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Dynamical Perturbation for Classical Fluids: A Solvable Model

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We investigate on a one-dimensional model the perturbation to the time-dependent correlations in a classical fluid when a small interaction is added to a hard core. Various formulas have already been proposed for this correction. We verify on this model, for which everything can be calculated explicitly, that the expressions proposed by Frisch and Berne yield strongly divergent time integrals for the diffusion coefficient. On the contrary, when all corrections are accounted for, the correction to the velocity time correlation is shown to decay like $(\ln t)/t^2$ at large times, yielding a finite first-order correction to the diffusion coefficient. The extension of this calculation to a gas of hard rods in the case of a perturbation with an infinite range is discussed.

KEY WORDS: Nonequilibrium statistical mechanics; hard point one-dimensional gas; small perturbation; long time behavior.

1. INTRODUCTION AND PRELIMINARIES

Many equilibrium properties of dense classical fluids may be understood by considering the two-body forces as the sum of a repulsive interaction with a short range, as, for instance, the repulsion between hard spheres, plus a small attractive part[(1)] which is to be treated as a perturbation.[(2)] It is of course very tempting to extend the same idea to nonequilibrium properties of classical

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fluids. Frisch and Berne[3] and other authors[4,5] have proposed explicit formulas for the correction to the velocity correlation function due to a small attractive potential in a hard sphere fluid. The computer experiments of Watts[6] showed that these formulas yield strongly divergent time integrals. A number of effects were not considered in the theory of Frisch and Berne. Pomeau indicated how to carry out an explicit calculation of the first-order correction due to a small added interaction.[7] However, it seems interesting to study this problem on an explicit example, where everything can be computed explicitly. Also, this calculation should not be restricted by the assumption of a low density, since, as stated by Watts,[6] the divergence of the correction of Frisch and Berne bears some connection to the virial part of the equilibrium pressure, which is negligible in this low-density limit.

In the present paper, we shall study a model where such a dynamical perturbation calculation can be done explicitly. As shown by Jepsen[8] and Lebowitz *et al.*,[9,10] the velocity time correlation of a one-dimensional system of hard points may be found exactly. Following the same general method as these authors, we have found explicit expressions for the first correction to this time correlation function, due to a small perturbation of the interaction. Moreover, we have indicated how to compute the same correction for a one-dimensional gas of hard rods.[2] Before discussing more precisely the points under consideration, we first recall the general method for computing the lowest order correction to the velocity time correlation. Then, we recall the main features of the solution for the one-dimensional system of hard points, as found by Jepsen[8] and Lebowitz *et al.*[9,10] This method is applied to the exact calculation of the correction proposed by Frisch and Berne. It is shown to be divergent in this one-dimensional case, and this divergence is very similar to the one found by Watts in the three-dimensional case.

1.1. General Formulas

Let us begin with some definitions and notations.

The reference fluid is the fluid where particles interact through the un-

[2] Actually, the case of a gas of hard points with an attractive interaction must be approached with caution. Since an infinite number of particles may be on a segment of finite length, the energy of this system is not bounded from below by a quantity proportional to the number of particles, and no thermodynamic limit exists. However, this catastrophe has no influence to first order in the amplitude of the perturbing potential, say η, as the factor in front of η does not depend on the sign of η. There is only a strong indication that any dynamical quantity has a nonanalytic behavior with respect to η near $\eta = 0$ for a hard point system with an interaction of amplitude η. For an attractive potential, one must consider hard rods with a finite size (instead of hard points of zero thickness) in order to avoid the catastrophe alluded to above. This hard rod system with a small interaction is briefly discussed at the end of the present paper.

perturbed potential only. Averages over an equilibrium ensemble of initial conditions for the reference fluid are labeled by the index R:$\langle\ \rangle_R$. The perturbation is denoted by $\delta U(|r_i - r_j|) = \delta U_{ij}$. Though it is not necessary so far, we shall restrict it from now on to a square well perturbation

$$\delta U_{ij} = \eta\epsilon[a - |r_i - r_j|] \tag{1}$$

where η is the depth of the square well, for which $\beta\eta \ll 1$ ($\beta^{-1} = k_B T$; k_B is the Boltzmann constant and T is the absolute temperature), and where $\epsilon(x)$ is the Heaviside step function: $\epsilon(x) = 0$ if $x < 0$, and $\epsilon(x) = 1$ if $x \geqslant 0$.

Actually, this allows one to treat any kind of perturbating potential to first order, since any potential which is sufficiently regular can be considered as a sum of a continuous set of square wells following the formula

$$\delta U(r) = \int_0^{+\infty} da\ [dU(a)/da]\epsilon(a - |r|)$$

so that the linear correction to the velocity time correlation, namely $\delta\psi(t)$, can be computed for a given potential $\delta U(r)$ through

$$\delta\psi(t) = \int_0^{+\infty} da\ [dU(a)/da]\ \delta\psi(t; a)$$

where $\delta\psi(t; a)$ is the correction to $\psi(t)$ computed for a square well of width a and unit depth [from now on we shall drop the argument a in $\delta\psi(t; a)$, so that $\delta\psi(t)$ shall stand everywhere for the correction arising from a square well of width a].

The velocity time correlation of the reference fluid is $\psi(t) = \langle v_1(0)v_1(t)\rangle_R$. When the reference potential is a hard core repulsion, its first-order correction can be written as the sum of three terms

$$\delta\psi(t) = \sum_{i=1}^{3} \delta_i\psi(t) \tag{2}$$

each of them being expressed by a quantity averaged over the reference fluid:

1. The correction $\delta\psi_1(t)$ arises from the expansion of the statistical weight to first order in the perturbating potential
2. The correction $\delta_2\psi(t)$ takes into account the small change in the velocity $v_1(t)$ due to the perturbating potential
3. The correction $\delta_3\psi(t)$ accounts for the delay in the collision time because of the small displacement of the trajectories.

A correct definition of these last two quantities is not obvious, so let us define $\delta_i\psi(t)$ ($i = 1, 2, 3$) more precisely.

(i) The contribution $\delta_1\psi(t)$ is well known. This is simply

$$\delta_1\psi(t) = -\beta\left\langle v_1(0)v_1^{\mathrm{R}}(t) \sum_{i\neq j} [\delta U_{ij} - \langle \delta U_{ij}\rangle_{\mathrm{R}}]\right\rangle_{\mathrm{R}} \tag{3}$$

the sum $\sum_{i\neq j}$ running over the whole set of nonordered pairs in the system. $v_1^{\mathrm{R}}(t)$ is the velocity of particle 1 at time t on the trajectory of the reference system.

(ii) The correction $\delta_2\psi(t)$ arises from the small change in the velocity $v_1(t)$ due to the perturbing interaction.

Suppose that particles i and j start with the unperturbed velocities v_i and v_j at $t = 0$ and that their mutual distance becomes equal to a (range of the square well) at some later time t_{ij}, so that $r_{ij}v_{ij} < 0$ and no other interaction affects the motion of i and j between 0 and t_{ij}; thus, the relative velocity of i and j just after t_{ij} is

$$v'_{ij} = \operatorname{sg} v_{ij}(v_{ij}^2 - 4\eta)^{1/2} \tag{4}$$

where $\operatorname{sg} x = 1$ if $x > 0$ and -1 otherwise. Note that in Eq. (4) we took the mass of the hard points as the unit mass. If v_{ij}^2 becomes smaller than $4|\eta|$, formula (4) becomes meaningless in the repulsive case as the particle is reflected by the square well. As shown in Section 3, this last effect is not important to first order in $\beta\eta$. Except for this small region in velocity space, the difference $v'_{ij} - v_{ij}$ is of order η. In order to account for this contribution of the small deviations, Frisch and Berne[3] have derived the following formula, which should be valid for a hard sphere reference fluid:

$$\delta_2'\psi(t) = \left\langle [r_1(t) - r_1(0)]_{\mathrm{R}} \sum_{j\neq 1} \frac{\partial}{\partial r_1(0)}\, \delta U_{1j}(r_{1j}(0))\right\rangle_{\mathrm{R}} \tag{5}$$

the prime indicates that our formula for $\delta_2\psi(t)$ will not be this one.

Watts[6] has shown by computer experiments that for large times $\delta_2'\psi(t)$ has a nonzero finite limit. This will be confirmed by an explicit calculation of $\delta_2'\psi(t)$, which may be done quite simply in the one-dimensional case. On the other hand, we have shown[7] that Eq. (5) does not fully account for the effect of the small deviations of the hard sphere trajectories. But, contrary to Berne and Frisch, we have not found any closed formula for $\delta_2\psi(t)$, this quantity being just given by a kind of recipe requiring a detailed knowledge of a trajectory of the reference system.

(iii) The origin of the last contribution to $\delta\psi(t)$, i.e., $\delta_3\psi(t)$, is less obvious than those of $\delta_1\psi(t)$ and $\delta_2\psi(t)$. In fact, due to the small deviations of the trajectories caused by the potential δU, a hard point collision between, say, particles i and j does not occur at time t_{ij}, as in the reference system, but at time $t_{ij} + \delta t_{ij}$. Take, for instance, $\delta t_{ij} > 0$, and let v_i and v_j be the velocities of i and j before the collision; thus during the time interval $[t_{ij}, t_{ij} + \delta t_{ij}]$, the velocity of, say i, is v_i in the perturbed system, although it was v_j in the reference system. During this small lapse of time the change of velocity of i is large, and its amplitude does not vanish at $\eta = 0$ (η is the depth of the perturbing potential), although its duration is of order $|\eta|$. However, the net effect of the equilibrium average over the initial conditions is roughly equivalent to a time integration of this velocity change, so that small deviations during a finite lapse of time [as the one accounted for through $\delta_2\psi(t)$] and a finite deviation during a small period of time may contribute to the same order in η. Actually, this is verified in the one-dimensional model. It turns out that the contribution $\delta_3\psi(t)$ requires the most intricate calculation.

1.2. The Model and the Correction of Berne and Frisch

In this subsection, we present the main features of the hard points dynamics, as analyzed by Jepsen[8] and Lebowitz *et al.*[9,10] We then study a simple time correlation function, which yields the correction found by Berne and Frisch.

The reference fluid is a gas of hard points on an infinite line, which will be taken as the limit of a system of N points on a line of length L, $L \to \infty$, with $N/L = \rho$ finite. A number of dynamical quantities of this system may be computed using the method of Lebowitz *et al.* The basic idea is to replace the dynamical quantities of a hard point gas by some other dynamical quantities of a one-dimensional gas of noninteracting (or "free") points, which, in principle at least, depend in a very simple way on the initial conditions. At time $t = 0$, one defines the rank of a particle i on the line, which is measured by the integer

$$\sigma_i(0) = \sum_{j \neq i} \epsilon[r_i(0) - r_j(0)] \tag{6}$$

In the hard point system, there is only an exchange of indices at each collision, so that the velocity and position of particle i at time t in the hard point system are those of particle k in the free point system with the same initial conditions and such that

$$\sigma_k(t) = \sum_{j \neq k} \epsilon[r_k(t) - r_j(t)]$$

is equal to $\sigma_i(0)$.

Let $r_i^{\mathrm{R}}(t)$ and $v_i^{\mathrm{R}}(t)$ be the position and velocity of a particle i at time t in the hard point (reference) system, $\{r_l(0), v_l(0)\}$ being the set of the initial conditions. Then, any function f of $r_i^{\mathrm{R}}(t)$ and $v_i^{\mathrm{R}}(t)$ depends on the initial conditions as

$$f[r_i^{\mathrm{R}}(t), v_i^{\mathrm{R}}(t)] = \sum_k \delta_{\sigma_i(0),\sigma_k(t)} f[r_k(0) + v_k(0)t, v_k(0)] \tag{7}$$

where $\delta_{m,n}$ is the Kronecker symbol:

$$\delta_{mn} = \int_0^{2\pi} (d\theta/2\pi)\, e^{i\theta(m-n)} \tag{8}$$

From Eqs. (5) and (7), the dynamical correction of Berne and Frisch is

$$\delta_2'\psi(t) = -\sum_k \left\langle [r_k(0) + v_k(0)t - r_1(0)]\, \delta_{\sigma_k(t),\sigma_1(0)} \sum_{j\neq 1} \delta F_{1j}(0) \right\rangle \text{fp} \tag{9}$$

where $\delta F_{1j}(0) = -\partial U[r_1(0) - r_j(0)]/\partial r_1(0)$ is the small force exerted by particle j on particle 1 at time 0 (in this calculation, we shall not restrict ourselves to a particular potential) and where the average is taken on an equilibrium ensemble of initial conditions for the free point system as indicated by the subscript fp. After reduction of the sums $\sum_j$ and $\sum_k$ in (9), we find three terms corresponding to the following combinations of indices: (i) $k = 1, j \neq 1$; (ii) $k \neq 1, j = k$; (iii) $1, j, k$ all different.

It may be shown that the first and second combinations yield a contribution to $\delta_2'\psi(t)$ vanishing at large times, although the third one gives a nonzero constant in this limit:

$$\delta_2'\psi(t) \underset{t\to\infty}{\simeq} -(N-1)(N-2)\langle (r_2 + v_2 t - r_1)\, \delta F_{13}(0)\, \delta_{\sigma_2(t),\sigma_1(0)}\rangle \text{fp}$$

In this last expression, we have replaced $r_2(0)$, $v_2(0)$,... by r_2, v_2,....

We carry out the ensemble average explicitly and get

$$\begin{aligned}\delta_2'\psi(t) \underset{t\to\infty}{\simeq} & -(N-1)(N-2)\int_{-\infty}^{+\infty} dv_1 h_0(v_1) \int_{-\infty}^{+\infty} dv_3 h_0(v_3) \\ & \times \int_{-L/2}^{L/2} \frac{dr_1}{L} \int_{-L/2}^{L/2} \frac{dr_2}{L} \int_{-L/2}^{L/2} \frac{dr_3}{L} \left(\frac{r_2 - r_1}{t} + v_2\right) \delta F(|r_1 - r_3|) \\ & \times \int_0^{2\pi} \frac{d\theta}{2\pi} \exp\{i\theta[\epsilon(r_2 - r_1 + v_2 t - v_1 t) - \epsilon(r_1 - r_2)]\} \\ & \times \exp\{i\theta[\epsilon(r_2 - r_3 + v_2 t - v_3 t) - \epsilon(r_1 - r_3)]\} \prod_{l=4}^{N} \int_{-\infty}^{+\infty} dv_l\, h_0(v_l) \\ & \times \int_{-L/2}^{L/2} \frac{dr_l}{L} \exp\{i\theta[\epsilon(r_2 - r_l + v_2 t - v_l t) - \epsilon(r_1 - r_l)]\}\end{aligned}$$

where

$$h_0(v) = [1/(2\pi)^{1/2}] \exp(-v^2/2) \tag{10}$$

(the energy unit is chosen in such a way that $m/k_B T = 1$). In the $N \to \infty$ limit, the last factor on the right-hand side (i.e., $\prod_{l\geq 4} \int dv_l \cdots$) is replaced by

$$\exp\left\{it\rho(\sin\theta)\left(\frac{r_2 - r_1}{t} + v_2\right) - \rho t(1 - \cos\theta)\mu\left(\frac{r_2 - r_1}{t} + v_2\right)\right\}$$

where $\mu(x)$ is the collision frequency

$$\mu(x) = \int_{-\infty}^{+\infty} dv\, h_0(v)|v - x| \tag{11a}$$

$$= 2h_0(x) + 2x \operatorname{Erf} x \tag{11b}$$

with

$$\operatorname{Erf} x = \int_0^x dv\, h_0(v) \tag{11c}$$

After we integrate over v_1 and v_3, set $x = (r_1 - r_2)/t$, $y = (r_1 - r_3)/t$, $\omega = (r_2 - r_1)/t + v_2$, and integrate over r_1 and x, we get

$$\begin{aligned}\delta_2'\psi(t) \underset{t\to\infty}{\simeq} & -t\int_{-\infty}^{+\infty} \omega\, d\omega \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^2 \exp\{it\rho(\sin\theta)\omega - t\rho(1 - \cos\theta)\mu(\omega)\} \\ & \times \left[\frac{1 + e^{i\theta}}{2} - (1 - e^{i\theta}) \operatorname{Erf}\omega\right]\left[\frac{1 + e^{-i\theta}}{2} - (1 - e^{-i\theta})\operatorname{Erf}\omega\right] \\ & \times \int_{-\infty}^{+\infty} dy\left[\frac{1 + e^{i\theta}}{2} - (1 - e^{i\theta}) \operatorname{Erf}(\omega + y)\right] e^{-i\theta\epsilon(y)}\, \delta F(ty)\end{aligned} \tag{12}$$

Except for the factor $\exp\{it\rho(\sin\theta)\omega - \rho t(1 - \cos\theta)\mu(\omega)\}$, the integrand on the right-hand side of (12) may be rearranged into a polynomial in $(1 - \cos\theta)$ and $(i\sin\theta)$. Using the saddle point method as explained in Appendix A, we can show that the contributions of the various terms of this polynomial behave as t^{-1} as $t \to \infty$, except for the following term:

$$\begin{aligned}\delta_2'\psi(t) \underset{t\to\infty}{\simeq} & \; t\int_{-\infty}^{+\infty} \omega\, d\omega \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^2 (i\sin\theta) \\ & \times \exp\{it\rho(\sin\theta)\omega - t\rho(1 - \cos\theta)\mu(\omega)\} \int_0^{+\infty} dy\, \delta F(ty) \\ \simeq & \; \delta U(|r| = 0)\int_{-\infty}^{+\infty} \frac{d\omega\, \omega^2}{[\mu^2(\omega) - \omega^2]^{1/2}} (\rho t)^2\{\exp[-\rho t\mu(\omega)]\} \\ & \times I_0(\rho t[\mu^2(\omega) - \omega^2]^{1/2})\end{aligned} \tag{13}$$

where I_0 is the modified Bessel function of order zero and $\delta U(|r| = 0)$ is the limit value of the perturbating potential, which is assumed to be continuous and bounded at short distances. The integral on the rhs of (13) can be evaluated again by the saddle point method and we get the simple final result

$$\delta_2'\psi(t) \underset{t\to\infty}{\simeq} \delta U(|r|)|_{r=0} \tag{14}$$

In this last formula, we recover qualitatively the result of Watts, i.e., $\delta_2'\psi(t)$ has a nonzero limit at $t \to \infty$, but in contradiction to the statement by Watts, this value is not connected directly to the virial part of the equilibrium pressure, at least for this one-dimensional case.

