \quad , \tag{60a}$$

$$w^2(t) = D_s |t| \quad , \tag{60b}$$

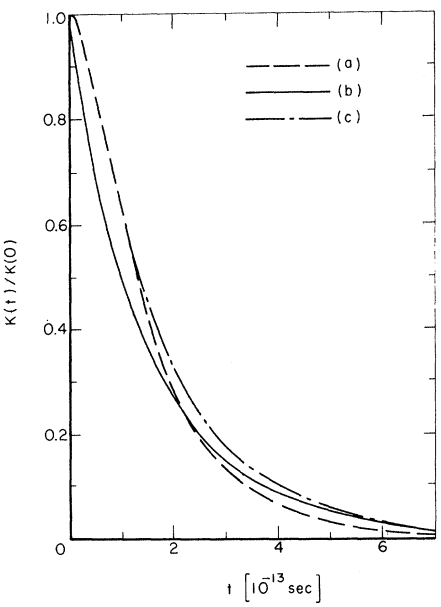

FIG. 1. Memory kernel $K(t)$ versus time t for the width functions given in Eq. (60).

$$w^2(t) = D_s\{[t^2 + (m\beta D_s)^2]^{1/2} - m\beta D_s\} \quad , \tag{60c}$$

where D_s is the coefficient of self-diffusion. The limitations of Eq. (57) have been described earlier.[20] Note that (60a) yields the proper short-time behavior, while (60b) is correct for long times. Model (60c) is an interpolative form which is correct for both long and short times. From Fig. 1, one can observe that in all cases $K(t)$ experiences a rapid initial decay followed by a somewhat slower power-law decay for long times. Both types of behavior were predicted by the analysis of Sec. V.

The corresponding correlation function $\Phi(t)$ has been calculated for each of these forms of $K(t)$ by numerically integrating Eq. (3). These results are given in Fig. 2. Again we find the proper qualitative behavior. It is remarkable, and perhaps fortuitous, that such a crude model yields results comparable with the more complicated calculations of Singwi and Sjölander[6] and with the molecular-dynamics calculations of Rahman.[21]

VII. CONNECTION WITH WORK OF OTHERS

Our analysis produces formulas which bear some resemblance to those appearing in recent papers of Singwi and Sjölander, and Kerr.[22] Thus, a few words about the relation of these works to each other may be in order.

Singwi and Sjölander, and Kerr adopt the test-particle viewpoint *ab initio*. The Singwi-Sjölander analysis leads, finally, to specific numerical results, as does ours. Kerr's analysis remains abstract. His principal equations for $\Phi(t)$ and his Eqs. (4.1) and (4.2) are nonlinear in the test-particle trajectory and quite complex. The equations serve to introduce the approximation scheme of Singwi-Sjölander.

In the Singwi-Sjölander (S-S) paper, specific results for an acceptable physical model ("hard core" and weak long-range attraction) are achieved at the cost of several uncontrolled approximations. We wish to avoid this situation, to assess the effect of simple approximations, even if we must thereby eschew a hard core. More specifically, S-S begin with a "simplified" Liouville equation which leads to an equation for $\Phi(t)$ different in form from the exact equation (3). After complex calculation, they find

$$\frac{d}{dt}\Phi(t) = -\int_0^t dt'\, \Gamma_0(t-t')\,\Phi(t') - \int_0^t dt'\, \Gamma_1(t-t') \int_{t'}^t dt''\, \Phi(t'') \quad . \tag{61}$$

The anomalous second term on the right-hand side turns out to be small, and the first kernel

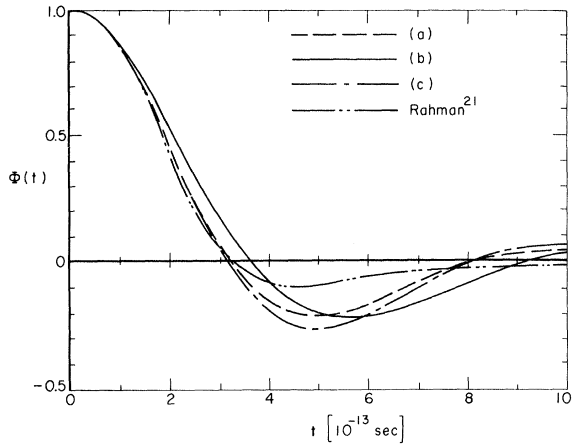

FIG. 2. Velocity autocorrelation function $\Phi(t)$ versus time t for the width functions given in Eq. (60). A sketch of the results obtained by Rahman (Ref. 21) via molecular dynamics calculations is also given for comparison.

