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# Velocity-correlation function for systems with strong repulsive potentials

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It is shown that a singularity appears in the velocity-correlation function of a classical fluid in equilibrium at time equal to zero when a smooth interparticle potential tends to the hard-sphere potential.

## I. INTRODUCTION

It has long been noticed in the literature[1-11] that time-correlation functions which appear in the Green-Kubo expressions for the transport coefficients of a classical monatomic fluid have an essentially different behavior for particles interacting through a smooth or a hard-core potential.

The difference appears in the short-time behavior. Generally, for smooth potentials time-correlation functions are analytic functions of the time $t$ around $t=0$,[2-4] while for hard-core interactions singularities appear at $t=0$.[1,5-8] As an example of this difference I consider here the velocity-correlation function which appears in the relation for the coefficient of self-diffusion in the fluid. This function is defined as

$$C_\delta(t)=\langle\vec{v}_1\cdot\vec{v}_1(t)\rangle_\delta\,, \tag{1.1}$$

where $\vec{v}_1$ and $\vec{v}_1(t)$ denote the velocities of a particle, labeled 1, at times 0 and $t$, respectively. The angular brackets $\langle\cdots\rangle_\delta$ in (1.1) refer to a canonical equilibrium ensemble average for a system of $N$ particles in a volume $V$ at temperature $T$ and a Hamiltonian

$$H_\delta=\sum_{i=1}^{N}\tfrac{1}{2}m\vec{v}_i^{\,2}+\sum_{i<j}^{N}V_\delta(r_{ij})\,, \tag{1.2}$$

where $m$ is the mass of a particle and the spherically symmetric two-body potential is given by

$$V_\delta(r)=\epsilon(\sigma/r)^{1/\delta}\,, \tag{1.3}$$

where the constants $\epsilon$ and $\sigma$ have the dimension of energy and length, respectively. The potential $V_\delta(r)$ with $\delta>0$ will serve here as an example of a smooth potential. For $\delta\to 0$, $V_\delta(r)$ describes the interaction of hard spheres with diameter $\sigma$.

As is discussed in the literature[2-4] the velocity-correlation function $C_\delta(t)$ can, for small $|t|$, be expanded in powers of $t$, i.e.,

$$C_\delta(t)=\sum_{l=0,2,4,\ldots}^{\infty}a_l(\delta)t^l\quad(\delta>0) \tag{1.4}$$

and all coefficients $a_l(\delta)$ can be expressed in equilibrium properties of the system.

Owing to the symmetry $C_\delta(t)=C_\delta(-t)$ odd powers of $t$ are absent in (1.4). It is also shown in the literature[1,5-8] that for hard spheres, i.e., $\delta=0$ in (1.1)–(1.4) the function $C_0(t)$ behaves as

$$C_0(t)=\frac{3}{\beta m}\left(1-\frac{2}{3}\frac{|t|}{t_E}+O(t^2)\right), \tag{1.5}$$

which means that $C_0(t)$ has a cusp at $t=0$. In Eq. (1.5) $\beta=1/k_BT$ with $k_B$ Boltzmann's constant and $t_E$ is the mean-free time between collisions in a hard-sphere fluid

$$t_E=\frac{\sqrt{\beta m}}{4\sqrt{\pi}\,n\sigma^2\chi} \tag{1.6}$$

with the density $n=N/V$, and $\chi$ denotes the value of equilibrium-pair-correlation function of two spheres in contact.

The result (1.5) has been derived from (1.1) using from the very beginning the properties of a hard-sphere fluid. Here I wish to show how the result (1.5) can be derived from the expansion (1.4). First, it is shown in Sec. II that the coefficients $a_l(\delta)$ in Eq. (1.4) diverge for $\delta\to 0$ and $l\geq 2$. In Sec. III the most divergent contribution in $\delta$ to each coefficient $a_l(\delta)$ is determined. In Sec. IV the series (1.4) with $a_l(\delta)$ replaced by its most divergent contribution is resummed. Then the limit $\delta\to 0$ is taken and the result (1.5) is recovered. Some consequences are discussed in Sec. V.