Now we shall consider successively the corrections $\delta_1\psi(t)$, $\delta_2\psi(t)$, and $\delta_3\psi(t)$, which, as explained above, arise from the expansion of the equilibrium weight, from the direct effect of the small interactions on $v_i(t)$, and from the time delay in the hard point collisions, respectively.

2. CORRECTION ARISING FROM THE STATISTICAL WEIGHT

From Eqs. (3) and (7), using the same notations as in (9), we get for this correction ($\beta = 1$)

$$\delta_1\psi(t) = \tfrac{1}{2}\left\langle v_1 \sum_{k=1}^{N} v_k\, \delta_{\sigma_k(t),\sigma_1(0)} \sum_{\substack{i \neq j \\ i,j=1\cdots,N}} [\delta U(r_i - r_j) - \langle \delta U(r_i - r_j)\rangle]\right\rangle \quad (15)$$

We have now six different terms to calculate, corresponding to the following six combinations of indices:

(i) $k = 1;\ i = 1;\ j \neq 1$.
(ii) $k = 1;\ 1, i, j$ all distinct.
(iii) $k \neq 1;\ i = 1;\ j = k$.
(iv) $k \neq 1;\ i = 1;\ j \neq k$.
(v) $k \neq 1;\ i = k;\ j \neq 1, k$.
(vi) $1, i, j, k$ all different.

The six quantities to be calculated are now

$$T_1 = (N-1)\langle v_1^2[\delta U_{12} - \langle \delta U_{12}\rangle]\,\delta_{\sigma_1(t),\sigma_1(0)}\rangle \quad (16a)$$

$$T_2 = \tfrac{1}{2}(N-1)(N-2)\langle v_1^2[\delta U_{23} - \langle \delta U_{23}\rangle]\,\delta_{\sigma_1(t),\sigma_1(0)}\rangle \quad (16b)$$

$$T_3 = (N-1)(N-2)\langle v_1 v_2[\delta U_{12} - \langle \delta U_{12}\rangle]\,\delta_{\sigma_2(t),\sigma_1(0)}\rangle \quad (16c)$$

$$T_4 = (N-1)(N-2)\langle v_1 v_2[\delta U_{13} - \langle \delta U_{13}\rangle]\,\delta_{\sigma_2(t),\sigma_1(0)}\rangle \quad (16d)$$

$$T_5 = (N-1)(N-2)\langle v_1 v_2[\delta U_{23} - \langle \delta U_{23}\rangle]\,\delta_{\sigma_2(t),\sigma_1(0)}\rangle \quad (16e)$$

$$T_6 = \tfrac{1}{2}(N-1)(N-2)(N-3)\langle v_1 v_2[\delta U_{34} - \langle \delta U_{34}\rangle]\,\delta_{\sigma_2(t),\sigma_1(0)}\rangle \quad (16f)$$

where we have dropped the subscript fp. The final result is

$$\delta_1\psi(t) = \sum_{i=1}^{6} T_i \quad (17)$$

The details of the evaluation of the T_i are given in Appendix B. Let us just sketch the method of calculation. It is not completely straightforward, as the quantity $\langle \delta U_{ij}\rangle$ for a given pair (i, j) vanishes in the thermodynamic limit. For some T_i, it may be completely neglected, although for others it must be kept in order to get a finite result in the thermodynamic limit.

Consider, for instance, the case of T_2. A partial average can be taken at once over the positions of the dummy particles, i.e., particles with an index $j \geqslant 4$. Let us denote by $\langle\ \rangle_{j\geqslant 4}$ this partial average. Thus,

$$\langle \delta_{\sigma_1(t),\sigma_1(0)} \rangle_{j\geq 4} = \int_0^{2\pi} \frac{d\theta}{2\pi} \exp\{i\theta[\epsilon_{12}(t) - \epsilon_{12}(0)]\} \exp\{i\theta[\epsilon_{13}(t) - \epsilon_{13}(0)]\} \times \left[\exp\{it\rho(\sin\theta)v_1 - \rho t(1-\cos\theta)\mu(v_1)\} + O\left(\frac{1}{N}\right)\right] \tag{18}$$

where $O(1/N)$ depends on θ, t, v_1 only and where $\epsilon_{ij}(t) = \epsilon[r_i(t) - r_j(t)]$. As a function of $r_2(0)$, the quantity $\epsilon_{12}(t) - \epsilon_{12}(0)$ differs from zero over a finite interval around $r_1(0)$; writing

$$\exp\{i\theta[\epsilon_{12}(t) - \epsilon_{12}(0)]\} = 1 + \phi_1(r_2(0), t)$$

we find that the function $\phi_1(r_2(0), t)$—which depends also on θ, v_1, $r_1(0)$, and v_2—differs from zero over a finite interval around $r_1(0)$. Then, from (18)

$$\langle \delta_{\sigma_1(t),\sigma_1(0)} \rangle_{j\geq 4} = \int_0^{2\pi} \frac{d\theta}{2\pi} [1 + \phi_1(r_2(0), t)][1 + \phi_1(r_3(0), t)] \times \left[\exp\{it\rho(\sin\theta)v_1 - \rho t(1-\cos\theta)\mu(v_1)\} + O\left(\frac{1}{N}\right)\right]$$

Expanding the product $[1 + \phi_1(r_2(0), t)][1 + \phi_1(r_3(0), t)]$ and inserting the corresponding value of $\langle \delta_{\sigma_1(t),\sigma_1(0)} \rangle_{j\geq 4}$ into (16b), we find three kinds of terms. The first does not depend on ϕ_1; it depends on positions through the combination $\langle \delta U_{23} - \langle \delta U_{23} \rangle \rangle$ only and, once averaged, this gives zero. Another term depends linearly on $\phi_1(r_2(0), t)$ [or on $\phi_1(r_3(0), t)$] and, after averaging over $r_3(0)$ [or $r_2(0)$], it gives again zero. The only term surviving in the thermodynamic limit is the one that is formally quadratic in ϕ_1. Due to the presence of the two factors ϕ_1, the integration over $r_2(0)$ and $r_3(0)$ is limited to a finite interval around $r_1(0)$. In this domain $\langle \delta U_{23} \rangle \sim (a/L)\, \delta U_{23}$, so that one may neglect therein both $\langle \delta U_{23} \rangle$ and the corrections $O(1/N)$ to $\exp\{it\rho(\sin\theta)v_1 \cdots\}$ and one obtains

$$T_2 = \tfrac{1}{2}(N-1)(N-2)\left\langle v_1^2\, \delta U_{23} \int_0^{2\pi} \frac{d\theta}{2\pi} \exp\{it\rho(\sin\theta)v_1 - (1-\cos\theta)\rho t\mu(v_1)\} \times \phi_1(r_2(0), t)\phi_1(r_3(0), t) \right\rangle \tag{19}$$

Very similar reasoning allows us to get explicit and finite integrals from the general formulas given in (16). All these contributions reduce to one- or two-dimensional integrals, which we have calculated by a Gauss integration method. The results are plotted on Fig. 1. After some oscillations, the function

$\delta_1\psi(t)$ goes monotonically to zero with increasing time. The saddle point method discussed in Appendix A shows that, at long times,

$$\delta_1\psi(t) \underset{t\to\infty}{\simeq} \rho a/(\rho t)^2 \tag{20}$$

Thus $\delta_1\psi(t)$ provides a finite correction to the self-diffusion coefficient. Moreover, we can find a few other exact properties of $\delta_1\psi(t)$, such as the slope at the origin, which is studied in Appendix B. Further, we have been able to show that, when the range of the potential increases, $\delta_1\psi(t)$ goes to a finite limit function.

3. CALCULATION OF THE CORRECTION $\delta_2\psi(t)$

As explained at the beginning of this paper, the correction to the velocity time correlation due to the perturbing potential may be divided into three parts. Now, we shall consider the term denoted $\delta_2\psi(t)$, which arises from the small changes in $v_1(t)$ due to the interaction δU. As we restrict ourselves to perturbations linear in δU, we can write this velocity shift as

$$\delta v_1(t) = \sum_{i\neq 1} \delta v_1^{(i)}(t)$$

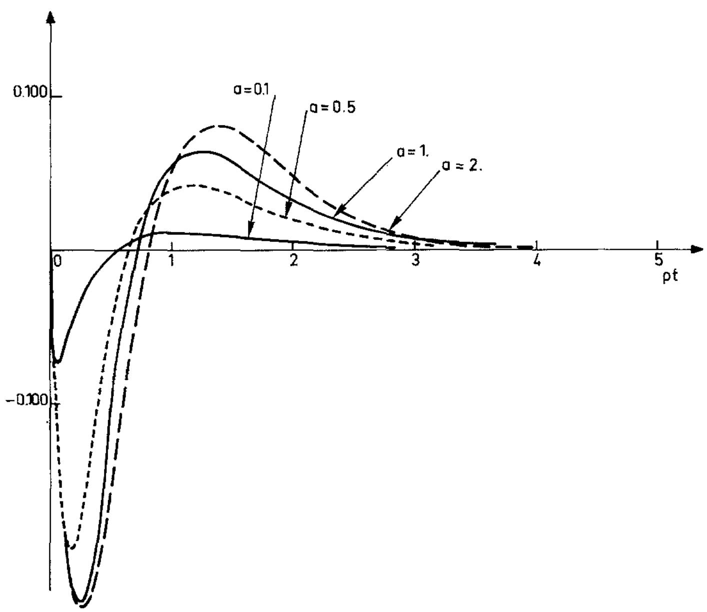

Fig. 1. Plot of the contribution to $\delta\psi(t)$ arising from the perturbation to the statistical weight as a function of time for several values of the potential range.

where $\delta v_1^{(i)}(t)$ is the difference between the velocity $v_1(t)$ in the reference system and that in the system where the interaction δU_{1i} is turned on at time zero. From (7), one can express the values of δv_1 in the hard point system by means of δv_1 for the free point system:

$$\delta v_1^{(k)}(t) = \sum_{i \neq k} \sum_{k} \delta_{\sigma_k(t),\sigma_1(0)} \, \delta v_k^{(i)}(t)$$

where $\delta v_1^{(i)}(t)$ is now the change of velocity of particle 1, due to the interaction δU_{1i} in the free point system. Thus

$$\delta_2 \psi(t) = \sum_{i \neq k} \sum_{k} \langle v_1 v_k^{(i)}(t) \, \delta_{\sigma_k(t),\sigma_1(0)} \rangle_{\text{fp}} \tag{21}$$

where, again, the average is taken over the equilibrium ensemble of noninteracting points. Due to the two summations on the right-hand side of (21), $\delta_2\psi(t)$ splits into three parts

$$\delta_2 \psi(t) = \sum_{j=1}^{3} U_j \tag{22}$$

with

$$U_1 = (N-1)\langle v_1 \, \delta v_1^{(2)} \, \delta_{\sigma_1(t),\sigma_1(0)} \rangle \tag{23a}$$

$$U_2 = (N-1)\langle v_1 \, \delta v_2^{(1)} \, \delta_{\sigma_2(t),\sigma_1(0)} \rangle \tag{23b}$$

and

$$U_3 = (N-1)(N-2)\langle v_1 \, \delta v_2^{(3)} \, \delta_{\sigma_2(t),\sigma_1(0)} \rangle \tag{23c}$$

We have now to express $\delta v_k^{(i)}$ as a function of η, of the range a, and of the velocities in the unperturbed system. Two cases may occur, depending on whether or not i and k interact through δU_{ik} at time zero. Let us consider them successively. In the forthcoming discussion, we shall write $r_i, r_k, \ldots$ instead of $r_i(0)$, $r_k(0), \ldots$.

(*i*) *Particles i and k Do Not Interact at* $t = 0$ (see Fig. 2a). The condition for the nonvanishing of $\delta v_k^{(i)}$ is therefore

$$|r_i - r_k| > a$$

and $(r_i - r_k)(v_i - v_k) < 0$; with these initial conditions, $\delta v_i^{(k)}$ takes a constant value, which is

$$\tfrac{1}{2}[\text{sg } v_{ki}(v_{ki}^2 - 4\eta)^{1/2} - v_{ki}]$$

at any time t such that $|r_i(t) - r_k(t)| < a$; thus the corresponding contribution to $\delta v_k^{(i)}$ is

$$\begin{aligned} \delta v_k^{(i)} = {} & \tfrac{1}{2}[\text{sg } v_{ki}(v_{ki}^2 - 4\eta)^{1/2} - v_{ki}]\epsilon(|r_{ki}| - a) \\ & \times \epsilon(a - |r_{ki} + v_{ki}t|)\epsilon(-r_{ki}v_{ki}) \end{aligned} \tag{24}$$

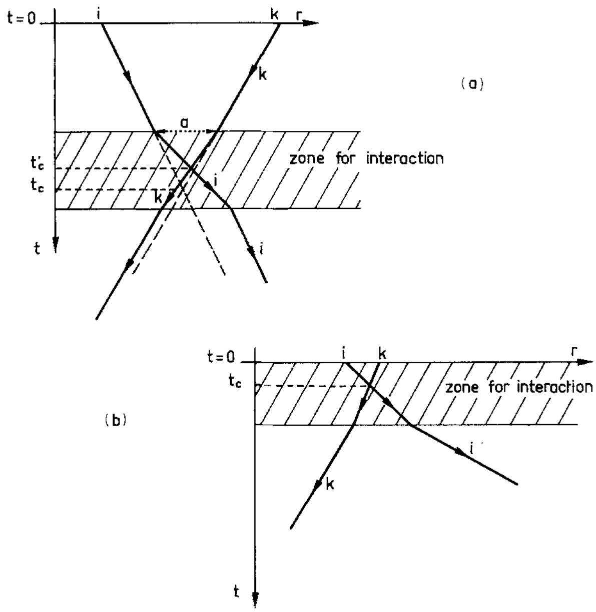

Fig. 2. Deviation of the trajectories of two *free* points when a small perturbation is added, for two cases: (a) The distance between the two particles is greater than a at time zero. (b) The distance between the particles is less than a at time zero.