Γ_0 bears some resemblance to our K_0. Indeed [compare Eq. (31), subject to the further approximation Eq. (57)], we find that

$$\Gamma_0(t) = \frac{-1}{3m} \int \frac{d^3k}{(2\pi)^3}\, k^2 \tilde{V}(\vec{k},t)\, \tilde{g}(\vec{k})\, e^{-t/\tau}\, \tilde{G}_s(\vec{k},t)\,, \tag{62}$$

where $e^{-t/\tau}$ describes the relaxation of the neighborhood of the test particle and $\tilde{V}(\vec{k},t)$ is the transform of a complicated effective potential. If we make some obvious approximations, $\Gamma_0(t)$ will become identical with the Eq. (57) version of our $K_0(t)$. Similarly, simple approximations in Kerr's improved, though still approximate, version of Eq. (61) brings it from a form close to the exact equation (15) to one more like (30). His kernel $G(\vec{r},t;\vec{r}',t';\vec{r}_0)$ is simplified to become $G_d(\vec{r},t)$.

VIII. CONCLUSIONS

In summary then, we have investigated the time behavior of the velocity autocorrelation function $\Phi(t)$ by studying the motion of a test particle in a bath of similar particles and retaining only lowest-order terms in the parameter $\lambda\tau$ (the "short-memory approximation"). Using only this assumption, we have obtained a rather simple form for Zwanzig's memory kernel which involves a density-density correlation function for the bath. This expression allowed a general investigation of both the short- and the long-time behavior of the memory kernel $K(t)$ and the correlation function $\Phi(t)$. It gave, as well, a rather reasonable qualitative description of self-diffusion in liquid argon, even for a very crude model of the interaction potential.

Of course, it has been repeatedly emphasized in the recent literature[3-6] that rather crude approximate forms for $K(t)$ yield very good descriptions of $\Phi(t)$. With the exception of the work of Singwi and Sjölander,[6] these earlier studies have attempted a phenomenological description of $K(t)$. In this paper we have chosen instead to give a more rigorous investigation of $K(t)$ based upon perturbation theory.

The forms we have obtained should prove useful in the investigation of self-diffusion in liquids and plasmas, and a study of (22) for more realistic potentials $V(\vec{r})$ and bath dynamics $G_d(\vec{r},t)$ is currently in progress. The resolvent expansion can also be applied to the derivation of test-particle kinetic equations (similar to the generalized Fokker-Planck equations of Kirkwood[23] and Rostoker and Rosenbluth[24]). Work in this latter area will be discussed in a forthcoming paper.

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Quantum-Statistical Theory of a Multicomponent Fully Ionized Gas

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The quantum-statistical theory of a nonrelativistic fully ionized gas in thermal equilibrium is developed using the well-known linked-cluster expansion of the grand potential. A systematic analysis of the self-energy structures leads to a master-graph formulation of quantum statistics. This provides a much simpler derivation and improved version, with important differences, of the earlier work of Mohling and Grandy. In particular, the analysis of the photon self-energy structures is now entirely different. The present formulation includes the technique of adding and subtracting in the Hamiltonian a single-particle operator, and the relation of this technique to the Λ-transformation method of Mohling, RamaRao, and Shea is indicated. As an application of the general theory, the lowest-order calculations of the photon self-energy and photon momentum distribution are presented. The result for the photon momentum distribution is different from that of Hwang and Grandy, and the reason for the difference is given. Finally, explicit connections between the master-graph line factors and Green's functions are outlined, and the consequences of such a connection are indicated.

I. INTRODUCTION

There exist several many-body theories, each having its own adherents and each having certain conceptual or calculational advantages over the others.[1,2] Of course, all mathematically rigorous many-body theories are, in some sense, equivalent. Thus, the applications of these theories to a given physical problem differ in their relative suitability for the problem, their mathematical sophistication, or their appeal to the intuition. We are interested in developing a theory of nonrelativistic quantum electrodynamics of a multicomponent system of charged particles in thermal equilibrium. In the sense of the discussion above, our formulation has several novel features, as well as its own point of view.

In the present case the Hamiltonian is rearranged by adding and subtracting a sum of arbitrary one-particle operators (called counterterms), and it is important to observe that these counterterms emerge in the theory in a mathematically very useful manner. Our diagrammatic expansion is subjected to a simple and complete self-energy analysis, and the counterterms can be used rigorously to cancel spurious system-independent self-energies and also to achieve mass renormalization. The connections between the present formalism and Green's functions will also be established.

For a system with photons interacting with charged particles, certain photon self-energy structures [called (0, 2) and (2, 0) structures] can lead to important contributions to physical quantities. These structures were not taken into account in an earlier formulation of this problem.[3] An important new feature of the present formulation is that these quantities are consistently taken into account.

II. DEFINITION OF SYSTEM

It is our purpose to formulate a microscopic basis for calculating the properties of a nonrelativ-