## II. SHORT-TIME COEFFICIENTS

Expressions for the coefficients $a_l(\delta)$ in Eq. (1.4) are obtained from Eq. (1.1) using the representation $\exp(L_\delta t)\vec{v}_1$ for $v_1(t)$, where $L_\delta$ denotes the Liouville operator corresponding to the Hamiltonian $H_\delta$ in Eq. (1.2), i.e.,

$$L_\delta=\sum_{i=1}^{N}\vec{v}_i\cdot\frac{\partial}{\partial\vec{r}_i}+\sum_{i<j}\Theta_\delta(ij)\,. \tag{2.1}$$

Here the first term is due to free streaming and the operator $\Theta_\delta(ij)$ describes the interaction of particles $i$ and $j$:

$$\Theta_\delta(ij)=\frac{dV_\delta(r_{ij})}{dr_{ij}}\,\frac{\vec{r}_{ij}}{mr_{ij}}\cdot\left(\frac{\partial}{\partial\vec{v}_i}-\frac{\partial}{\partial\vec{v}_j}\right). \tag{2.2}$$

Then the coefficients $a_l(\delta)$ are given by

$$a_l(\delta)=\frac{1}{l!}\langle \vec{v}_1(L_\delta)^l\vec{v}_1\rangle_\delta. \tag{2.3}$$

The operator $L_\delta$ has the property $\langle f_1L_\delta f_2\rangle_\delta = -\langle f_2L_\delta f_1\rangle_\delta$ for any two functions $f_1$ and $f_2$ of the phases of the $N$ particles. Hence the right-hand side of Eq. (2.3) vanishes for $l$ odd. The first non-vanishing coefficient in (2.3) occurs for $l=0$, and is

$$a_0(\delta)=3/\beta m\,, \tag{2.4}$$

which is independent of $\delta$. For $l=2$ one has

$$a_2(\delta)=\frac{N-1}{2}\langle \vec{v}_1L_\delta\Theta_\delta(12)\vec{v}_1\rangle_\delta\,, \tag{2.5}$$

where one operator $L_\delta$ has been replaced by $(N-1)\Theta(12)$. The function $\Theta(12)\vec{v}_1$ in Eq. (2.5) depends on $\vec{r}_1$ and $\vec{r}_2$ only, as follows from (2.2). Therefore, using (2.1) for $L_\delta$:

$$a_2(\delta)=\frac{N-1}{2}\left\langle \vec{v}_1\left(\vec{v}_1\cdot\frac{\partial}{\partial\vec{r}_1}\right)\Theta_\delta(12)\vec{v}_1\right\rangle_\delta\,. \tag{2.6}$$

A similar term, with $\vec{v}_1\cdot\partial/\partial\vec{r}_1$ replaced by $\vec{v}_2\cdot\partial/\partial\vec{r}_2$, vanishes since it is odd in $\vec{v}_2$. The average in (2.6) can be expressed in terms of the equilibrium-pair-correlation function $g_\delta(r_{12})$, which is defined as

$$g_\delta(r_{12})=e^{-\beta V_\delta(r_{12})}h_\delta(r_{12}) \tag{2.7}$$

with

$$h_\delta(r_{12})=\frac{N(N-1)}{n^2}\,\frac{\int d\vec{r}_3\cdots\int d\vec{r}_N(\exp-\beta\sum_{\alpha'}V_\delta(r_{\alpha'}))}{\int d\vec{r}_1\cdots\int d\vec{r}_N(\exp-\beta\sum_\alpha V_\delta(r_\alpha))}. \tag{2.8}$$

The variables $\alpha$ and $\alpha'$ run over all different pairs in the system and in the summation over $\alpha'$ the pair 12 is excluded. Thus

$$a_2(\delta)=\frac{n^2}{2N}\int d\vec{r}_1\int d\vec{r}_2\int d\vec{v}_1\int d\vec{v}_2 g_\delta(r_{12})\phi(\vec{v}_1)\phi(\vec{v}_2)\times\vec{v}_1\cdot\left(\vec{v}_1\cdot\frac{\partial}{\partial\vec{r}_1}\right)\theta_\delta(12)\vec{v}_1\,, \tag{2.9}$$

where $\phi(\vec{v}_i)$ denotes the normalized Maxwellian

$$\phi(\vec{v}_i)=\left(\frac{\beta m}{2\pi}\right)^{3/2}e^{-\beta m\vec{v}_i^2/2}. \tag{2.10}$$

Substitution of (2.2) for $\Theta_\delta$ in (2.9) and performing the integrations over $\vec{v}_1$, $\vec{v}_2$, and $\vec{r}_1$ yields

$$a_2(\delta)=\frac{-n}{2\beta m^2}\int d\vec{r}g_\delta(r)\left(\frac{2}{r}\frac{dV_\delta(r)}{dr}+\frac{d^2V_\delta(r)}{dr^2}\right)\,, \tag{2.11}$$

where $r$ denotes the relative distance $r_{12}$.