In order to write (24), we have assumed that, even during the interaction, the relative distance between i and k remains equal to $(r_{ik} + v_{ik}t)$, which is strictly true in the free point system only. However, the corresponding correction arising from the duration of the collision, i.e., the change in $\epsilon(a - |r_{ki} + v_{ki}t|)$, yields contributions to $\delta v_i^{(k)}$ which are of order η^2 at least. Furthermore, in order to get from (24) an expression for $\delta v_k^{(i)}$ which is linear in η, one must expand the velocity difference as follows:

$$\operatorname{sg} v_{ki}(v_{ki}^2 - 4\eta)^{1/2} - v_{ki} = -\frac{2\eta}{v_{ki}} - \frac{2\eta^2}{v_{ki}^3} + \cdots \tag{25}$$

and keep the first term on the right-hand side only. But this expansion must be considered carefully; in fact, as is often the case in this type of problem, the terms that are formally of an increasing order in the small parameters may yield more and more diverging quantities. In the present case, the terms of order η^n are actually of the form η^n/v^{2n-1}, and this may give a diverging contribution to $\delta_2\psi(t)$, due to the average over the velocity v_{ki} near $v_{ki} = 0$. However, the negative powers on the right-hand side of (25) are cancelled in part. In fact, the range of variation of r_{ki} is of order $|v_{ki}|t$ around $r_{ki} = a$; this makes a quantity of order $|v_{ki}|$ appear in the integrand, so that the factor

v_{ki}^{-1} in the first term on the rhs of (25) is just cancelled by this v_{ki} and no divergence appears at this order in η. However, at the next order in η, a divergence appears which should ultimately yield a contribution to $\delta_2\psi(t)$ like $\eta^{3/2}$, as shown in Appendix D.

If the potential is repulsive (i.e., if $\eta > 0$), the formula in (24) becomes meaningless if $|v_{ki}| < (4\eta)^{1/2}$, which means that the relative particle does not have enough kinetic energy to go over the potential barrier. However, it may be shown that this range of the small relative velocities contributes as η^2 to $\delta_2\psi(t)$. In fact, let us consider the corresponding contribution to $\delta v_k^{(i)}$, which we shall denote as $\delta v_k^{(i)}|_{\eta^2}^2$. From simple dynamical considerations

$$\delta v_k^{(i)}|_{\eta^2} \simeq -\tfrac{1}{2}v_{ki}\epsilon(4\eta - v_{ki}^2)\epsilon(|r_{ki}| \dotplus a)\epsilon(-r_{ki}v_{ki})\epsilon(a - |r_{ki} + v_{ki}t|) \quad (26)$$

when v_{ik} becomes small, the product $\epsilon(|r_{ik}| - a)\epsilon(a - |r_{ik} + v_{ik}t|)$ becomes concentrated around $r_{ik} = +a$ in a small interval of width $|v_{1k}|t$. Accordingly, it may be expanded like

$$\begin{aligned}&\epsilon(|r| - a)\epsilon(a - |r + vt|)\\ &\quad\simeq |v|t\,\delta(|r| - a) - \tfrac{1}{2}(vt)^2\,\delta'(|r| -)a + \tfrac{1}{6}(vt)^3\,\delta''(|r| - a) \qquad (27)\end{aligned}$$

where we have dropped the subscript *ik* and where, by definition, $\delta^{(n)}(x)$ is such that

$$\int_{-\infty}^{+\infty} \delta^{(n)}(x)f(x)\,dx = (-)^n(d^n/dx^n)f(x)|_{x=0}$$

Inserting the expansion (27) into (26), we get series of functions $\delta(v)$, $\delta'(v)$,... multiplied by increasing powers of v and $|v|: v|v|, v^3, v|v^3|$,.... Without any assumption about the parity in v of the rest of the integrand, we get, after averaging, contributions which are at most of order $\eta^{3/2}, \eta^2$,.... This means that the contribution of particles that cannot go over the potential is at most of order $\eta^{3/2}$, and it can be neglected in the linear approximation.

(*ii*) *Particles i and k Interact at* $t = 0$ (Fig. 2b). In this case, $\delta v_k^{(i)}$ differs from zero only when $|r_{ik}(t)| \geqslant a$. Furthermore, if the potential δU_{ik} is attractive ($\eta < 0$), $\delta v_k^{(i)}$ takes a particular form in the range $|v_{ki}| < (4|\eta|)^{1/2}$, which corresponds to classical bound states for particles i and k. However, as in the previous case, this gives a contribution to $\delta v_k^{(i)}$ which is negligible to first order in η and the main contribution to $\delta v_k^{(i)}$ arising from particles interacting at $t = 0$ is

$$\delta v_k^{(i)} = \tfrac{1}{2}[\text{sg}\, v_{ki}(v_{ki}^2 + 4\eta)^{1/2} - v_{ki}]\epsilon(a - |r_{ki}|)\epsilon(|r_{ki} + v_{ki}t| - a)\epsilon(v_{ki}^2 - 2\eta) \quad (28)$$

It will be often convenient to replace in this last expression $\epsilon(|r_{ki} + v_{ki}t| - a)$ by

$$\epsilon(-r_{ki}v_{ki})\epsilon\left(t - \frac{a + |r_{ki}|}{|v_{ki}|}\right) + \epsilon(r_{ki}v_{ki})\epsilon\left(t + \frac{|r_{ki}| - a}{|v_{ki}|}\right)$$

Moreover, as explained in Appendices C and D, one may replace

$$\operatorname{sg} v_{ki}(v_{ki}^2 + 4\eta)^{1/2} - v_{ki} \qquad \text{by} \qquad 2\eta/v_{ki}$$

without making any divergence appear in $\delta_2\psi(t)$.

Inserting into (23) the value of $\delta v_k^{(i)}$ that is the sum of the right-hand sides of Eqs. (24) and (28), we get the final expression for $\delta_2\psi(t)$, which depends on a number of integrals listed in Appendix C. In this appendix, we have also studied the asymptotic behavior of the U_i, as it governs the existence of the correction to the self-diffusion coefficient, which is the time integral of $\delta\psi(t)$. For U_1 and U_3, this asymptotic behavior is

$$U_1, U_3 \underset{t\to\infty}{\simeq} [\rho a/(\rho t)^2] \ln(\rho a/\rho t)$$

On the contrary, it turns out that U_2 decreases at infinity like $1/t$; more precisely

$$U_2 \underset{t\to\infty}{\simeq} -[2\eta/(2\pi)^{1/2}]\rho a/\rho t$$

whence the asymptotic behavior for $\delta_2\psi(t)$:

$$\delta_2\psi(t) \underset{t\to\infty}{\simeq} -\frac{2\eta}{(2\pi)^{1/2}}\frac{\rho a}{\rho t} + \frac{\rho a}{(\rho t)^2}\left[A \ln\left(\frac{\rho a}{\rho t}\right) + B\right] + \cdots \tag{29}$$

As the self-diffusion coefficient is the time integral of this velocity correlation, this $1/t$ contribution should yield a logarithmically diverging contribution to the first-order correction to this transport coefficient. Actually, it turns out that this $1/t$ is just cancelled by another contribution of the type studied in the next section, so that no logarithmic divergence appears. It should be interesting to get the value of the coefficient of the $(\ln t)/t^2$ term. The calculations are so complicated that we cannot claim it does not vanish. However, the main point is that the time integral converges.

The time variation of U_2 is plotted on Fig. 3 for several values of a. The behavior of U_2 for a large potential range also is indicated. For not too large t ($t \ll a$), the function is nearly zero. The maximum of U_2 moves toward large t; it can be shown (by a saddle point method) that the function becomes concentrated around $t \sim a^{1/2}$ and that the height of the maximum is $\rho t \exp\{(\rho t)^2/2 - \rho a\}$. For very large times ($t \gg a$), the function U_2 decreases slowly, like a/t. The numerical values taken here for a ($a \leqslant 10$) and ρt are likely not large enough to check this behavior.

4. CALCULATION OF $\delta_3\psi(t)$

As explained in the introduction, part of the correction $\delta\psi(t)$is due to the difference of the collision times for hard points in the reference system and in the perturbed system. Let $\delta_3\psi(t)$ be this contribution to $\delta\psi(t)$. We shall

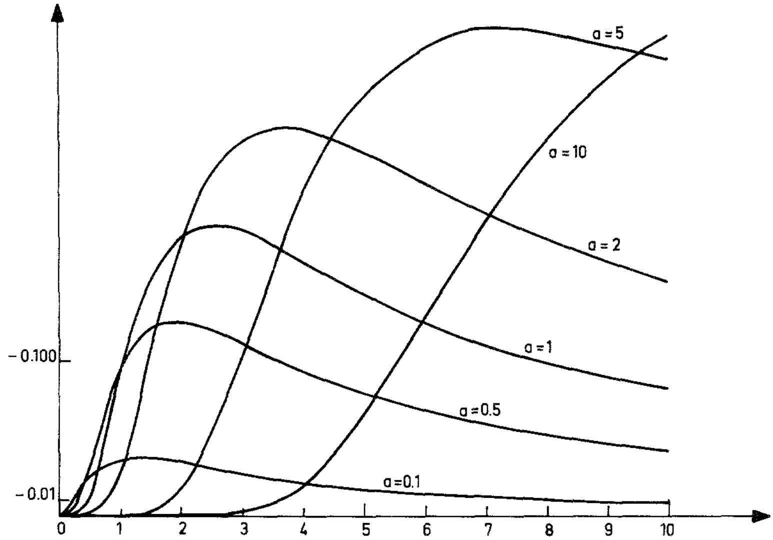

Fig. 3. Plot of $U_2(t)$ vs. time for several values of the potential range a. It goes to zero like a/t.

first explain how to compute this time delay by starting from the dynamics of the free point system.

Let us consider a collision arising at time t_{1k} between particles 1 and k in the unperturbed hard point system. Furthermore, let $\delta r_i(t)$ be the spatial shift of particle i due to the action of δU between times 0 and t. This means that, if particle i is located at $r_i(t)$ at time t_{1k} in the unperturbed system, it lies at $r_i(t) + \delta r_i(t)$ at the same instant in the perturbed system. Thus, the time delay for the collision $(1k)$ is

$$\delta t_{1k} = -[\delta r_1(t) - \delta r_k(t)]/(v_1 - v_k) \tag{30}$$

where v_1 and v_k are the velocities of 1 and k before the collision. If $\delta t_{1k} > 0$, the collision is delayed and during the interval $[t_{1k}, t_{1k} + \delta t_{1k}]$ the velocity of particle 1 is v_1 in the perturbed system, although it was v_k in the reference system; on the contrary, if $\delta t_{1k} < 0$, the collision is in advance and during the interval $[t_{1k} + \delta t_{1k}, t_{1k}]$ the velocity of particle 1 is v_k in the perturbed system, although it was v_1 in the reference system. Let us denote by $\delta' v_1(t)$ the velocity change due to this time delay; thus

$$\delta' v_1(t) \simeq \sum_{m \neq n} \delta(t - t_{mn})\, \delta t_{mn}\, v_{mn}\, \delta_{\sigma_m(t_{mn}^-),\sigma_1(0)} \tag{31}$$

where

$$t_{mn} = -[r_m(0) - r_n(0)]/[v_m(0) - v_n(0)] \tag{32}$$

is the instant of the collision (mn) in the reference system. Due to the presence of the function $\delta(t - t_{mn})$, there could be some indeterminacy in (31), as $\sigma_m(t)$ is undefined at the instant of the collision (mn); in the present case, one must keep the value of $\sigma_m(t)$ just *before* the collision, as emphasized by the notation $\sigma_m(t_{mn}^-)$. In order to get completely explicit formulas from (31), we have to express δt_{mn}, i.e., $\delta r(t)$. To first order in η, one may suppose that $\delta r_m(t)$ is just the sum of the contributions due to the interaction δU between m and any other particle between times 0 and t:

$$\delta r_m(t) = \sum_{p \neq m} \delta r_m^{(p)}(t) \tag{33}$$

As in the preceding case, we have transformed the problem into the evaluation of a perturbation in two-body dynamics.

The quantity $\delta r_m^{(p)}(t)$ takes different forms, depending on whether m and p interact or not at $t = 0$ and at time t, although in any case they must interact between 0 and t. Simple considerations show that, when particles m and p have interacted between 0 and t, but do not interact at time zero, $\delta r_m^{(p)}(t)$ takes the form

$$\begin{aligned}\delta r_m^{(p)}(t) = {} & \tfrac{1}{2}\epsilon(|r_{mp}| - a)\epsilon(-r_{mp}v_{mp})[\operatorname{sg} v_{mp}(v_{mp}^2 - 4\eta)^{1/2} - v_{mp}] \\ & \times \epsilon(t - T_{mp})\left[(t - T_{mp})\epsilon\left(T_{mp} - t + \frac{2a}{|v_{mp}|}\right) + \frac{2a}{|v_{mp}|} \right. \\ & \left. \times \epsilon\left(t - T_{mp} - \frac{2a}{|v_{mp}|}\right)\right]\end{aligned} \tag{34a}$$

where T_{mp} (which must not be confused with the time t_{mp} defined previously) is the time after which particles m and p begins to interact

$$T_{mp} = (|r_{mp}| - a)/|v_{mp}| \tag{34b}$$

(see Fig. 4a).

If, on the contrary, particles m and p interact at $t = 0$, but do not interact at time t (Fig. 4b), then $\delta r_m^{(p)}(t)$ takes the form

$$\begin{aligned}\delta r_m^{(p)}(t) = {} & \tfrac{1}{2}[\operatorname{sg} v_{mp}(v_{mp}^2 + 4\eta)^{1/2} - v_{mp}]\epsilon(a - |r_{mp}|) \\ & \times \epsilon(|r_{mp} + v_{mp}t| - a)\left[t - \frac{a \operatorname{sg} v_{mp} - r_{mp}}{v_{mp}}\right]\end{aligned} \tag{35}$$

Inserting (33) into (30), we get

$$\delta t_{1k} = -(1/v_{1k})\left[\sum_{p \neq 1} \delta r_1^{(p)}(t) - \sum_{p \neq k} \delta r_k^{(p)}(t)\right]$$

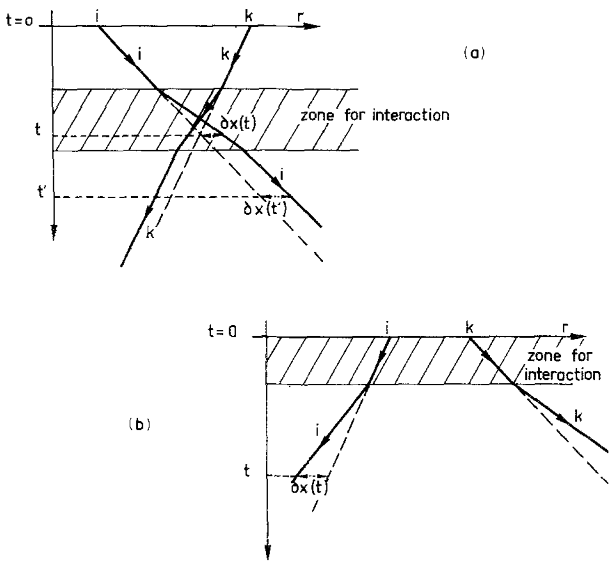

Fig. 4. Perturbation of the positions due to a small interaction for free point particles. (a) Particles do not interact at time zero. The deviation $\delta x(t)$ increases until there is no more interaction. The deviation is constant when the particles are no longer interacting (time t'). (b) Particles interact at time $t = 0$. After they have left their mutual potential, the deviation increases linearly.

where $\delta r_i^{(j)}(t)$ is the sum of the right-hand sides of (34) and (35): $\delta r_i^{(j)}(t) = \delta r_{i,1}^{(j)}(t) + \delta r_{i,2}^{(j)}(t)$. Once inserted into (31), this gives for the sought quantity, i.e., $\delta' v_1(t)$,

$$\delta' v_1(t) = -\sum_{n \neq m} \sum_{m} \delta_{\sigma_m(t_{mn}^-), \sigma_1(0)}\, \delta(t - t_{mn}) \left[\sum_{p \neq m} \delta r_m^{(p)}(t) - \sum_{p \neq n} \delta r_n^{(p)}(t) \right] \quad (36)$$

so that the time correlation function $\delta_3 \psi(t) = \langle v_1\, \delta' v_1(t) \rangle$ splits first into two parts, the first one arising from $\delta r_m^{(p)}(t)$, the second one from $\delta r_n^{(p)}(t)$. Due to three summations ($\sum_n$, $\sum_m$, and $\sum_p$), each of these two parts of $\delta_3 \psi(t)$ splits into seven contributions corresponding to particular combinations of indices. Using

$$\delta r_m^{(p)}(t) = -\delta r_p^{(m)}(t)$$

[which may be verified at once from (34) and (35)] to reduce slightly the numbers of contributions, we obtain

$$\delta_3 \psi(t) = 2(V_1 + V_3 + V_6) + V_2 + V_4 + V_5 + V_7 \quad (37)$$

with

$$V_1 = -(N-1)\langle v_1\, \delta_{\sigma_1(t_{12}^-),\sigma_1(0)}\, \delta(t-t_{12})\, \delta r_1^{(2)}(t)\rangle_{\text{fp}} \tag{38a}$$

$$V_3 = -(N-1)\langle v_1\, \delta_{\sigma_2(t_{12}^-),\sigma_1(0)}\, \delta(t-t_{12})\, \delta r_2^{(1)}(t)\rangle_{\text{fp}} \tag{38b}$$

$$V_6 = -(N-1)(N-2)\langle v_1\, \delta_{\sigma_2(t_{23}^-),\sigma_1(0)}\, \delta(t-t_{23})\, \delta r_2^{(3)}(t)\rangle_{\text{fp}} \tag{38c}$$

$$V_2 = -(N-1)(N-2)\langle v_1\, \delta(t-t_{12})\, \delta r_1^{(3)}(t)[\delta_{\sigma_1(t_{12}^-),\sigma_1(0)} - \delta_{\sigma_2(t_{12}^-),\sigma_1(0)}]\rangle_{\text{fp}} \tag{38d}$$

$$V_4 = -(N-1)(N-2)\langle v_1\, \delta(t-t_{12})\, \delta r_2^{(3)}(t)[\delta_{\sigma_1(t_{12}^-),\sigma_1(0)} - \delta_{\sigma_2(t_{12}^-),\sigma_1(0)}]\rangle_{\text{fp}} \tag{38e}$$

$$V_5 = -(N-1)(N-2)\langle v_1\, \delta(t-t_{23})\, \delta_{\sigma_2(t_{23}^-),\sigma_1(0)}[\delta r_2^{(1)}(t) - \delta r_3^{(1)}(t)]\rangle_{\text{fp}} \tag{38f}$$

$$V_7 = -(N-1)(N-2)(N-3)\langle v_1\, \delta(t-t_{23})\, \delta_{\sigma_2(t_{23}^-),\sigma_1(0)}[\delta r_2^{(4)}(t) - \delta r_3^{(4)}(t)]\rangle_{\text{fp}} \tag{38g}$$

From now on the calculations are very similar to those in Section 3. The results are listed in Appendix E.

As in Section 3, there is a term which behaves like t^{-1} for long times. It comes from the V_5 contribution and it just cancels out the diverging part of U_2. We may write

$$\delta_3\psi(t) \underset{t\to\infty}{\simeq} \frac{2\eta}{(2\pi)^{1/2}} \frac{\rho a}{\rho t} + \eta \frac{\rho a}{(\rho t)^2}\left[A' \ln\left(\frac{\rho a}{\rho t}\right) + B'\right] \tag{39}$$

where A' and B' are constants that we did not calculate explicitly.

5. RESULTS

Before going to the hard-rod case, we gather in this section all the results we have obtained so far.

We recall that, for small perturbations, the correction to the velocity autocorrelation function is the sum of three terms [see Eq. (2)]

$$\delta\psi(t) = \sum_{i=1}^{3} \delta_i\psi(t)$$

each of them being itself a sum of several contributions [Eqs. (17), (22), and (37)]:

$$\delta_1\psi(t) = \sum_{k=1}^{6} T_k$$

$$\delta_2\psi(t) = \sum_{k=1}^{3} U_k$$

$$\delta_3\psi(t) = 2(V_1 + V_3 + V_6) + V_2 + V_4 + V_5 + V_7$$

Each correction T_k, U_k, V_k may be expressed as a sum of multidimensional integrals, which are listed in Appendices B, C, and E, respectively.

For small perturbation η, no difference exists between the attractive and repulsive cases: The correction $\delta\psi(t)$ is proportional to η and the first-order correction to the self-diffusion coefficient also exists. For $t = 0$, $\delta\psi(t) = 0$ and after some oscillations, it decreases monotonically to zero. From Eqs. (20), (29), and (39),

$$\delta\psi(t) \underset{t\to\infty}{\simeq} \eta[\rho a/(\rho t)^2][C \ln(\rho a/\rho t) + D] \tag{40}$$

where C $(=A + A')$ and D are constants. The C coefficient is obtained after a lengthy and tedious calculation. Some indications are given in Appendix C. We did not carry out completely this calculation, the main point being that the time integral of $\delta\psi(t)$ still exists.

Plots of $\eta^{-1}\delta\psi(t)$ for several values of the potential range a are shown in Fig. 5. The dashed line represents the limit curve for $a = \infty$ and $t \ll a$. It departs from the curve for $a = 5$ at $\rho t \simeq 1$ $(t/a \simeq 0.2)$. To test more precisely the asymptotic behavior for large a and a large range of values of ρt ($\rho t \sim 5$ or 10 for instance), it should be interesting to plot $\delta\psi(t)$ for $a = 20$, for instance. Unfortunately, the integration method becomes less precise as great relative compensations occur between the different contributions and no quantitative result may be obtained in this range of values of a and t, at least by using our numerical integration method.

6. CONNECTION WITH HARD RODS—THE VAN DER WAALS GAS

Now, we shall study to what extent the preceding results may be generalized to a gas of hard rods, each of length b $(Nb \ll L)$. As shown by Lebowitz *et al.*,[9,10] when one evaluates averages of functions of the velocities only (velocity autocorrelation function, self-diffusion coefficient), the hard rod system is equivalent to a gas of hard points on a line of length $L - Nb$, the actual density being

$$\rho' = \rho/(1 - \rho b) \tag{41}$$

and all the formulas are unchanged after the substitution $\rho \to \rho'$.

However, an important difference occurs for functions depending also on the positions; on a given space interval l between the center of two rods $(l \geqslant b)$, there cannot be more than m intermediate rods—m being the greatest integer smaller than $(l - b)/b$—although, for a gas of hard points, any number of particles in a finite interval is allowed.

Using a method very similar to the one of the preceding sections, it is possible, at least in principle, to compute the first-order perturbation $\delta\psi(t)$ in the case of hard rods of length b perturbed by a square well potential. For that purpose, the hard rod system should be first transformed into a hard point

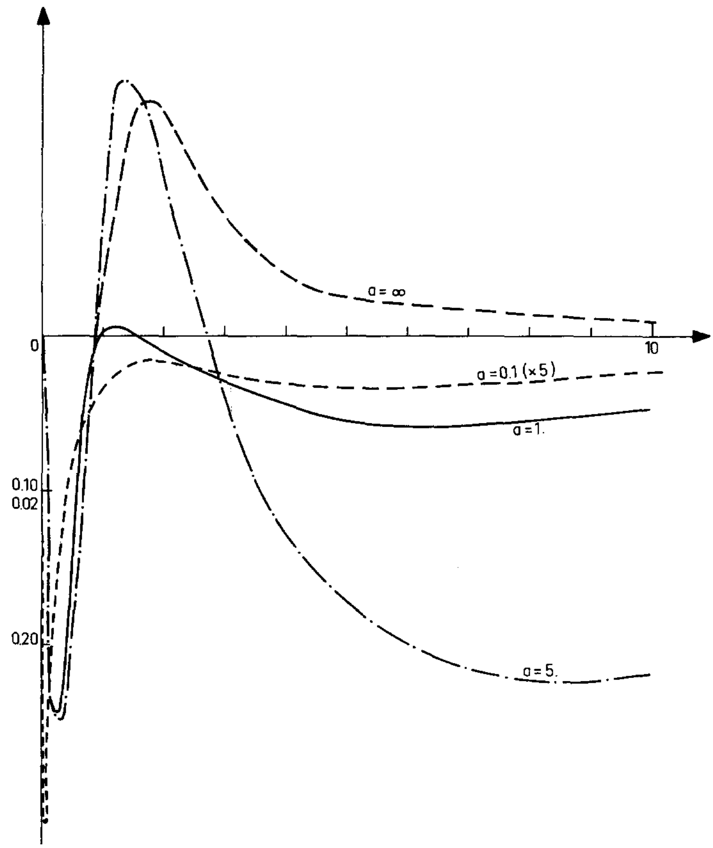

Fig. 5. Plot of the whole perturbation $\delta\psi(t)$ vs. time for several values of the potential range.

system by picking a particular hard rod, say α, then translating jb toward the right the jth rod on the left of α, and translating $j'b$ toward the left the j'th rod on its right. After this overall length contraction, the range of the square well between particles numbered, say j and $j + k$, becomes $\sup(0, a - kb)$ [$\sup(x, y) = x$ if $x > y$, and $= y$ otherwise] so that it becomes a kind of multibody potential. This explains why, although the computations are tractable in principle for the hard rod case, their complexity makes them discouraging. However, we have investigated the case where the range of the square well becomes much larger than the mean interparticular distance ($a \gg \rho^{-1}$). In this limit, the number of particles lying on a length of order a becomes an almost nonfluctuating quantity. Thus, one may consider that, in this limit, the perturbed hard rod system behaves like a hard point gas perturbed by an interaction of range $a' \simeq a - \langle m \rangle b$, $\langle m \rangle$ being the mean number of rods on a length a, i.e., $\langle m \rangle = \rho a$, so that $a' \simeq a(1 - \rho b)$.

Finally, the perturbation $\delta\psi(t)$ for this hard rod case may be derived from the formula of the previous section through the change

$$\rho \to \rho' = \rho/(1 - \rho b) \tag{42a}$$

$$a \to a' = a(1 - \rho b) \tag{42b}$$

Let us now return to the study of $\delta\psi(t)$ at finite times in the limit $a \to \infty$. We choose to study the term T_1, which is the simplest one. Some modifications occur for the other contributions but the proof does not differ essentially.

We first replace the system of N rods of centers $r_1,..., r_N$ at time $t = 0$ $(-L/2 < r_1 < \cdots < r_N < L/2)$ by a system of N points of positions $x_1,..., x_N$ $[-L - (N-1)b/2 < x_1 < \cdots < x_N < L - (N-1)b/2]$ through

$$r_1 = x_1 + \tfrac{1}{2}(N-1)b,..., \qquad r_k = x_k + \tfrac{1}{2}(N-1)b + (k-1)b \cdots$$

The interaction δU_{ij} depends now on the number p $(0 \leqslant p \leqslant m)$ of intermediate points through

$$\begin{aligned} \delta U_{ij} = \delta U_{ij}^{(p)} &= \eta \qquad \text{when} \quad p \leqslant m \quad \text{and} \quad |x_i - x_j| \leqslant a - (p+1)b \\ &= 0 \qquad \text{otherwise} \end{aligned} \tag{43}$$

Using a free-point formalism, we rewrite T_1 as

$$\begin{aligned} &\frac{1}{N} \sum_{i \neq j} \langle v_i^2 \, \delta_{\sigma_i(t), \sigma_i(0)} [\delta U_{ij} - \langle \delta U_{ij} \rangle] \rangle \\ &\simeq \frac{1}{N} \sum_{i \neq j} \langle v_i^2 \, \delta_{\sigma_i(t), \sigma_i(0)} \, \delta U_{ij} \rangle \\ &= (N-1)! \sum_{p=0}^{m} \sum_{i=1}^{N-p-1} \langle v_i^2 \, \delta U_{i,i+p+1}^{(p)} \, \delta_{\sigma_i(t), \sigma_i(0)} \rangle \\ &\quad + (N-1)! \sum_{p=0}^{m} \sum_{i=p+2}^{N} \langle v_i^2 \, \delta U_{i,i-p-1}^{(p)} \, \delta_{\sigma_i(t), \sigma_i(0)} \rangle \\ &\qquad (x_1 < x_2 < \cdots < x_N) \end{aligned}$$

We study only the first term; similar arguments hold for the second one. We express it explicitly as (we have set $j = i + p + 1$)

$$\begin{aligned} &(N-1)! \sum_{p=0}^{m} \sum_{i=1}^{N-p-1} \int_{-\infty}^{+\infty} v_i^2 h_0(v_i) \, dv_i \int_{-\infty}^{+\infty} h_0(v_j) \, dv_j \int_0^{L-(N-1)b} \frac{dx_i}{L-(N-1)b} \\ &\quad \times \int_0^{L-(N-1)b} \frac{dx_j}{L-(N-1)b} \int_0^{2\pi} \frac{d\theta}{2\pi} \\ &\quad \times \exp\{i\theta[\epsilon(x_i - x_j + v_i t - v_j t) - \epsilon(x_i - x_j)]\} \\ &\quad \times \iint_{x_1 < x \cdots < x_N} \cdots \int \prod_{l \neq i,j} \frac{dx_l}{L-(N-1)b} \exp[-i\theta\epsilon(x_i - x_l)] \\ &\quad \times \int_{-\infty}^{+\infty} dv_l h_0(v_l) \exp[i\theta\epsilon(x_i - x_l + v_i t - v_l t)] \end{aligned} \tag{44a}$$

Let us rewrite the last product in the integral as

$$\frac{t^p}{p!}\left[\frac{F(\theta, z, v_i)}{L-(N-1)b}\right]^p \frac{1}{(N-2-p)!}$$
$$\times\left[1+\frac{tG(\theta, v_i)}{L-(N-1)b}-\frac{tF(\theta, z, v_i)}{L-(N-1)b}\right]^{N-2-p} \quad (44b)$$

where

$$F(\theta, z, v_i) = t^{-1}\int_{x_i}^{x_j} dx_l \int_{-\infty}^{+\infty} dv_l\, h_0(v_l)$$
$$\times \exp\{i\theta[\epsilon(x_i - x_l + v_i t - v_l t) - \epsilon(x_i - x_l)]\}$$
$$= \frac{1+e^{i\theta}}{2} z + (1-e^{i\theta})[\phi(z-v_i) - \phi(v_i)] \quad (45a)$$

$$G(\theta, v_i) = t^{-1}\int_{-[L-(N-1)b]/2}^{[L-(N-1)b]/2} dx_l \int_{-\infty}^{+\infty} dv_l\, h_0(v_l)$$
$$\times (\exp\{i\theta[\epsilon(x_i - x_l + v_i t - v_l t) - \epsilon(x_i - x_l)]\} - 1)$$
$$\simeq -(1-\cos\theta)\mu(v_i) + i\sin\theta\, v_i \quad (45b)$$

the functions $\phi(x)$ and $\mu(x)$ $[=2\phi(x)]$ were defined above, and $z = (x_j - x_i)/t$; the function F is concentrated around small values of z ($|z| \leqslant 2$).

Now formulas (44)–(45) are exact but very difficult to handle. Thus, we restrict ourselves to large values of a.

In the case of a hard-point system ($b = 0$), taking the limit consists in (i) replacing the summation $\sum_{p=0}^{m}$ by the summation $\sum_{p=0}^{N-2}$ as the terms for large p do not change anything, the main contributions arising for $p \sim \sqrt{m}$; and (ii) dropping the step function $\epsilon(a - (x_j - x_i)) = \epsilon(a/t - z)$; this implies that $t \ll a$ (finite times).