Using Eq. (1.3) for $V_\delta(r)$ and Eq. (2.7) for $g_\delta(r)$ yields

$$a_2(\delta)=\frac{2\pi n\epsilon(\delta-1)}{\beta m^2\delta^2}\int_0^\infty dr\,h_\delta(r)\,e^{-\beta\epsilon(\sigma/r)^{1/\delta}}(\sigma/r)^{1/\delta}. \tag{2.12}$$

For $\delta\to 0$ the integral over $r$ can be evaluated using the dimensionless inverse length

$$s\equiv\beta\epsilon(\sigma/r)^{1/\delta} \tag{2.13}$$

as the new integration variable so that

$$a_2(\delta)=\frac{2\pi n\sigma(\beta\epsilon)^\delta(\delta-1)}{\beta^2m^2\delta}\int_0^\infty ds\,e^{-s}s^{-\delta}h_\delta\left(\frac{\sigma(\beta\epsilon)^\delta}{s^\delta}\right). \tag{2.14}$$

Furthermore, one needs that

$$\lim_{\delta\to 0}h_\delta\left(\frac{\sigma(\beta\epsilon)^\delta}{s^\delta}\right)=h_0(\sigma)=\chi \tag{2.15}$$

which holds since $h_\delta(r)$ is a continuous function of $r$ for all $r$ and $\delta\geq 0$ with $\delta=0$ included. The quantity $\chi$ in Eq. (2.15) is equal to the equilibrium-pair-correlation function of a hard-sphere fluid $g_0(r)$ at $r=\sigma$ since in Eq. (2.7) the Mayer function $\exp[-\beta V_\delta(r)]$ tends to one for $\delta\to 0$ and $r\geq\sigma$.

Thus the expression on the right-hand side of Eq. (2.14) diverges for $\delta\to 0$ proportional to $1/\delta$, i.e.,

$$a_2(\delta)=-\frac{2\pi n\sigma\chi}{\beta^2m^2}\frac{1}{\delta}[1+O(\delta)]\,, \tag{2.16}$$

which is the final result for $a_2(\delta)$. Notice that the divergence is due to the following four properties:

(1) a factor $\sim\delta^{-1}$ which is present in the interaction term $\Theta_\delta(12)$ at the right-hand side of (2.6) since $\Theta_\delta(12)$ contains the derivative of the potential $V_\delta(r)$ [cf. (2.2) and (1.3)];

(2) a factor $\sim\delta^{-1}$ which arises from the free streaming term $\vec{v}_1\cdot(\partial/\partial\vec{r}_1)$ on the right-hand side of (2.6) since each further derivative of $V_\delta(r)$ introduces a factor $\sim\delta^{-1}$;

(3) a factor $\sim\delta$ which is due to the volume element $dr$ in the $r$ integral on the right-hand side of (2.12) since $dr\sim\delta\,ds$ with $s\sim r^{-1/\delta}$, given by (2.13);

(4) the fact that the integral over $s$ in Eq. (2.14) is finite in the limit $\delta\to 0$. For this the Mayer function $\exp(-s)$ is explicitly needed as a convergence factor for large $s$, i.e., for a small interparticle distance $r$.

These four properties can also be used to estimate the asymptotic behavior of $a_l(\delta)$ for $\delta\to 0$ and $l$ larger than 2, from Eq. (2.3). First notice that the expression in angular brackets on the right-hand side of Eq. (2.3) is proportional to $\delta^{-l}$ since each operator $L_\delta$ yields a factor $\delta^{-1}$ as discussed in (1) and (2) above. For each $l$ the coefficient $a_l(\delta)$ can be decomposed into terms which contain the two-particle-equilibrium-correlation function $g_\delta(r)$ defined in Eqs. (2.7) and (2.8), the three-particle-equilibrium-correlation function defined in a similar way as in Eqs. (2.7) and (2.8), and so on. Terms which contain $g_\delta(r)$ are for $\delta\to 0$ at most proportional to $\delta^{-l}\delta$, where the extra factor $\delta$ is discussed in (3) above. Terms which contain the three-particle correlation function are at most proportional to $\delta^{-l}\delta^2$. Here the extra factor $\delta^2$ is due to spatial integrations over *two* relative distances each giving a factor $\delta$ in a similar way as in (3) above. Thus $a_l(\delta)$ diverges for $\delta\to 0$ proportional to $\delta^{-l+1}$. In the next section the proportionality constants are determined.

## III. ASYMPTOTIC BEHAVIOR

Here the behavior of the coefficients $a_l(\delta)$ is determined for $\delta\to 0$ and $l\geq 2$. From Eq. (2.3) it follows that for $l\geq 2$,

$$a_l(\delta)=\frac{N-1}{l!}\langle\vec{v}_1(L_\delta)^{l-1}\Theta_\delta(12)\,\vec{v}_1\rangle_\delta\,, \tag{3.1}$$

similar to the derivation of Eq. (2.5).