The resummation is then possible, and the product

$$\left[1+\frac{tG(\theta, v_i)}{L-(N-1)b}\right]^{N-2}$$

is replaced by the exponential

$$\exp\{\rho' tG(\theta, v_i)\} = \exp\{it\rho'(\sin\theta)v_i - (1-\cos\theta)\rho' t\mu(v_i)\}.$$

When $b \neq 0$ (hard rods), $a - (p+1)b$ is still large for the values of the index which are of interest ($p \sim \sqrt{m}$) and we can drop the step function. When p increases, the integration interval becomes smaller, but it corresponds to values of p for which the contribution of the integrand is negligible. Operations (i) and (ii) are then allowed and the result still holds, i.e., one may obtain the results for the hard rod system through the substitution listed in (42).

APPENDIX A. ASYMPTOTIC BEHAVIOR OF THE CONTRIBUTION FOR LARGE TIMES

For large t, all the integrals which we have to consider can be rewritten as

$$\mathscr{I} = \int_{-\infty}^{+\infty} d\omega\, \omega^{\gamma} F(\omega) \int_{0}^{2\pi} \frac{d\theta}{2\pi} (1 - \cos\theta)^{\alpha} (i \sin\theta)^{\beta} \times \exp[i\rho t\omega \sin\theta - \rho t(1 - \cos\theta)\mu(\omega)] \tag{A.1}$$

where $F(\omega)$ is an *even* function of ω, independent of t, and $F(0) \neq 0$; α, β, γ are positive or zero integers, and $\gamma + \beta$ is even; otherwise $\mathscr{I} = 0$ by the symmetry $(\theta, \omega) \to (-\theta, -\omega)$.

Let us rewrite the integrand as $i^{\beta} \exp \psi(\theta, \omega)$, where

$$\psi(\omega, \theta) = \gamma \ln \omega + \ln F(\omega) + \alpha \ln(1 - \cos\theta) + \beta \ln \sin\theta + i\rho t\omega \sin\theta - \rho t(1 - \cos\theta)\mu(\omega) \tag{A.2}$$

The saddle-point equations read

$$\left.\frac{\partial\psi}{\partial\omega}\right|_{\theta} = \frac{\gamma}{\omega} + \frac{F'(\omega)}{F(\omega)} + i\rho t \sin\theta - \rho t(1 - \cos\theta)\mu'(\omega) = 0$$

$$\left.\frac{\partial\psi}{\partial\theta}\right|_{\omega} = \frac{\alpha \sin\theta}{1 - \cos\theta} + \beta \frac{\cos\theta}{\sin\theta} + i\rho t\omega \cos\theta - \rho t \sin\theta\, \mu(\omega) = 0 \tag{A.3}$$

and the second-order derivatives are

$$\frac{\partial^2\psi}{\partial\omega^2} = -\frac{\gamma}{\omega^2} + \frac{d}{d\omega}\left[\frac{F'(\omega)}{F(\omega)}\right] - \rho t(1 - \cos\theta)\mu''(\omega)$$

$$\frac{\partial^2\psi}{\partial\omega\, \partial\theta} = i\rho t \cos\theta - \rho t(\sin\theta)\mu'(\omega)$$

$$\frac{\partial^2\psi}{\partial\theta^2} = \alpha \frac{d}{d\theta}\left(\frac{\sin\theta}{1 - \cos\theta}\right) + \beta \frac{d}{d\theta}\left(\frac{\cos\theta}{\sin\theta}\right) - i\rho t\omega \sin\theta - \rho t \cos\theta\, \mu(\omega) \tag{A.4}$$

We shall denote (ω_0, θ_0) a couple of solutions of (A.3); for large t

$$\mathscr{I} \sim \sum_{\text{for all saddles}} \frac{2\pi}{|D|^{1/2}} i^{\beta} \exp \psi(\omega_0, \theta_0) \tag{A.5}$$

where D is the determinant of the second-order derivative

$$D \equiv \begin{vmatrix} \partial^2\psi/\partial\omega^2 & \partial^2\psi/\partial\omega\, \partial\theta \\ \partial^2\psi/\partial\theta\, \partial\omega & \partial^2\psi/\partial\theta^2 \end{vmatrix} \tag{A.6}$$

We shall consider several cases.

A1. $\alpha = \beta = 0$

Equations (A.3) reduce to

$$\gamma/\omega + F'(\omega)/F(\omega) + i\rho t \sin\theta - \rho t(1 - \cos\theta)\mu'(\omega) = 0$$
$$i\omega\cos\theta - \sin\theta\,\mu(\omega) = 0$$

If ω_0 is not small, θ_0 is not small either. It is then easy to see, using (A.5)–(A.6), that the contribution to $\mathscr{I}$ is exponentially decreasing with t; then it is surely negligible with respect to the inverse powers in which we are interested. Then, we shall look for solutions to the saddle point equations where ω_0 and θ_0 are small.

(i) If $\gamma = 0$, the only possible solution is $\omega_0 = 0$, $\theta_0 = 0$. We get $\psi(\omega_0, \theta_0) = \ln F(0)$ and

$$D = \begin{vmatrix} F''(0)/F(0) & i\rho t \\ i\rho t & -\rho t\mu(0) \end{vmatrix}$$

whence $\mathscr{I} \sim_{t\to\infty} t^{-1}$.

(ii) if $\gamma \neq 0$ (γ even), both ω_0 and θ_0 are small and to first order

$$i\omega_0 = \theta_0\mu(0), \qquad \gamma/\omega_0 + i\rho t\theta_0 = 0$$

whence

$$\theta_0 = \pm i[\gamma/\rho t\mu(0)]^{1/2}, \qquad \omega_0 = \pm[\gamma\mu(0)/\rho t]^{1/2}$$

There are two symmetric saddle points. At each saddle point

$$\exp[\psi(\theta_0, \omega_0)] \sim [\gamma\mu(0)/\rho t]^{\gamma/2} F(0)\exp(-\gamma/2)$$
$$D \simeq 2\rho^2 t^2$$

and the contribution of the saddle point is $\sim (t\rho)^{-1-\gamma/2}$.

A2. $\alpha + \beta > 0$

Again, if both θ_0 and ω_0 are finite, the corresponding saddle points give a contribution decreasing exponentially at large t. We come now to the other saddle points.

(i) $\gamma = 0$. From Eqs. (A.3), there is no saddle point where ω_0 and θ_0 are both small or when ω_0 is small and θ_0 finite. We investigate now the opposite situation, i.e., θ_0 small and ω_0 finite. To first order, we have

$$(2\alpha + \beta)/\theta_0 + i\rho t\omega_0 = 0, \qquad F'(\omega_0)/F(\omega_0) + i\rho t\theta_0 = 0$$

whence we obtain the implicit equation for ω_0

$$F'(\omega_0)/F(\omega_0) = (2\alpha + \beta)/\omega_0$$

and $\theta_0 \sim i(2\alpha + \beta)/t\rho\omega_0$ is of order t^{-1}. As $F(\omega)$ is an even function, there are generally two symmetric saddle points. We have

$$\exp \psi(\omega_0, \theta_0) \sim \frac{F(\omega_0)}{\omega_0^{2\alpha+\beta}} \frac{(-)^{\alpha+\beta}}{2^\alpha} \{\exp[-(2\alpha + \beta)]\} \left(\frac{2\alpha + \beta}{\rho t}\right)^{2\alpha+\beta}$$

$$D \sim (\rho t)^2 \left\{ \frac{\omega^2(d/d\omega)(F'/F)|_{\omega=\omega_0}}{2\alpha + \beta} + 1 \right\}$$

and the asymptotic contribution of each saddle point is like $\sim (t\rho)^{-1-2\alpha-\beta}$.

(ii) $\gamma \neq 0$. Starting from Eqs. (A.3), it is easy to verify that there are no saddle points when θ_0 is finite and ω_0 small. There is again a solution for $\theta_0 \sim t^{-1}$ and ω_0 small and the above results are unchanged. There are supplementary solutions when both θ_0 and ω_0 are small.

To first order, Eqs. (3) reduce to

$$\gamma/\omega_0 + i\rho t\theta_0 = 0, \qquad (2\alpha + \beta)/\theta_0 + i\rho t\omega_0 - \rho t\theta_0\mu(0) = 0 \qquad \text{(A.7)}$$

when $2\alpha + \beta \neq \gamma$ we get $\theta_0, \omega_0 \sim t^{-1/2}$. More precisely

$$\theta_0 = \pm[(2\alpha + \beta - \gamma)/\rho t\mu(0)]^{1/2}, \qquad \omega_0 = \pm i\gamma[\mu(0)/\rho t(2\alpha + \beta - \gamma)]^{1/2}$$

and

$$\exp \psi(\omega_0, \theta_0) \sim (\rho t)^{-\alpha-(\beta+\gamma)/2}, \qquad D \sim -(\rho t)^2(2\alpha + \beta - \gamma)/\gamma$$

whence the contribution at the saddle is $\sim_{t\to\infty} (t\rho)^{-1-\alpha-(\beta+\gamma)/2}$.

When $2\alpha + \beta = \gamma$, the first-order equations (A.7) are no longer sufficient. We rewrite Eqs. (A.3) more carefully, keeping the second-order terms:

$$\gamma + i\rho t\omega_0\theta_0 + \omega_0^2F''(0)/F(0) - \tfrac{1}{6}i\rho t\omega_0\theta_0^3 - \tfrac{1}{2}\omega_0^2\rho t\theta_0^2\mu''(0) + \cdots = 0$$

$$2\alpha + \beta + i\rho t\omega_0\theta_0 - \tfrac{1}{6}(\alpha + 2\beta)\theta_0^2 - \tfrac{1}{6}i\rho t\omega_0^3 - \rho t\theta_0^2\mu(0) + \tfrac{1}{6}\rho t\theta_0^4\mu(0) - \tfrac{1}{2}\rho t\theta_0^2\omega_0^2\mu''(0) + \cdots = 0$$

whence $\theta_0 \ll \omega_0$ and $\theta_0^2t\rho\mu(0) + \omega_0^2[F''(0)/F(0)] = 0$, and $\theta_0 \sim (t\rho)^{-3/4}$ and $\omega_0 \sim (t\rho)^{-1/4}$; nevertheless, we recover the same asymptotic behavior as above

$$\mathscr{I} \sim t^{-1-\alpha-(\beta+\gamma)/2}$$

The results of this discussion are given in Table I.

Remark. We have concentrated our attention upon the contribution to $\delta\psi(t)$ behaving like t^{-1} for large times, as they could give a logarithmically divergent contribution to the diffusion coefficient. As the various contributions to this t^{-1} term just cancel, the knowledge of the asymptotic behavior of $\delta\psi(t)$ requires an expansion to the next order in the saddle point method.

Table I. Asymptotic Behavior for Large Times of Each Saddle Point for Integrals Given by Eq. (A1)

Type of integrand (values of α, β, γ)	Nature of the saddle points	Asymptotic behavior of $\mathscr{I}$ for each saddle point when $t \to \infty$
$\alpha = \beta = 0, \gamma = 0$	(1) ω_0, θ_0 finite	Exponential decreasing
	(2) $\omega_0 = 0, \theta_0 = 0$	$(\rho t)^{-1}$
$\alpha = \beta = 0, \gamma \neq 0$	(1) ω_0, θ_0 finite	Exponential decreasing
	(2) $\omega_0, \theta_0 \sim t^{-1/2}$	$(\rho t)^{-1-\gamma/2}$
$\alpha + \beta > 0, \gamma = 0$	(1) ω_0, θ_0 finite	Exponential decreasing
	(2) ω_0 finite, $\theta_0 \sim t^{-1}$	$(\rho t)^{-1-2\alpha-\beta}$
$\alpha + \beta > 0, \gamma \neq 0$[a]	(1) ω_0, θ_0 finite	Exponential decreasing
	(2) ω_0 finite, $\theta_0 \sim t^{-1}$	$(\rho t)^{-1-2\alpha-\beta}$
	(3a) $2\alpha + \beta \neq \gamma$: $\omega_0 \sim t^{-1/2}, \theta_0 \sim t^{-1/2}$	$(\rho t)^{-1-\alpha-(\beta+\gamma)/2}$
	(3b) $2\alpha + \beta = \gamma$: $\omega_0 \sim t^{-1/4}, \theta_0 \sim t^{-3/4}$	$(\rho t)^{-1-\alpha-(\beta+\gamma)/2}$

[a] If $\alpha = \beta = \gamma = 1$, then $\mathscr{I} \sim t^{-4}$ (cf. Appendix A).

This should yield very intricate calculations, and we thought that it was sufficient to notice that, due to the cancellation of the t^{-1} terms [Eq. (40)]

$$\delta\psi(t) \underset{t\to\infty}{\simeq} (a/t^2)[C \ln (a/t) + D]$$

Of course, it is possible that C just vanishes, due to some cancellation. However, the main point here is that $\delta\psi(t)$ decreases at least as rapidly as (and perhaps more rapidly than) $(\ln t)/t^2$ at $t \to \infty$, so that its time integral (i.e., the first perturbation in the diffusion coefficient) is well definite.

There are three contributions to $\delta\psi(t)$ decreasing like t^{-1}: U_2 (Section 3) and V_5 and V_7 (Section 4). For U_2, there is only one saddle point, so no compensation appears and it surely behaves like t^{-1}. For V_5, when integrating over θ, we see that it behaves like t^{-1} and exactly cancels the divergent part of U_2.

For large times, V_7 behaves like

$$V_7 \underset{t\to\infty}{\sim} \int_{-\infty}^{+\infty} d\omega\, \omega h_0(\omega) \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^2 i \sin\theta (1 - \cos\theta) \times \exp[i\rho t\omega \sin\theta - \rho t(1-\cos\theta)\mu(\omega)]$$

By integrating over the variable θ, then looking for small ω, we find that the t^{-1} terms vanish. It is a little complicated to prove this point in this way and we prefer to show that the integral

$$\lim_{\epsilon\to 0} \int_0^\infty V_7(t)e^{-\epsilon t}$$

exists, i.e., that

$$V_7(\epsilon) \equiv \int_{-\infty}^{+\infty} d\omega\, \omega h_0(\omega) \int_0^{2\pi} \frac{d\theta}{2\pi} \frac{i(\sin\theta)(1-\cos\theta)}{[\epsilon + \rho\mu(\omega)(1-\cos\theta) - i\rho\omega\sin\theta]^3}$$

exists for small ϵ.

Setting $u = \tan(\theta/2)$, we get

$$V_7(\epsilon) = \frac{8}{\pi}\int_{-\infty}^{+\infty} d\omega\, \omega h_0(\omega) \int_{-\infty}^{+\infty} du \frac{iu^3}{\{u^2[\epsilon + 2\rho\mu(\omega)] - 2i\rho\omega u + \epsilon\}^3}$$

$$= \frac{8}{\pi}\int_{-\infty}^{+\infty} \frac{d\omega\, \omega h_0(\omega)}{[\epsilon + 2\rho\mu(\omega)]^3} \int_{-\infty}^{+\infty} \frac{i\, du\, u^3}{[u^2 - 2iA(\omega)u + B^2(\omega)]^3}$$

with

$$A(\omega) \equiv \rho\omega/[\epsilon + 2\rho\mu(\omega)], \qquad B^2(\omega) \equiv \epsilon/[\epsilon + 2\rho\mu(\omega)]$$

Thus

$$V_7(\epsilon) = -16\int_{-\infty}^{+\infty} \frac{d\omega\, \omega h_0(\omega)}{[\epsilon + 2\rho\mu(\omega)]^3}$$

$$\times \text{ Residue } \frac{u^3}{[u^2 - 2iA(\omega) - B^2(\omega)]^3}\bigg|_{u = iA(\omega) + i[A^2(\omega) + B^2(\omega)]^{1/2}}$$

$$= -\frac{3}{2}\int_{-\infty}^{+\infty} d\omega \frac{\rho\epsilon\omega^2 h_0(\omega)}{[\epsilon^2 + 2\rho\epsilon\mu(\omega) + \rho^2\omega^2]^{5/2}}$$

Setting $\epsilon = 0$ in the integrand, we get an indeterminate result. Defining the new integration variable x by

$$\rho\omega = [2\rho\mu(0)\epsilon]^{1/2}x$$

we get

$$V_7(\epsilon) \underset{\epsilon\to 0}{\simeq} -\frac{3}{4}\frac{h_0(0)}{\rho^3\mu(0)}\int_{-\infty}^{+\infty} \frac{dx\, x^2}{(1+x^2)^{5/2}}$$

which exists.

APPENDIX B

As an example, we calculate here the contribution

$$T_2 = \tfrac{1}{2}(N-1)(N-2)\langle v_1{}^2[\delta U_{23} - \langle\delta U_{23}\rangle]\, \delta_{\sigma_1(t),\sigma_1(0)}\rangle$$

The beginning of the calculation has been sketched in the text. We rewrite (19) as

$$T_2 = \frac{1}{2}\eta \int_{-\infty}^{+\infty} dv_1\, v_1{}^2 h_0(v_1) \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^2$$
$$\times \exp\{it\rho(\sin\theta)v_1 - t\rho(1 - \cos\theta)\mu(v_1)\}$$
$$\times \iint_{-\infty}^{+\infty} dx\, dy\, \epsilon\left(\frac{a}{t} - |x - y|\right)\phi_{1,\theta}(y)\ \phi_{1,\theta}(x) \qquad \text{(B.1)}$$

where we have set $x = (r_1 - r_2)/t$, $y = (r_1 - r_3)/t$, the exponential arises in a way similar to that of Eq. (12), and

$$1 + \phi_{1,\theta}(x) = \{\exp[-i\theta\epsilon(x)]\} \int_{-\infty}^{+\infty} dv_2\, h_0(v_2) \exp[i\theta\epsilon(x + v_1 - v_2)]$$
$$= 1 + \frac{\cos\theta - 1}{2} + i(\sin\theta)\,\mathrm{Erf}(x + v_1)$$
$$- \frac{i\sin\theta}{2}\,\mathrm{sg}\, x + (1 - \cos\theta)\,\mathrm{sg}\, x\, \mathrm{Erf}(x + v_1)$$

or, in an alternative manner

$$\phi_{1,\theta}(x) = [(1 - \cos\theta)\,\mathrm{sg}\, x + i\sin\theta][\mathrm{Erf}(x + v_1) - \tfrac{1}{2}\,\mathrm{sg}\, x] \qquad \text{(B.2)}$$

where $\mathrm{sg}\, x = x/|x|$ and $\mathrm{Erf}(x)$ is defined in Eq. (11c).

Easy, but tedious manipulations give the final result

$$T_2 = \frac{1}{2}\eta \int_{-\infty}^{+\infty} dv_1\, v_1{}^2 h_0(v_1) \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^2$$
$$\times \exp\{it\rho(\sin\theta)v_1 - t\rho(1 - \cos\theta)\mu(v_1)\}$$
$$\times \{(1 - \cos\theta)^2[f_1(v_1) + f_2(v_1) + f_3(v_1) + f_1(-v_1) + f_2(-v_1) + f_3(-v_1)$$
$$+ i(\sin\theta)(1 - \cos\theta)[f_1(v_1) + f_2(v_1) + f_3(v_1) - f_1(-v_1) - f_2(-v_1) - f_3(-v_1]$$
$$- (1 - \cos\theta)[f_1(v_1) + 2f_3(v_1) + f_1(-v_1) + 2f_3(+v_1)]\} \qquad \text{(B.3)}$$

with

$$f_1(v_1) = \int_0^{+\infty} dx \left[\mathrm{Erf}(x + v_1) - \frac{1}{2}\right]\left[\mu\left(x + v_1 + \frac{a}{t}\right) - \mu\left(x + v_1 - \frac{a}{t}\right) - \frac{2a}{t}\right]$$

$$f_2(v_1) = \int_0^{a/t} dx \left[\mathrm{Erf}(x + v_1) - \frac{1}{2}\right]\left[\mu\left(x + v_1 - \frac{a}{t}\right) - \mu(v_1)\right]$$

$$f_3(v_1) = \int_0^{a/t} dx \left[\mathrm{Erf}(x + v_1) - \frac{1}{2}\right]\left(\frac{a}{t} - x\right)$$

and a supplementary integration, over the angle θ, can be performed by using the relation

$$\int_0^{2\pi} \frac{d\theta}{2\pi} \exp\{it\rho(\sin\theta)x - t\rho(1 - \cos\theta)\mu(x)\}$$
$$= I_0(\rho t[\mu^2(x) - x^2]^{1/2}) \exp[-\rho t\mu(x)]$$

Here, I_0 denotes the modified Bessel function of index 0. The integrand is now a *real* function in terms of v_1 and x only. It is this latter form which we took up for numerical calculations.

Let us make a few more remarks:

(i) Consider the derivative of $T_2(t)$ for $t = 0$. The step function $\epsilon(a/t - |x - y|)$ may be replaced by one, but as t appears at least under the form $(\rho t)^2 \exp\{\rho t(\cdots)\}$ in the integrand, the slope is zero at the origin.

(ii) When $a \to \infty$, again $\epsilon(a/t - |x - y|)$ can be replaced by one and T_2 goes to a limit independent of a.

(iii) When $a = 0$, $T_2 = 0$.

Let us now list the five remaining contributions. The calculation of T_6 is very much similar to that of T_2. We get

$$\begin{aligned} T_6 = -\eta \int_{-\infty}^{+\infty} d\omega\, h_0^2(\omega) \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^3 (1 - \cos\theta) \\ \times \exp\{it\rho(\sin\theta)\omega - t\rho(1 - \cos\theta)\mu(\omega)\} \\ \times \{(1 - \cos\theta)^2[f_1(\omega) + f_2(\omega) + f_3(\omega) + f_1(-\omega) + f_2(-\omega) + f_3(-\omega)] \\ + i(\sin\theta)(1 - \cos\theta)[f_1(\omega) + f_2(\omega) + f_3(\omega) - f_1(-\omega) - f_2(-\omega) - f_3(-\omega)] \\ -(1 - \cos\theta)[f_1(\omega) + 2f_3(\omega) + f_1(-\omega) + 2f_3(-\omega)]\} \end{aligned} \tag{B.4a}$$

with the same definitions as above for the functions f_1, f_2, and f_3. The other terms are simple; we get

$$\begin{aligned} T_1 = \frac{\eta}{2} \int_{-\infty}^{+\infty} dv_1\, v_1^2 h_0(v_1) \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t) \\ \times \exp\{it\rho(\sin\theta)v_1 - t\rho(1 - \cos\theta)\mu(v_1)\} \\ \times \left\{(1 - \cos\theta)\left[\mu\left(v_1 + \frac{a}{t}\right) + \mu\left(v_1 - \frac{a}{t}\right) - 2\mu(v_1) - \frac{2a}{t}\right]\right. \\ \left. + i(\sin\theta)\left[\mu\left(v_1 + \frac{a}{t}\right) - \mu\left(v_1 - \frac{a}{t}\right)\right]\right\} \end{aligned} \tag{B.4b}$$

$$\begin{aligned} T_3 = \eta \int_{-\infty}^{+\infty} d\omega\, h_0^2(\omega) \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t) \\ \times \exp\{it\rho(\sin\theta)\omega - t\rho(1 - \cos\theta)\mu(\omega)\} \\ \times \left\{(1 - \cos\theta)\left[h_0\left(\omega + \frac{a}{t}\right) + h_0\left(\omega - \frac{a}{t}\right) - 2h_0(\omega)\right]\right. \\ \left. + i(\sin\theta)\left[h_0\left(\omega + \frac{a}{t}\right) - h_0\left(\omega - \frac{a}{t}\right)\right]\right\} \end{aligned} \tag{B.4c}$$

$$T_4 = -\eta \int_{-\infty}^{+\infty} d\omega\, h_0^2(\omega) \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^2 (1 - \cos\theta)$$
$$\times \exp\{it\rho(\sin\theta)\omega - t\rho(1-\cos\theta)\mu(\omega)\}$$
$$\times \left\{(1-\cos\theta)\left[\mu\left(\omega + \frac{a}{t}\right) + \mu\left(\omega - \frac{a}{t}\right) - 2\mu(\omega) - \frac{2a}{t}\right]\right.$$
$$\left. + i(\sin\theta)\left[\mu\left(\omega + \frac{a}{t}\right) - \mu\left(\omega - \frac{a}{t}\right)\right]\right\}$$
$$T_5 = 2\eta \int_{-\infty}^{+\infty} d\omega\, h_0(\omega) \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^2 (1-\cos\theta)$$
$$\times \exp\{it\rho(\sin\theta)\omega - t\rho(1-\cos\theta)\mu(\omega)\}$$
$$\times \{(1-\cos\theta)[g_1(\omega) + g_2(\omega) + g_1(-\omega) + g_2(-\omega)]$$
$$+ i(\sin\theta)[g_1(\omega) + g_2(\omega) - g_1(-\omega) - g_2(-\omega)]$$
$$- [g_1(\omega) + g_1(-\omega)]\} \tag{B.4d}$$

with

$$g_1(\omega) = \int_0^\infty dy \left[\mathrm{Erf}(\omega + y) - \frac{1}{2}\right]\left[h_0\left(\omega + y + \frac{a}{t}\right) - h_0\left(\omega + y - \frac{a}{t}\right)\right]$$
$$g_2(\omega) = \int_0^{a/t} dy \left[\mathrm{Erf}(\omega + y) - \frac{1}{2}\right]\left[h_0\left(\omega + y - \frac{a}{t}\right) - h_0(\omega)\right]$$

In all the above expressions, $h_0(x)$, $\mu(x)$, and $\mathrm{Erf}(x)$ denote the functions defined by Eqs. (10) and (11).

APPENDIX C. CALCULATION OF U_1 AND FINAL EXPRESSION FOR $\delta_2\psi(t)$

C1. Calculation of U_1

We start from

$$U_1 = (N-1)\langle v_1\, \delta v_1^{(2)}\, \delta_{\sigma_1(t),\sigma_1(0)}\rangle$$
$$= \rho \int_{-\infty}^{+\infty} dv_1 \int_{-\infty}^{+\infty} dv_2\, v_1 h_0(v_1) h_0(v_2) \int_{-\infty}^{+\infty} d(r_1 - r_2)$$
$$\times \int_0^{2\pi} \frac{d\theta}{2\pi} \exp\{i\theta[\epsilon(r_1 - r_2 + v_1 t - v_2 t) - \epsilon(r_1 - r_2)]\}\, \delta v_1^{(2)}$$
$$\times \prod_{l\geq 3} \int_{-\infty}^{+\infty} dv_l\, h_0(v_l) \int_0^L \frac{dr_l}{L}$$
$$\times \exp\{i\theta[\epsilon(r_1 - r_l + v_1 t - v_l t) - \epsilon(r_1 - r_l)]\}$$

$$= \int_{-\infty}^{+\infty} v_1 h_0(v_1)\, dv_1 \int_{-\infty}^{+\infty} h_0(v_2)\, dv_2 \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)$$
$$\times \exp\{i\theta[\epsilon(r_1 - r_2 + v_1 t - v_2 t) - \epsilon(r_1 - r_2)]\}$$
$$\times \exp\{it\rho(\sin\theta)v_1 - t\rho(1 - \cos\theta)\mu(v_1)\}$$
$$\times \int_{-L/2}^{L/2} \delta v\left(\frac{r_1 - r_2}{t}, v_1 - v_2\right) d(r_1 - r_2) \tag{C.1}$$

where the second exponential is obtained by the same arguments as in Appendix B and

$$\delta v\left(\frac{r_1 - r_2}{t}, v_1 - v_2\right) = \delta v_1^{(2)}$$

is given in (24)–(28).

Setting now $x = (r_1 - r_2)/t$ and $\omega = v_1 - v_2$, we rewrite U_1 as

$$U_1 = \int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \int_0^{2\pi} \frac{d\theta}{2\pi} \rho t$$
$$\times \exp[i\rho t v_1 \sin\theta - \rho t(1 - \cos\theta)\mu(v_1)]$$
$$\times \int_{-\infty}^{+\infty} dx \exp\{i\theta[\epsilon(x + \omega) - \epsilon(x)]\} \int_{-\infty}^{+\infty} d\omega\, h_0(v_1 - \omega)\, \delta v(x,\omega)$$

For the present, we shall be concerned with the last two integrations. When the particle 1 is not in the potential of particle 2 for $t = 0$ (i.e., when $|x| > a/t$) it can be rewritten, using Eq. (22), as

$$\frac{1}{2}\int_{-\infty}^{+\infty} d\omega\, h_0(v_1 - \omega)[\mathrm{sg}\,\omega(\omega^2 - 4\eta)^{1/2} - \omega] \int_{-\infty}^{+\infty} dx\, \epsilon(-x\omega)\epsilon\left(|x| - \frac{a}{t}\right)$$
$$\times\, \epsilon\left(|\omega| - |x| + \frac{a}{t}\right)\epsilon\left(|x| - |\omega| - \frac{a}{t} + \frac{2a|\omega|}{t(\omega^2 - 4\eta)^{1/2}}\right)$$
$$\times \exp[i\theta\epsilon(x + \omega) - i\theta\epsilon(x)]$$

or

$$\frac{1}{2}\int_0^{\infty} d\omega\, [(\omega^2 - 4\eta)^{1/2} - \omega] \int_{-\infty}^{+a/t} dx$$
$$\times\, \epsilon\left(-\omega - x - \frac{a}{t} + \frac{2a\omega}{t(\omega^2 - 4\eta)^{1/2}}\right)\epsilon\left(\omega + x + \frac{a}{t}\right)$$
$$\times\, [e^{i\theta\epsilon(x+\omega)} h_0(v_1 - \omega) - e^{-i\theta} e^{i\theta\epsilon(-x-\omega)} h_0(v_1 + \omega)]$$

where we have restricted the integration domain to $\omega \geqslant 0$ by appropriate changes of variables. Expressing the step function explicitly and setting $z = \omega + x$, we get

$$\frac{1}{2}\int_0^{[4\eta+(2a/t)^2]^{1/2}} d\omega\, [(\omega^2 - 4\eta)^{1/2} - \omega]$$
$$\times \int_{-a/t}^{\omega - a/t} dz\, [e^{i\theta\epsilon(z)} h_0(v_1 - \omega) - e^{-i\theta} e^{i\theta\epsilon(-z)} h_0(v_1 + \omega)]$$
$$+ \frac{1}{2}\int_{[4\eta+(2a/t)^2]^{1/2}}^{\infty} d\omega\, [(\omega^2 - 4\eta)^{1/2} - \omega] \int_{-a/t}^{[2a\omega/t(\omega^2-4\eta)^{1/2}]-a/t} dz$$
$$\times\, [e^{i\theta\epsilon(z)} h_0(v_1 - \omega) - e^{-i\theta} e^{i\theta\epsilon(-z)} h_0(v_1 + \omega)] \qquad \text{(C.2)}$$