The most divergent contribution to each $a_l(\delta)$ is obtained from (3.1) by substituting Eq. (2.1) for $L_\delta$ and keeping the terms which involve particles 1 and 2 only. This is explained at the end of Sec. II. Therefore,

$$a_l(\delta)=\frac{N-1}{l!}\left\langle\vec{v}_1\left(\vec{v}_1\cdot\frac{\partial}{\partial\vec{r}_1}+\vec{v}_2\cdot\frac{\partial}{\partial\vec{r}_2}+\Theta_\delta(12)\right)^{l-1}\Theta_\delta(12)\,\vec{v}_1\right\rangle_\delta[1+O(\delta)]\,. \tag{3.2}$$

Using Eqs. (2.7) and (2.8) one derives that

$$a_l(\delta)=\frac{n^2}{l!N}\int d\vec{r}_1\int d\vec{r}_2\int d\vec{v}_1\int d\vec{v}_2 g_\delta(r_{12})\,\phi(\vec{v}_1)\,\phi(\vec{v}_2)\,\vec{v}_1\left(\vec{v}_1\cdot\frac{\partial}{\partial\vec{r}_1}+\vec{v}_2\cdot\frac{\partial}{\partial\vec{r}_2}+\Theta_\delta(12)\right)^{l-1}\Theta_\delta(12)\,\vec{v}_1[1+O(\delta)]\,. \tag{3.3}$$

similarly as in Eq. (2.9). The operator $\Theta_\delta(12)$ can be written in relative coordinates, i.e., $\vec{v}=\vec{v}_{12}$, $\vec{V}=\frac{1}{2}(\vec{v}_1+\vec{v}_2)$, $\vec{r}=\vec{r}_{12}$, and $\vec{R}=\frac{1}{2}(\vec{r}_1+\vec{r}_2)$ as

$$\Theta_\delta(12)=-2\frac{dV_\delta(r)}{dr}\,\frac{\vec{r}}{mr}\cdot\frac{\partial}{\partial\vec{v}}\,. \tag{3.4}$$

The free streaming operator in Eq. (3.3) can be written as $\vec{v}_1\cdot(\partial/\partial\vec{r}_1)+\vec{v}_2\cdot(\partial/\partial\vec{r}_2)=\vec{V}\cdot(\partial/\partial\vec{R})+\vec{v}\cdot(\partial/\partial\vec{r})$. The operator $\vec{V}\cdot(\partial/\partial\vec{R})$ commutes with $\vec{v}\cdot(\partial/\partial\vec{r})$ and with $\Theta_\delta(12)$ and vanishes when acting on $\Theta_\delta(12)\,\vec{v}_1$ on the right-hand side of Eq. (3.3). Thus

$$a_l(\delta)=\frac{n}{4l!}\int d\vec{r}\int d\vec{v}\, g_\delta(r)\,\phi_r(\vec{v})\,\vec{v}\left(\vec{v}\cdot\frac{\partial}{\partial\vec{r}}+\Theta_\delta(12)\right)^{l-1}\times\Theta_\delta(12)\,\vec{v}[1+O(\delta)]\,, \tag{3.5}$$

where $\phi_r(v)$ stands for the Maxwell-Boltzmann factor (2.10) with $m$ replaced by $m/2$, i.e., by the relative mass and the integrations over $\vec{R}$ and $\vec{V}$ have been performed. Next, introduce the dimensionless relative position

$$\vec{s}=\beta\epsilon\left(\frac{\sigma}{r}\right)^{1/\delta}\frac{\vec{r}}{r} \tag{3.6}$$

so that $s=\beta\epsilon(\sigma/r)^{1/\delta}=\beta V_\delta(r)$ similarly as in Eq. (2.13) and the dimensionless relative velocity

$$\vec{w}=\tfrac{1}{2}\sqrt{\beta m}\;\vec{v} \tag{3.7}$$

so that $s+w^2=\beta[V_\delta(r)+\frac{1}{4}mv^2]$ is the dimensionless relative energy. With respect to the new variables $\vec{s},\vec{w}$ the free streaming term in Eq. (3.5) reads

$$\vec{v}\cdot\frac{\partial}{\partial\vec{r}}=\frac{2s^\delta}{\sqrt{\beta m}\,\sigma(\beta\epsilon)^\delta}\left[s\vec{w}\cdot\frac{\partial}{\partial\vec{s}}-\left(1+\frac{1}{\delta}\right)\frac{\vec{w}\cdot\vec{s}}{s}\,\vec{s}\cdot\frac{\partial}{\partial\vec{s}}\right] \tag{3.8}$$

and the interaction operator reads

$$\Theta_\delta(12)=\frac{s^\delta}{\sqrt{\beta m}\,\sigma(\beta\epsilon)^\delta}\,\frac{1}{\delta}\,\vec{s}\cdot\frac{\partial}{\partial\vec{w}}\,. \tag{3.9}$$