Except when $(a/t)^2 \leqslant |\eta|$ and for small velocities ($\omega^2 \sim 4|\eta|$), we get

$$\text{sg}\, \omega(\omega^2 - 4\eta)^{1/2} - \omega \sim -(2\eta/\omega)$$

To first order in η, the first contribution to U_1 simplifies to

$$-\eta \int_0^{2a/t} \frac{d\omega}{\omega} \int_{-a/t}^{\omega - a/t} dz\, [e^{i\theta\epsilon(z)} h_0(v_1 - \omega) - e^{-i\theta} e^{i\theta\epsilon(-z)} h_0(v_1 + \omega)]$$
$$- \eta \int_{2a/t}^{\infty} \frac{d\omega}{\omega} \int_{-a/t}^{a/t} dz\, [e^{i\theta\epsilon(z)} h_0(v_1 - \omega) - e^{-i\theta} e^{i\theta\epsilon(-z)} h_0(v_1 + \omega)]$$
$$= -\eta \int_0^{a/t} d\omega\, [h_0(v_1 - \omega) - h_0(v_1 + \omega)]$$
$$- \frac{\eta a}{t} \int_{a/t}^{\infty} \frac{d\omega}{\omega} [h_0(v_1 - \omega) - h_0(v_1 + \omega)]$$
$$- \eta \int_{a/t}^{2a/t} \frac{d\omega}{\omega} \left(\omega - \frac{a}{t}\right) \{(\cos\theta)[h_0(v_1 - \omega) - h_0(v_1 + \omega)]$$
$$+ i(\sin\theta)[h_0(v_1 + \omega) + h_0(v_1 - \omega)]\}$$
$$- \frac{\eta a}{t} \int_{2a/t}^{\infty} \frac{d\omega}{\omega} \{(\cos\theta)[h_0(v_1 - \omega) - h_0(v_1 + \omega)]$$
$$+ i(\sin\theta)[h_0(v_1 + \omega) + h_0(v_1 - \omega)]\}$$

and for the second contribution, using definition (26), we get $[a/t > (4|\eta|)^{1/2}]$

$$\frac{1}{2}\int_{a/t}^{\infty} d\omega\, [(\omega^2 + 4\eta)^{1/2} - \omega]$$
$$\times \int_{\sup(a/t,\, \omega - a/t)}^{\infty} dz\, \{(\cos\theta)[h_0(\omega - v_1) - h_0(\omega + v_1)] + i(\sin\theta)$$
$$\times\, [h_0(v_1 + \omega) + h_0(v_1 - \omega)]\}$$
$$+ \tfrac{1}{2}\int_{a/t}^{\infty} d\omega\, [(\omega^2 + 4\eta)^{1/2} - \omega] \int_{\omega}^{\omega + a/t} dz\, \{(\cos\theta)[h_0(\omega - v_1)$$
$$- h_0(v_1 + \omega)] - i(\sin\theta)[h_0(\omega - v_1) + h_0(\omega + v_1)]\}$$
$$+ \tfrac{1}{2}\int_{(4|\eta|)^{1/2}}^{a/t} d\omega\, [(\omega^2 + 4\eta)^{1/2} - \omega]$$
$$\times \int_{a/t}^{\omega + a/t} dz\, \{(\cos\theta)[h_0(\omega - v_1) - h_0(\omega + v_1)]$$
$$- i(\sin\theta)[h_0(\omega - v_1) + h_0(\omega + v_1)]\} \qquad \text{(C.3)}$$

Except for long times and small velocities again, we may replace $\operatorname{sg}\omega(\omega^2 + 4\eta)^{1/2} - \omega$ by $2\eta/\omega$ and the integration limit $(4|\eta|)^{1/2}$ by 0. We obtain the final result for U_1:

$$
\begin{aligned}
U_1 = {} & -\frac{\eta}{2}\int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \\
& \times \int_0^{2\pi} \frac{d\theta}{2\pi}\, \rho t \exp\{i\rho t v_1 \sin\theta - \rho t(1 - \cos\theta)\mu(v_1)\} \\
& \times \left\{(1 - \cos\theta)\int_0^{a/t} d\omega\, [h_0(\omega - v_1) - h_0(\omega + v_1)]\right. \\
& + i(\sin\theta)\int_0^{a/t} d\omega\, [h_0(\omega - v_1) + h_0(\omega + v_1)] \\
& + (1 - \cos\theta)\frac{a}{t}\int_{a/t}^{\infty} \frac{d\omega}{\omega}[h_0(\omega - v_1) - h_0(\omega + v_1)] \\
& \left. + \frac{ia}{t}(\sin\theta)\int_{a/t}^{\infty} \frac{d\omega}{\omega}[h_0(\omega - v_1) + h_0(\omega + v_1)]\right\}
\end{aligned}
$$

We have not justified here the way we have "linearized" with respect to η to get the results. This point is considered both in the text and in Appendix D.

C2. Limiting Cases (with Linearized Formulas)

(i) Long-time behavior. From the results of Appendix A quoted in Table I, the predominant contribution to U_1 at large times is

$$
\begin{aligned}
U_1 \underset{t\to\infty}{\sim} {} & -\eta\int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \\
& \times \int_0^{2\pi} \frac{d\theta}{2\pi}\, i\rho t(\sin\theta)\exp[i\rho t v_1 \sin\theta - \rho t(1 - \cos\theta)\mu(v_1)] \\
& \times \left\{\int_0^{a/t} d\omega\, [h_0(\omega - v_1) + h_0(\omega + v_1)]\right. \\
& \left. + \frac{a}{t}\int_{a/t}^{\infty} \frac{d\omega}{\omega}[h_0(\omega - v_1) + h_0(\omega + v_1)]\right\} \\
\sim {} & -\eta\rho a\int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \\
& \times \int_0^{2\pi} \frac{d\theta}{2\pi}\, i(\sin\theta)\exp[i\rho t v_1 \sin\theta - \rho t(1 - \cos\theta)\mu(v_1)] \\
& \times \left\{-2h_0(v_1)\frac{\ln \rho a}{\rho t} + 2h_0(v_1)\right. \\
& \left. + \mathrm{FP}\int_0^{\infty} \frac{d\omega}{\omega}[h_0(\omega + v_1) + h_0(\omega - v_1)]\right\}
\end{aligned}
$$

where the FP $\int$ symbol denotes the "finite part" of the integral. This leads to an asymptotic behavior for U_1 of the form

$$[\rho a/(\rho t)^2][A_1 \ln(\rho a/\rho t) + B_1] \qquad (A_1, B_1 \text{ constants})$$

which is different from the behavior encountered in Section 3. As an example, let us calculate A_1. We have

$$\begin{aligned} A_1 \frac{\rho a}{(\rho t)^2} &\sim 2\eta\rho a \int_{-\infty}^{+\infty} dv_1\, v_1 h_0^2(v_1) \\ &\quad \times \int_0^{2\pi} \frac{d\theta}{2\pi}\, i(\sin\theta) \exp[i\rho t(\sin\theta)v_1 - \rho t(1-\cos\theta)\mu(v_1)] \\ &= -2\eta\rho a \int_{-\infty}^{+\infty} dv_1 \frac{v_1^2}{[\mu^2(v_1) - v_1^2]^{1/2}} \\ &\quad \times h_0^2(v_1) I_0'(\rho t[\mu^2(v_1) - v_1^2]^{1/2}) \exp[-\rho t\mu(v_1)] \end{aligned}$$

where $I_0(x)$ is the modified Bessel function and $I_0'(x)$ is its derivative; we calculate the above integral near $v_1 = 0$ using the asymptotic expansion $I_0(x) \sim [1/(2\pi x)^{1/2}] \exp x$ and rewrite

$$\frac{A_1\rho a}{(\rho t)^2} \sim \frac{-2\eta\rho a}{[2\pi\mu(0)]^{3/2}} (\rho t)^{-1/2} \int_{-\infty}^{+\infty} dv_1\, v_1^2 \exp\left[-\frac{\rho t v_1^2}{2\mu(0)}\right]$$

whence $A_1 \sim -\eta/\pi$.

(ii) In the opposite limit $t \to 0$, we get

$$\begin{aligned} U_1 \underset{t=0}{\sim} & -\eta \int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \\ & \times \int_0^{2\pi} \frac{d\theta}{2\pi} \rho t \Big\{ (1-\cos\theta) \int_0^{\infty} d\omega\, [h_0(\omega - v_1) - h_0(\omega + v_1)] \\ & + i(\sin\theta) \int_0^{\infty} d\omega\, [h_0(\omega - v_1) + h_0(\omega + v_1)] \Big\} \\ = & -2\eta \int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \operatorname{Erf}(v_1)\, \rho t \end{aligned}$$

whence $U_1|_{t=0} = 0$ and $(dU_1/dt)|_{t=0} = -\eta/\sqrt{\pi}$, which does not depend on a.

(iii) When $a = 0$, then $U_1 = 0$, for obvious reasons, although when $a \to \infty$,

$$\begin{aligned} U_1 \underset{a\to\infty}{\sim} & -\eta \int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \\ & \times \int_0^{2\pi} \frac{d\theta}{2\pi} \rho t \exp[i\rho t(\sin\theta)v_1 - \rho t(1-\cos\theta)\mu(v_1)] \\ & \times [2(1-\cos\theta)\operatorname{Erf}(v_1) + i\sin\theta] \end{aligned}$$

which does not depend on a.

C3. Expression of the Two Remaining Terms

Once linearized, the expression for U_3 is

$$U_3 = -\frac{\eta}{2}\int_{-\infty}^{+\infty} d\omega\, h_0(\omega)$$

$$\times \int_0^{2\pi} \frac{d\theta}{2\pi}(\rho t)^2 \exp[i\rho t(\sin\theta)\omega - \rho t(1-\cos\theta)\mu(\omega)]$$

$$\times \left(\int_0^{a/t} \frac{dv}{v} h_0\left(\frac{v}{\sqrt{2}}\right)\right.$$

$$\times \{(1-\cos\theta)^2[2v\sqrt{2} + \mu(z_2) + \mu(z_4) - \mu(z_1) - \mu(z_3)]$$

$$+ (i\sin\theta)^2[2v\sqrt{2} + \mu(z_2) + \mu(z_4) - \mu(z_1) - \mu(z_3)]$$

$$+ 2i(\sin\theta)(1-\cos\theta)[\mu(z_2) + \mu(z_3) - \mu(z_1) - \mu(z_4)]\}$$

$$+ \int_{a/t}^{\infty} \frac{dv}{v} h_0\left(\frac{v}{\sqrt{2}}\right)$$

$$\times \left\{(1-\cos\theta)^2\left[\frac{2a\sqrt{2}}{t} + 2\mu\left(\frac{v}{\sqrt{2}} + \omega\sqrt{2}\right)\right.\right.$$

$$\left. + 2\mu\left(\frac{v}{\sqrt{2}} - \omega\sqrt{2}\right) - \sum_{i=1}^{4}\mu(z_i)\right]$$

$$+ (i\sin\theta)^2\left[\frac{2a\sqrt{2}}{t} + \mu(z_2) + \mu(z_4) - \mu(z_1) - \mu(z_3)\right]$$

$$+ 2i(\sin\theta)(1-\cos\theta)\left[\mu\left(\frac{v}{\sqrt{2}} + \omega\sqrt{2}\right)\right.$$

$$\left.\left.\left. - \mu\left(\frac{v}{\sqrt{2}} - \omega\sqrt{2}\right) + \mu(z_3) + \mu(z_4)\right]\right\}\right)$$

where $\mu(x)$ $[=2\Phi(x) = 2h_0(x) + 2x\,\mathrm{Erf}(x)]$ is again the frequency collision and

$$z_1 = \sqrt{2}\left(\frac{a}{t} + \frac{v}{2} + \omega\right), \qquad z_2 = \sqrt{2}\left(\frac{a}{t} - \frac{v}{2} + \omega\right)$$

$$z_3 = \sqrt{2}\left(\frac{a}{t} + \frac{v}{2} - \omega\right), \qquad z_4 = \sqrt{2}\left(\frac{a}{t} - \frac{v}{2} - \omega\right)$$

The last term U_2 reads

$$U_2 = -\eta \int_{-\infty}^{+\infty} d\omega \int_0^{2\pi} \frac{d\theta}{2\pi} \rho t$$

$$\times \exp[i\rho t\omega \sin\theta - \rho t(1-\cos\theta)\mu(\omega)]\Big\{(1-\cos\theta)\int_{a/t}^{\infty} \frac{du}{u}$$

$$\times \Big[h_0\Big(\omega + \frac{a}{t}\Big)h_0\Big(\omega + \frac{a}{t} - u\Big) + h_0\Big(\omega - \frac{a}{t}\Big)h_0\Big(\omega - \frac{a}{t} + u\Big)$$

$$- h_0(\omega)h_0(\omega + u) - h_0(\omega)h_0(\omega - u)\Big]$$

$$+ i\sin\theta \int_{a/t}^{\infty} \frac{du}{u}\Big[h_0\Big(\omega + \frac{a}{t}\Big)h_0\Big(\omega + \frac{a}{t} - u\Big) - h_0\Big(\omega - \frac{a}{t} - u\Big)$$

$$\times h_0\Big(\omega - \frac{a}{t}\Big) + h_0(\omega)h_0(\omega - u) - h_0(\omega)h_0(\omega + u)]$$

$$+ \cos\theta \int_0^{\infty} \frac{du}{u}\Big[h_0\Big(\omega + \frac{a}{t}\Big)h_0\Big(\omega + \frac{a}{t} - u\Big)$$

$$- h_0\Big(\omega + \frac{a}{t}\Big)h_0\Big(\omega + u + \frac{a}{t}\Big)$$

$$+ h_0\Big(\omega - \frac{a}{t}\Big)h_0\Big(\omega + u - \frac{a}{t}\Big) - h_0\Big(\omega - \frac{a}{t}\Big)h_0\Big(\omega - u - \frac{a}{t}\Big)\Big]$$

$$- i\sin\theta \int_0^{a/t} \frac{du}{u}\Big[h_0\Big(\omega + \frac{a}{t}\Big)h_0\Big(\omega + \frac{a}{t} - u\Big) - h_0\Big(\omega + \frac{a}{t}\Big)$$

$$\times h_0\Big(\omega + u + \frac{a}{t}\Big) - h_0\Big(\omega - \frac{a}{t}\Big)h_0\Big(\omega + u - \frac{a}{t}\Big)$$

$$+ h_0\Big(\omega - \frac{a}{t}\Big)h_0\Big(\omega - u - \frac{a}{t}\Big)\Big]\Big\}$$

The third term U_2 is responsible for the t^{-1} behavior for long times. The integral behaves like

$$U_2 \underset{t\to\infty}{\sim} -2\eta\rho a \int_{-\infty}^{+\infty} d\omega\, h_0(\omega)$$

$$\times \int_0^{2\pi} \frac{d\theta}{2\pi} \cos\theta \exp[i\rho t\omega \sin\theta - \rho t(1-\cos\theta)\mu(\omega)]$$

$$\times \int_0^{\infty} du[h_0(\omega + u) + h_0(\omega - u)]$$

The integrand becomes concentrated around $\omega = 0$ for long times, whence we obtain for the asymptotic behavior

$$U_2 \underset{t\to\infty}{\sim} -2\eta\rho a \int_{-\infty}^{+\infty} d\omega\, h_0(\omega) I_0(\rho t[\mu^2(\omega) - \omega^2]^{1/2}) e^{-\rho t\mu(\omega)} = -\frac{2\eta}{(2\pi)^{1/2}} \frac{\rho a}{\rho t}$$

As the integrand of U_2 and U_3 are exponentially decreasing when $t \to 0$ or $a \to \infty$, we can ensure that

$$U_2|_{t=0} = U_3|_{t=0} = \left.\frac{dU_3}{dt}\right|_{t=0} = \left.\frac{dU_2}{dt}\right|_{t=0} = 0$$

and that the limiting function for large a is zero.

APPENDIX D. JUSTIFICATION OF THE LINEARIZATION

In this appendix, we shall consider in more detail the way in which we get final contributions which are explicitly linear in η. Indeed, by inspection of (C.2) and (C.3), it appears at once that the η dependence of U_1 is quite complicated so that it is not completely obvious to derive from (C.2) a closed expression formally linear in η, such as the one given in (C.4). The following considerations will be applied directly to U_1, as its computation is carried out explicitly in Appendix C. Of course, they can be easily extended to any contribution to $\delta\psi(t)$.

The final expression (C.4) is derived after three simplifications: (i) linearization of the limit of integration $[(2a/t)^2 + 4\eta]^{1/2}$; (ii) replacement of $(\omega^2 \pm 4\eta)^{1/2} - |\omega|$ by $\pm 2\eta/|\omega|$; (iii) replacement of $(4|\eta|)^{1/2}$ by 0.

Some explanations for the latter case were given in Section 3. Operations (i), (ii), and (iii) are surely valid when we deal with finite times only; we shall examine the three operations successively.

(i) Linearization of $[(2a/t)^2 + 4\eta]^{1/2}$. By neglecting η in the integration bound of (C.2), we make an error of order

$$\int_{[4\eta+(2a/t)^2]^{1/2}}^{2a/t} d\omega\, [(\omega^2 - 4\eta)^{1/2} - \omega] \int_{-a/t}^{\inf(\omega - a/t,\, 2a\omega/t(\omega^2-4\eta)^{1/2})} dz$$
$$\times\, [e^{i\theta\epsilon(z)} h_0(v_1 - \omega) - e^{-i\theta} e^{i\theta\epsilon(-z)} h_0(v_1 + \omega)]$$

for which a rough upper bound is

$$\int_{[4\eta+(2a/t)^2]^{1/2}}^{2a/t} d\omega\, [(\omega^2 + 4|\eta|)^{1/2} - \omega] \int_{-a/t}^{a/t} dz\, [h_0(v_1 + \omega) + h_0(v_1 - \omega)]$$
$$\leqslant 2 \int_{[4\eta+(2a/t)^2]^{1/2}}^{2a/t} d\omega\, [(\omega^2 + 4|\eta|)^{1/2} - \omega]$$
$$\sim \frac{2|\eta| t}{a} \left\{ \left[\left(\frac{2a}{t}\right)^2 + 4\eta \right]^{1/2} - \frac{2a}{t} \right\} = O(\eta^2)$$

as a/t is finite.

(ii, iii) Linearization of $(\omega^2 \pm 4\eta - \omega)^{1/2}$ *and Dropping of the Condition* $\omega^2 > 4|\eta|$ [for expression (C.3)]. We carry out the proof for $(\omega^2 \pm 4\eta)^{1/2} - \omega$; only small modifications are necessary for case (iii). Problems occur only because of small velocities ($\omega^2 \sim 4|\eta|$). For $\omega \geqslant a/t$, the corrections to the linearization with respect to η are obviously of order η^2 and so we shall not consider them. When $\omega \geqslant a/t$, the right-hand side of (C.2) reduces to

$$\tfrac{1}{2}\int_0^{a/t} d\omega\, [(\omega^2 - 4\eta)^{1/2} - \omega] \int_{-a/t}^{\omega - a/t} dz\, [h_0(v_1 - \omega) - h_0(v_1 + \omega)]$$
$$= \frac{1}{2}\int_0^{a/t} d\omega\, \omega^2[(\omega^2 - 4\eta)^{1/2} - \omega]\, \frac{h_0(v_1 - \omega) - h_0(v_1 + \omega)}{\omega}$$

More generally, we shall prove that integrals of the form

$$\int_0^{\alpha} d\omega\, \omega^n \phi(\omega)[(\omega^2 - 4\eta)^{1/2} - \omega]$$

where $n \geqslant 1$, $\phi(0) \neq 0, \infty$, can be linearized. The absolute magnitude of the correction

$$\int_0^{\alpha} d\omega\, \omega^n \phi(\omega)[(\omega^2 - 4\eta)^{1/2} - \omega + (2\eta/\omega)]$$

is smaller than

$$\sup|\phi(\omega)| \int_0^{\alpha} d\omega\, \omega^n[\omega - (2\eta/\omega) - (\omega^2 - 4\eta)^{1/2}]$$

which is of order η^2 when $n > 1$. If $n = 1$, the integration can be performed and we find that the neglected term is of order $\eta^{3/2}$.

We must keep in mind that, when we consider the self-diffusion coefficient, i.e., the time integral of $\delta\psi(t)$, a careful inspection of the long-time ($a/t \sim |\eta|^{1/2}$) and very long-time ($a/t \ll |\eta|^{1/2}$) behavior is necessary. Indeed, it is possible that, for instance, a very slow decrease of the velocity correlation at times much larger than $a|\eta|^{-1/2}$ yields ultimately a correction to the time integral of this quantity of order (or even larger than) η.

APPENDIX E. LIST OF THE CONTRIBUTIONS TO $\delta_3\psi(t)$

For V_1, V_3, and V_6 we have

$$2V_1 = 2\eta\rho a \int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1)$$
$$\times \int_0^{2\pi} \frac{d\theta}{2\pi} \exp[i\rho t(\sin\theta)v_1 - \rho t(1 - \cos\theta)\mu(v_1)]$$
$$\times \int_{a/t}^{\infty} \frac{dv}{v} [h_0(v_1 - v) - h_0(v_1 + v)$$

$$
\begin{aligned}
2V_3 = & -2\eta\rho a \int_{-\infty}^{+\infty} d\omega\, dh_0(\omega) \\
& \times \int_0^{2\pi} \frac{d\theta}{2\pi} \exp[i\rho t(\sin\theta)\omega - \rho t(1-\cos\theta)\mu(\omega)] \\
& \times \left\{ \cos\theta \int_{a/t}^{\infty} \frac{dv}{v} [h_0(\omega - v) - h_0(\omega + v)] \right. \\
& \left. + i\sin\theta \int_{a/t}^{\infty} \frac{dv}{v} [h_0(\omega - v) + h_0(\omega + v)] \right\}
\end{aligned}
$$

$$
\begin{aligned}
2V_6 = & \ 2\eta\rho a \int_{-\infty}^{+\infty} d\omega\, h_0(\omega) \\
& \times \int_0^{2\pi} \frac{d\theta}{2\pi} \rho t \exp[i\rho t(\sin\theta)\omega - \rho t(1-\cos\theta)\mu(\omega)] \\
& \times \int_{a/t}^{\infty} \frac{dv}{v\sqrt{2}} h_0\left(\frac{v}{\sqrt{2}}\right) \left\{ 2(1-\cos\theta)^2 \right. \\
& \times \left[1 - \operatorname{Erf}\left(\frac{v}{\sqrt{2}} - \omega\sqrt{2}\right) - \operatorname{Erf}\left(\frac{v}{\sqrt{2}} + \omega\sqrt{2}\right) \right] \\
& - 2(1-\cos\theta) + 2i(\sin\theta)(1-\cos\theta) \\
& \left. \times \left[\operatorname{Erf}\left(\frac{v}{\sqrt{2}} - \omega\sqrt{2}\right) - \operatorname{Erf}\left(\frac{v}{\sqrt{2}} + \omega\sqrt{2}\right) \right] \right\}
\end{aligned}
$$

$$
\begin{aligned}
V_2 = & -\rho a\eta \int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \\
& \times \int_0^{2\pi} \frac{d\theta}{2\pi} \rho t \exp[i\rho t v_1 \sin\theta - \rho t(1-\cos\theta)\mu(v_1)] \\
& \times \left\{ \int_{a/t}^{\infty} \frac{dv}{v^2} [h_0(v_1 - v) - h_0(v_1 + v)] \right. \\
& \times [(1-\cos\theta)^2\mu(v_1) - i(1-\cos\theta)(\sin\theta)v_1] \\
& + \int_{a/t}^{\infty} \frac{dv}{v^2} [h_0(v_1 - v) + h_0(v_1 + v)] \\
& \left. \times [(i\sin\theta)^2 v_1 - i(\sin\theta)(1-\cos\theta)\mu(v_1)] \right\}
\end{aligned}
$$

$$
\begin{aligned}
V_4 = & -\frac{\eta}{2} \int_{-\infty}^{+\infty} dv_1\, v_1 h_0(v_1) \\
& \times \int_0^{2\pi} \frac{d\theta}{2\pi} (\rho t)^2 \exp[i\rho t v_1 \sin\theta - \rho t(1-\cos\theta)\mu(v_1)] \\
& \times \{(1-\cos\theta)^2[F(v_1) - F(-v_1)] \\
& + i(\sin\theta)(1-\cos\theta)[F(v_1) + F(-v_1)] \\
& - (1-\cos\theta)[F(v_1) + G(v_1) - F(-v_1) - G(-v_1)]\}
\end{aligned}
$$

with

$$F(v_1) \equiv \int_0^{a/t} \frac{dv}{v^2} h_0\left(\frac{v}{\sqrt{2}}\right)\left[v_1 v^2\sqrt{2} - v^2\phi(\beta) - \int_{z_1}^{z_2} dy\,(z_1 - y)f(y)\right]$$
$$+ \int_{a/t}^{\infty} \frac{dv}{v^2} h_0\left(\frac{v}{\sqrt{2}}\right)\left[\frac{a^2}{t^2}\,[v_1\sqrt{2} - \phi(\beta)] - \int_{\beta}^{z_1} dy\,(z_1 - y)f(y)\right]$$

$$G(v_1) \equiv \int_{a/t}^{2a/t} \frac{dv}{v^2} h_0\left(\frac{v}{\sqrt{2}}\right)\left[\phi(\alpha)\left(v^2 - \frac{a^2}{t^2}\right) - \int_{z_2}^{\beta} dy\,(z_1 - y)f(y)\right]$$
$$+ \int_{2a/t}^{\infty} \frac{dv}{v^2} h_0\left(\frac{v}{\sqrt{2}}\right)\left[\left(\frac{4av}{t} - \frac{a^2}{t^2}\right)\phi(\alpha) - \int_{-z_4}^{\beta} dy\,(z_1 - y)f(y)\right.$$
$$\left. - \frac{2a\sqrt{2}}{t}\int_{z_2}^{z_4} dy\,f(y)\right]$$

$$f(y) \equiv h_0(y) + \alpha\,\mathrm{Erf}(y)$$

the variables z_i ($i = 1$–4), α, and β are given by

$$z_1 = (a/t + v/2 + v_1)\sqrt{2}, \qquad z_2 = (a/t - v/2 + v_1)\sqrt{2}$$
$$z_3 = (a/t + v/2 - v_1)\sqrt{2}, \qquad z_4 = (a/t - v/2 - v_1)\sqrt{2}$$
$$\alpha = (v_1 - v/2)\sqrt{2}, \qquad \beta = (v_1 + v/2)\sqrt{2}$$

and the functions $h_0(x)$, $\mathrm{Erf}(x)$, and $\phi(x) = \mu(x)/2$ are again those of Eqs. (10) and (11).

For V_5 we have

$$V_5 = -2\int_{-\infty}^{+\infty} d\omega \int_0^{2\pi} \frac{d\theta}{2\pi}(\rho t)^2 \exp[i\rho t\omega\sin\theta - \rho t(1 - \cos\theta)\mu(\omega)]$$
$$\times \{4(1 - \cos\theta)^2 F_1(\omega) - 2(i\sin\theta)^2 F_2(\omega)$$
$$+ i(\sin\theta)(1 - \cos\theta)[4F_1(\omega) - 2F_2(\omega)] - 4(1 - \cos\theta)F_4(\omega)$$
$$+ 2i(\sin\theta)F_5(\omega)\}$$

with

$$F_2(\omega) \equiv \frac{1}{2}\int_{a/t}^{\infty}\frac{du}{u^2}\left[\int_0^{\inf(a/t,u-a/t)} dx\left(x + \frac{a}{t}\right)(\omega - x)h_0(\omega - x)h_0(\omega + u - x)\right.$$
$$\times (\omega + u - x) + \frac{2a}{t}\int_{a/t}^{\sup(a/t,u-a/t)} dx\,(\omega - x)h_0(\omega - x)$$
$$\times h_0(\omega + u - x)(\omega + u - x)$$
$$\left. - \int_{\sup(a/t,u-a/t)}^{u} dx\left(x - \frac{a}{t}\right)(\omega - x)h_0(\omega - x)h_0(\omega + u - x)(\omega + u - x)\right]$$

$$F_5(\omega) \equiv \frac{1}{2}\int_0^\infty \frac{du}{u^2}\Bigg[\int_{-a/t}^{\inf(a/t,u-a/t)} dx\left(x+\frac{a}{t}\right)(\omega - x)$$
$$\times h_0(\omega - x)h_0(\omega + u - x)(\omega + u - x)$$
$$+ \frac{2a}{t}\int_{a/t}^{\sup(a/t,u-a/t)} dx\,(\omega - x)h_0(\omega - x)$$
$$\times h_0(\omega + u - x)(\omega + u - x)$$
$$- \int_{\sup(a/t,u-a/t)}^{u+a/t} dx\,\epsilon\left(u - \frac{a}{t}\right)\left(x - \frac{a}{t}\right)(\omega - x)$$
$$\times h_0(\omega - x)h_0(\omega + u - x)(\omega + u - x)\Bigg]$$

and $F_1(\omega)$ and $F_4(\omega)$ are obtained by replacing the factor $(\omega + u - x)$ by $h_0(\omega) + (\omega + u - x)\,\mathrm{Erf}\,\omega$ in $F_2(\omega)$ and $F_5(\omega)$, respectively.

For large t and small ω, $F_5(\omega)$ reads

$$F_5(\omega) \underset{\substack{t\to\infty \\ \omega\to 0}}{\sim} (a\omega/t)\int_0^\infty du\, h_0{}^2(u/\sqrt{2}) = a\omega/[(2\pi)^{1/2}t^2]$$

and

$$V_5 \underset{t\to\infty}{\sim} -\frac{2\rho a}{(2\pi)^{1/2}}\int_{-\infty}^{+\infty} d\omega\,\omega\int_0^{2\pi}\frac{d\theta}{2\pi}\rho t(i\sin\theta)$$
$$\times \exp[i\rho t(\sin\theta)\omega - \rho t(1-\cos\theta)\mu(\omega)]$$
$$\sim \frac{2\rho a}{(2\pi)^{1/2}}\int_{-\infty}^{+\infty} d\omega\,\frac{\omega^2\rho t}{\mu(0)[2\pi\rho t\mu(0)]^{1/2}}\exp\left[-\frac{\rho t\omega^2}{2\mu(0)}\right]$$
$$\sim \frac{2}{(2\pi)^{1/2}}\frac{\rho a}{\rho t}$$

and the diverging term is exactly cancelled by the diverging term of U_2.

For V_7 we have

$$V_7 = -4\int_{-\infty}^{+\infty} d\omega\, h_0(\omega)$$
$$\times \int_0^{2\pi}\frac{d\theta}{2\pi}(\rho t)^3\exp[i\rho t(\sin\theta)\omega - \rho t(1-\cos\theta)\mu(\omega)]$$
$$\times \{2(1-\cos\theta)^3[F_1(\omega) + 2F_2(\omega)]$$
$$- 2i(\sin\theta)(1-\cos\theta)^2[F_1(\omega) + 2F_2(\omega)]$$
$$- 4(1-\cos\theta)^2[F_1(\omega) + F_2(\omega) - G_2(\omega)]$$
$$+ 2i(\sin\theta)(1-\cos\theta)[F_1(\omega) - G_1(\omega)]\}$$

with

$$F_1(\omega) = \frac{1}{2}\int_0^\infty \frac{dv}{v^2}\int_v^\infty dx\, h_0(\omega + v - x)h_0(\omega - x)(\omega + v - x)$$
$$\times \left[\epsilon\left(v - \frac{a}{t}\right)\int_0^{\inf(a/t, v - a/t)} dz\left(z + \frac{a}{t}\right) + \frac{2a}{t}\epsilon\left(v - \frac{2a}{t}\right)\int_{a/t}^{v - a/t} dz\right.$$
$$\left. - \epsilon\left(x - \frac{a}{t}\right)\int_{\sup(a/t, v - a/t)}^{\inf(x, v + a/t)} dz\left(z - \frac{a}{t}\right)\right]$$
$$- \frac{1}{2}\int_0^\infty \frac{dv}{v^2}\int_{-\infty}^{\inf(0, v - a/t)} dx\, h_0(\omega - v + x)h_0(\omega + x)(\omega + v - x)$$
$$\times \int_{\sup(x, -a/t)}^{\inf(0, v - a/t)} dz\left(z + \frac{a}{t}\right)$$

$$G_1(\omega) \equiv -\frac{1}{2}\int_0^\infty \frac{dv}{v^2}\int_0^v dx\, h_0(\omega + x)h_0(\omega - v + x)(\omega - v + x)\epsilon\left(v - \frac{a}{t}\right)$$
$$\times \left\{\int_0^{\inf(a/t, u - a/t, x)} dz\left(z + \frac{a}{t}\right)\epsilon\left(v - \frac{a}{t}\right)\right.$$
$$+ \frac{2a}{t}\epsilon\left(v - \frac{a}{t}\right)\int_{a/t}^{\inf[x, \sup(a/t, v - a/t)]} dz\, \epsilon\left(x - \frac{a}{t}\right)$$
$$\left. - \int_{\sup(a/t, u - a/t)}^{x} dz\left(z - \frac{a}{t}\right)\epsilon\left(x - \sup\left(\frac{a}{t}, u - \frac{a}{t}\right)\right)\right\}$$

and similar formulas for $F_2(\omega)$ and $G_2(\omega)$ by simply replacing $(\omega + v - x)$ by $h_0(\omega) + (\omega + v - x)$ Erf ω in $F_1(\omega)$ and $G_1(\omega)$, respectively.

The only remaining diverging term arises from the $(i \sin \theta)(1 - \cos \theta)$, but as explained in Appendix A, compensations appear and actually the term V_7 behaves like t^{-2} instead of t^{-1}.

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