Substitution of Eqs. (3.6)–(3.9) into (3.5) and changing to new integration variables $\vec{s},\vec{w}$ yields

$$a_l(\delta)=\frac{n\sigma^2(\beta\epsilon)^{2\delta}}{(\pi\beta m)^{3/2}l!}\left[\tfrac{1}{2}\sqrt{\beta m}\,\sigma(\beta\epsilon)^\delta\,\delta\right]^{1-l}$$
$$\times\int d\vec{s}\int d\vec{w}\,e^{-s-\vec{w}^2}s^{-3-3\delta}h_\delta\left(\sigma\frac{(\beta\epsilon)^\delta}{s^\delta}\right)\vec{w}\cdot\left[s^\delta\left(\tfrac{1}{2}\vec{s}\cdot\frac{\partial}{\partial\vec{w}}-(1+\delta)\frac{\vec{w}\cdot\vec{s}}{s}\,\vec{s}\cdot\frac{\partial}{\partial\vec{s}}+\delta s\vec{w}\cdot\frac{\partial}{\partial\vec{s}}\right)\right]^{l-1}s^\delta\,\vec{s}[1+O(\delta)]\,, \tag{3.10}$$

where the relation (2.7) is substituted for $g_\delta(r)$. The second factor on the right-hand side of Eq. (3.10) is proportional to $\delta^{1-l}$. The proportionality constant is obtained from Eq. (3.10) taking the limit $\delta \to 0$ in the remaining quantities, so that

$$a_l(\delta)=\frac{n\sigma^2\chi}{(\pi\beta m)^{3/2}l!}\left(\tfrac{1}{2}\sqrt{\beta m}\,\sigma\,\delta\right)^{1-l} \times \int d\vec{s}\int d\vec{w}\, e^{-s-\vec{w}^2} s^{-3}\vec{w}\cdot L_0^{l-1}\vec{s}\,[1+O(\delta)], \tag{3.11}$$

where Eq. (2.15) is used and where

$$L_0=\tfrac{1}{2}\vec{s}\cdot\frac{\partial}{\partial\vec{w}}-\frac{\vec{w}\cdot\vec{s}}{s}\,\vec{s}\cdot\frac{\partial}{\partial\vec{s}}. \tag{3.12}$$

The operator $L_0$ takes into account the interaction operator $\Theta_\delta(12)$ in Eq. (3.9) and the most divergent part in $\delta$ of the free streaming term $\vec{v}\cdot(\partial/\partial\vec{r})$ in Eq. (3.8).

As follows from Eq. (3.12), $L_0$ conserves the direction of the vector $\vec{s}$, i.e.,

$$L_0\vec{s}/s=0 \tag{3.13}$$

and conserves the energy, i.e.,

$$L_0(s+w^2)=0 \tag{3.14}$$

and conserves the absolute value of the angular momentum, i.e.,

$$L_0\left[w^2-\left(\frac{\vec{w}\cdot\vec{s}}{s}\right)^2\right]=0. \tag{3.15}$$

Furthermore, $L_0$ maps any function of $s$, $w$, and $\vec{s}\cdot\vec{w}$ into a function of $s$, $w$, and $\vec{s}\cdot\vec{w}$. Writing the vector $\vec{s}$ in the integrand on the right-hand side of Eq. (3.11) as $(\vec{s}/s)s$ and commuting $\vec{s}/s$ with $L_0^{l-1}$ using Eq. (3.13), the integrand becomes a function of $s$, $w$, and $\vec{s}\cdot\vec{w}$. Thus one can integrate over $s$, $w$, and $u=\vec{w}\cdot\vec{s}/ws$ as

$$a_l(\delta)=\frac{8\sqrt{\pi}\,n\sigma^2\chi}{(\beta m)^{3/2}l!}\left(\tfrac{1}{2}\sqrt{\beta m}\,\sigma\,\delta\right)^{1-l} \times \int_0^\infty ds\int_0^\infty dw\int_{-1}^{+1}du\, e^{-s-w^2}\frac{uw^3}{s}L_0^{l-1}s[1+O(\delta)]. \tag{3.16}$$

The following variables are convenient in order to perform the integrations over $s$, $w$, and $u$:

$$x=w^2-u^2w^2,\quad y=(s+u^2w^2)^{1/2},\quad z=\tanh^{-1}\frac{uw}{(s+u^2w^2)^{1/2}}. \tag{3.17}$$

The variable $x$ denotes the angular momentum and therefore is conserved [cf. (3.15)], $x+y^2=s+w^2$ is the energy and therefore $y$ is a conserved quantity [cf. (3.14)]. With respect to the new variables $x$, $y$, $z$ the operator $L_0$ in Eq. (3.12) takes the form

$$L_0=\tfrac{1}{2}y\frac{\partial}{\partial z} \tag{3.18}$$

as follows from (3.17) and (3.12).

The transformation of variables in Eq. (3.16) from $(s,w,u)$ to $(x,y,z)$ is most easily carried out in two steps. First, change from $(s,w,u)$ to $(s,\xi,x)$ with $x$ as in Eq. (3.17) and $\xi=uw$. The Jacobian of this transformation is given by $ds\,d\xi\,dx=2w^2ds\,dw\,du$ and $-\infty\le\xi\le+\infty$ and $0\le x\le\infty$. Second, change from $(s,\xi,x)$ to $(x,y,z)$. According to Eq. (3.17) one has $y=(s+\xi^2)^{1/2}$ and $z=\tanh^{-1}\xi(s+\xi^2)^{-1/2}$ so that $dx\,dy\,dz=(1/2s)ds\,d\xi\,dx$ and $0\le y\le\infty$ and $-\infty\le z\le\infty$. Using these results and Eqs. (3.17) and (3.18) one finds for $a_l(\delta)$ in Eq. (3.16) and $l\ge 2$,

$$a_l(\delta)=\frac{8\sqrt{\pi}\,n\sigma^2\chi}{(\beta m)^{3/2}l!}\left(\sqrt{\beta m}\,\sigma\,\delta\right)^{1-l}\int_0^\infty dx\int_0^\infty dy\int_{-\infty}^{-\infty}dz\, e^{-x}e^{-y^2}y^{l+2}\tanh z\left(\frac{\partial}{\partial z}\right)^{l-1}\operatorname{sech}^2 z[1+O(\delta)]. \tag{3.19}$$

The integrations over $x$ and $y$ can be performed so that

$$a_l(\delta)=\frac{4\sqrt{\pi}\,n\sigma^2\chi}{(\beta m)^{3/2}l!}\left(\sqrt{\beta m}\,\sigma\,\delta\right)^{1-l}\Gamma\left(\frac{l+3}{2}\right) \times\int_{-\infty}^{+\infty}dz\tanh z\left(\frac{\partial}{\partial z}\right)^{l-1}\operatorname{sech}^2 z[1+O(\delta)]. \tag{3.20}$$

The integral over $z$ can be obtained from the corresponding generating function defined by

$$G(\tau)\equiv\int_{-\infty}^{+\infty}dz\tanh z\exp\left(\tau\frac{\partial}{\partial z}\right)\operatorname{sech}^2 z, \tag{3.21}$$

which is, after a shift in the variable $z$,

$$G(\tau)=-\int_{-\infty}^{+\infty}dz\operatorname{sech}^2 z\tanh(z+\tau). \tag{3.22}$$

Using the addition formula for $\tanh(z+\tau)$ and changing to the variable $x=\tanh z$ yields

$$G(\tau)=-\int_{-1}^{+1}dx\,\frac{x+\tanh\tau}{1+x\tanh\tau} \tag{3.23}$$

so that the final result is

$$G(\tau)=2\tau\operatorname{csch}^2\tau-2\coth\tau \tag{3.24}$$

or equivalently

$$G(\tau)=-2\frac{\partial}{\partial\tau}\tau\coth\tau. \tag{3.25}$$

The Taylor expansion of coth$\tau$ yields

$$G(\tau)=-4\sum_{j=1,3,5,\ldots}^{\infty} B_{j+1}\frac{(2\tau)^j}{j!}, \tag{3.26}$$

where the coefficients $B_j$ are Bernoulli numbers, and only odd powers of $\tau$ occur in the expansion. From the result (3.26) and the definition (3.21) one finds for $a_l(\delta)$ in (3.20) and $l \geq 2$,

$$a_l(\delta)=-\frac{4\pi n\sigma^2\chi}{(\beta m)^{3/2}}\frac{(l+1)B_l}{(l/2)!\,(\sqrt{\beta m}\,\sigma)^{l-1}}\frac{1}{\delta^{l-1}}[1+O(\delta)]. \tag{3.27}$$

Thus $a_l(\delta)$ diverges proportional to $\sim\delta^{1-l}$ and the proportionality constant is explicitly determined. For $l=2$ the result (3.27) is equivalent to (2.16) since $B_2=\frac{1}{6}$.

## IV. RESUMMATION

Here the series (1.4) with $a_l(\delta)$ replaced by its most divergent contribution in $\delta$ is resummed. At the end the limit $\delta\to 0$ is performed. Using the result (2.4) for $a_0(\delta)$ and the representation (3.19) for $a_l(\delta)$ with $l=2,4,6,\ldots$ one can write the series (1.4) for $C_\delta(t)$ as

$$C_\delta(t)=\frac{3}{\beta m}+\frac{8\sqrt{\pi}n\sigma^3\chi}{\beta m}F\left(\frac{t}{\sqrt{\beta m}\,\sigma\delta}\right)+\cdots \tag{4.1}$$

with

$$F(\tau)=\sum_{l=2,4,\ldots}^{\infty}\frac{\tau^l}{l!}\int_0^{\infty}dy\int_{-\infty}^{+\infty}dz\,e^{-y^2}y^{l+2}\times\tanh z\left(\frac{\partial}{\partial z}\right)^{l-1}\operatorname{sech}^2 z\,. \tag{4.2}$$

The dots $\cdots$ in Eq. (4.1) indicate terms in the expansion (1.4) which are for each power in $t$ less divergent in $\delta$. The quantity $\sqrt{\beta m}\,\sigma$ which occurs in the argument of the function $F$ in Eq. (4.1) is of the order of the average time a particle needs to traverse the distance $\sigma$. The time needed to change the relative velocity in a head-on collision from minus to plus half the asymptotic absolute value is, on the average, proportional to $\sqrt{\beta m}\,\sigma\delta$. Thus the quantity $\sqrt{\beta m}\,\sigma\delta$ is a measure for the time spent in the steep part of the force range. The reduced time $\tau=t/(\sqrt{\beta m}\,\sigma\delta)$ in Eqs. (4.1) and (4.2) is a dimensionless quantity and $F(\tau)$ is a dimensionless function which is even in $\tau$ and vanishing for $\tau=0$.

Owing to the symmetry properties of the integral over $z$ on the right-hand side of Eq. (4.2) one may add terms in Eq. (4.2) with $l=1,3,5,\ldots$. Then changing to the summation variable $j=l-1$ one finds

$$F(\tau)=\int_0^{\tau}d\tau'\int_0^{\infty}dy\int_{-\infty}^{-\infty}dz\,e^{-y^2}y^3\tanh z\times\exp\left(\tau' y\frac{\partial}{\partial z}\right)\operatorname{sech}^2 z: \tag{4.3}$$

For the integral over $z$ one may substitute $G(y\tau')$ according to Eq. (3.21) and use the result (3.25) so that

$$F(\tau)=-2\int_0^{\tau}d\tau'\int_0^{\infty}dy\,e^{-y^2}y^3\frac{\partial}{\partial y}y\coth y\tau'. \tag{4.4}$$

Integration with respect to $\tau'$ and differentiation with respect to $y$ yields

$$F(\tau)=-2\int_0^{\infty}dy\,e^{-y^2}y^2(y\tau\coth y\tau-1). \tag{4.5}$$

From the expansion of coth$y\tau$ in powers of $y\tau$ one finds

$$F(\tau)=-\tfrac{1}{2}\sqrt{\pi}\sum_{l=2,4,\ldots}^{\infty}\frac{l+1}{(l/2)!}B_l\tau^l, \tag{4.6}$$

which applies to small values of $\tau$, and where $B_l$ denotes a Bernoulli number. From the representation $1+2\sum_{n=1}^{\infty}\exp(-2ny\tau)$ for coth$y\tau$ one finds, using the symmetry of $F(\tau)$,

$$F(\tau)=-|\tau|+\tfrac{1}{2}\sqrt{\pi}+\tfrac{1}{2}\pi\sum_{l=3,5,\ldots}^{\infty}\frac{(l-1)B_{l+1}}{(l+1)!}\left|\frac{\pi}{\tau}\right|^l \tag{4.7}$$

which applies to large values of $\tau$. Thus the series (4.2) for $F(\tau)$ is explicitly resummed [cf. (4.5)], the behavior of $F(\tau)$ for small $\tau$ follows from Eq. (4.6) and for large $\tau$ from Eq. (4.7). For a fixed but small value of $\delta$, the function $F$ in Eq. (4.1) can be expanded in powers of $t/(\sqrt{\beta m}\,\sigma\delta)$. Using Eq. (4.6) one recovers the series (1.4), i.e.,

$$C_\delta(t)=\frac{3}{\beta m}-\frac{4\pi n\sigma^3\chi}{\beta m}\delta\times\sum_{l=2,4,\ldots}^{\infty}\frac{l+1}{(l/2)!}B_l\left(\frac{t}{\sqrt{\beta m}\,\sigma\delta}\right)^l+\cdots, \tag{4.8}$$

where each coefficient $a_l(\delta)$ in (1.4) is replaced by its most divergent contribution in $\delta$ [cf. Eq. (3.27)].

For a fixed but small value of time $t$ and for $\delta$ tending to zero one needs in Eq. (4.1) the function $F$ for *large* values of its argument. Using the result (4.7) and taking the limit $\delta\to 0$ yields

$$C_0(t)=\frac{3}{\beta m}-\frac{8\sqrt{\pi}\,n\sigma^2\chi}{(\beta m)^{3/2}}|t|+\cdots \tag{4.9}$$

which is the hard-sphere result for $C_0(t)$ given by Eqs. (1.5) and (1.6).

## V. DISCUSSION

The main results of this paper are contained in Eqs. (4.8) and (4.9). First for the soft but steep potential $V_\delta(r)$ the velocity-correlation function $C_\delta(t)$ is analytic around $t=0$ and has a series expansion in even powers of $t$ where the coefficients of $t^l$ diverge for $\delta \to 0$ and $l \geq 2$ [cf. Eq. (4.8)]. Second by resumming the series, taking into account the most divergent part of each coefficient only, and then performing the limit $\delta \to 0$ one obtains the hard-sphere result given in Eq. (4.9) which is singular at $t=0$.

I remark that both statements have long been conjectured in the literature. Kleban[6] and Sears[7] have in fact shown that the first few coefficients in the series (1.4) diverge in the hard-sphere limit and have conjectured that the hard-sphere result could be obtained from a resummation of most divergent terms. It has been the purpose of this paper to show that such a resummation procedure can actually be carried out and that both conjectures are correct, at least for the potential considered here.

The explicit calculation given here confirms furthermore that the two expansions for the velocity-correlation function given by Eqs. (1.4) and (1.5) are of a completely different nature. First the representation (1.4) is an expansion in powers of $t/t_\delta$ where $t_\delta = \sqrt{\beta m}\,\sigma\delta$ is the time needed for a particle to traverse the steep part of the potential [cf. Eqs. (4.1) and (4.6)]. Therefore, the representation is restricted to times $|t| \lesssim t_\delta$, and for $\delta \to 0$ the region of applicability of the series shrinks to zero. Equivalently one might say that the dynamics of the particles enters into the coefficients of the series essentially through an analytic expansion of the velocity $\vec{v}_1(t)$ around $\vec{v}_1(0)$. Since over a time interval $t_\delta$, $\vec{v}_1(t)$ differs drastically from $\vec{v}_1(0)$, the representation (1.4) is restricted to $|t| \lesssim t_\delta$. On the other hand, the hard-sphere result (4.9) for $C_0(t)$ represents the first two terms in an expansion in powers of $t/t_E$, where $t_E$ is the mean-free time between collisions [cf. Eqs. (1.5) and (1.6)]. Therefore, the result (4.9) is meaningful for $|t| \lesssim t_E$. As noted below Eq. (4.8) the second term on the right-hand side of Eq. (4.9) essentially involves the asymptotic *large*-time behavior of a two-body interaction which for hard spheres includes infinitesimally short times since the collision is instantaneous. Thus for a finite but very small value of $\delta$ the expansion (4.8) represents the velocity-correlation function for $0 \leq |t| \lesssim t_\delta$ and the expansion (4.9) for $t_\delta \lesssim |t| \lesssim t_E$. This applies to a Lennard-Jones potential with $\delta = \frac{1}{12}$ and low densities where the time scales $t_\delta$ and $t_E$ are well separated, i.e., $t_\delta \ll t_E$. However, at liquid densities $t_\delta$ is of the order of $t_E$ so that the representation (4.9) does not apply. This has been discussed elsewhere.[11]

The essential difference in the short-time behavior of $C_\delta(t)$ with $\delta > 0$ and of $C_0(t)$ manifests itself also in the large-frequency behavior in the corresponding Fourier transforms, i.e., in $\tilde{C}_\delta(\omega)$ and $\tilde{C}_0(\omega)$, respectively. For large frequencies $\tilde{C}_\delta(\omega)$ decays to zero faster than any inverse power of $\omega$, while $\tilde{C}_0(\omega)$ decays proportional to $\omega^{-2}$. A similar and related difference occurs in the incoherent scattering functions for hard-sphere and for soft potentials.[7,11]

A singularity as discussed here for the velocity-correlation function of a hard-sphere system is also present in the time-correlation functions which appear in the Green-Kubo expressions for the heat conductivity and the shear and bulk viscosities. For these functions the singularity takes the form of a delta function in time located at $t=0$ and with a strength equal to the collisional transfer contributions to the corresponding transport coefficients. This will be discussed elsewhere.


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