

Sutherland formula for a square-well fluid

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We introduce a closed Onsager-symmetric set of linear kinetic equations for smooth interactions. The new formula is an equivalent of the Enskog equation for hard spheres. Corresponding Green-Kubo expressions for transport coefficients are given with high temperature corrections from finite potentials—Sutherland formula, not only for thermal conductivity and shear viscosity, but also bulk viscosity with discussion of the square-well case.

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I. INTRODUCTION

The well-known Boltzmann equation describes very well the evolution of gases [1,2] giving an efficient tool for calculation of transport coefficients [3]. It is a long-standing problem, however, how to construct a closed kinetic equation for dense gases and fluids interacting by smooth potentials with a possibility of evaluation of transport coefficients. A good kinetic equation must satisfy several conditions. First, in the (Grad) limit of small concentrations, it should lead to the Boltzmann equation and its predictions concerning viscosity and thermal conductivity. In a linearized version, the most common and important case, it should obey Onsager symmetry [4]. Moreover, it should include dissipation. It can be satisfied by a respective H theorem, growth of entropy functional, or an equivalent argument for approach to equilibrium. Finally, a correspondence between full dynamics governed by the Liouville operator or its equivalent—Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of kinetic equations [5] and evolution approximated by the new kinetic equation must be explained. The discussion of neglected events is necessary.

The Enskog equation [6–8] is such an equation for hard spheres. It ignores complicated collisions of three and more particles, but has dissipation built in and its predictions about shear viscosity and thermal conductivity are in good agreement with numerical calculations [9]. It also gives the value of bulk viscosity, which is zero in the Boltzmann-Grad limit, with the leading term proportional to the square of volume fraction occupied by spheres. More generally, one can construct a class of kinetic equations for hard spheres with H theorem [10,11] and satisfy the above conditions [12–14]. It is possible due to the special property of hard cores. Immediate interactions allow us to truncate hierarchy of kinetic equations [2,15] on a certain level and close it according to the maximum entropy principle [16]. Positive entropy production occurs exactly on the interaction surface—when spheres touch one another.

The same procedure applied to smooth potentials gives an unexpected result: there is no entropy production and, hence, it cannot be used to obtain an Enskog-like equation. One can

avoid this problem by replacing the smooth potential by a square well of several steps [14,17–19], but it leads to expressions for transport coefficients without a proper low-density limit. Another method is to consider a stochastic model of hard spheres with random diameters [20]. The problem is that all finite-range potentials imply finite duration time of a collision. It means that the description only by the one-particle distribution function, though correct in the case of hard spheres, is insufficient in situations where the correlations between particles change in finite time. The assumption of molecular chaos can be made only before the beginning of the whole collision, not before partial events. The two-particle distribution function is indispensable.

In this paper, we allow for the evolution of pair distribution function. Moreover, instead of asymmetric BBGKY hierarchy, we consider only a linear case, but in an Onsager-symmetric form. It is impossible to generalize the hard-sphere H theorem to smooth interactions. However, due to the special behavior of the evolution operator, dynamic correlations between particles outside the range of equilibrium correlations have no influence on physical quantities—they just escape to infinity. It can be regarded as an equivalent of the H theorem.

We prove also that this method leads also to the proper Boltzmann-Grad limit and Green-Kubo relations. We are able to obtain high temperature corrections to transport coefficients of hard spheres with weak finite potential—the well-known Sutherland formula [2,3]—not only for shear viscosity and thermal conductivity, but also for bulk viscosity. We apply them to the special case of the square-well potential [21] and compare them with existing results [17,27].

The paper is organized as follows. We start by writing definitions in Sec. II. In Sec. III, the linear algebra necessary in our description is remembered and the dynamics of correlations is explained. The Enskog-like equation is given in Sec. IV. The Green-Kubo expressions for transport coefficients are given in Sec. V. Explicit calculations for smooth cores (imitating hard spheres) and high temperature corrections—Sutherland formulas—are presented in Sec. VI. We close the paper with discussion in Sec. VII and leave some comments and calculations in the appendices.

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II. BASIC CONCEPTS

A system of n particles is represented by a set of phases $\mathbf{x}_1 \cdots \mathbf{x}_n$, where the phase $\mathbf{x}_i = (\mathbf{r}_i, \mathbf{p}_i)$ represents the position \mathbf{r}_i and momentum \mathbf{p}_i of the particle i , respectively. We shall consider systems with a floating number of particles so n is not fixed. For convenience, we shall write i instead of \mathbf{x}_i . Another frequently used symbol will be boldface \mathbf{m} to denote a set of m phases. If two different sets \mathbf{i} and \mathbf{j} appear, then $\mathbf{i} + \mathbf{j}$ is a set of $i + j$ phases, but $\mathbf{i} - \mathbf{j}$ is a set of $i - 1$ phases \mathbf{i} without the phase \mathbf{j} .

The probability density of finding exactly n particles in the phase space point $\mathbf{n} = \{1 \cdots n\}$ is $\rho(\mathbf{n}) \equiv \rho_n$. Any permutation of particles leads to the same state since the particles are identical. Therefore, ρ_n must be a symmetrical function of phases. The average of the phase function $\mathcal{A} = \{\mathcal{A}(\mathbf{n}); n \geq 0\}$ is given by

$$\langle \mathcal{A} \rangle = \sum_{n=0}^{\infty} \int d\mathbf{n} \rho(\mathbf{n}) \mathcal{A}(\mathbf{n}) \equiv \sum_{n=0}^{\infty} \int d\mathbf{n} \rho_n \mathcal{A}_n, \quad (1)$$

where $d\mathbf{n} \equiv d1 \cdots dn/n!$ denotes integration over all canonical coordinates of phases, that is $\int d\mathbf{i} = h^{-3} \int d^3\mathbf{r}_i \int d^3\mathbf{p}_i$, where h is Planck's constant. Arguments of ρ_n and \mathcal{A}_n are omitted whenever it is unambiguous. Reduced distribution functions are defined as

$$f(\mathbf{m}) = \sum_{n=0}^{\infty} \int d\mathbf{n} \rho(\mathbf{n} + \mathbf{m}). \quad (2)$$

The probability distribution must satisfy the normalization condition $f_0 = \sum_{n=0}^{\infty} \int d\mathbf{n} \rho_n = 1$. Functions f are useful in averages of cluster functions

$$\mathcal{A}(\mathbf{n}) = a_0 + \sum_{i \in \mathbf{n}} a(i) + \sum_{i > j} a(ij) + \cdots = \sum_{\mathbf{m} \subseteq \mathbf{n}} a(\mathbf{m}), \quad (3)$$

because $\langle \mathcal{A} \rangle = \sum_{\mathbf{m}=0}^{\infty} \int d\mathbf{m} a_{\mathbf{m}} f_{\mathbf{m}}$. The above cluster decomposition will be frequently used in the paper with small letters standing for cluster functions and capital calligraphic ones for whole functions.

The equilibrium probability density ρ of hard spheres of mass M interacting by the pair potential $\phi(\mathbf{r}_{ij})$ ($\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$) at the temperature T is given by

$$\rho_n = \exp\{(\Omega + n\mu - \mathcal{H}_n)/k_B T\}, \quad (4)$$

where the Hamiltonian \mathcal{H} is defined as

$$\mathcal{H}_n = \sum_{i \in \mathbf{n}} p_i^2/2M + \sum_{i > j} \phi(\mathbf{r}_{ij}) \quad (5)$$

and μ is the chemical potential, $\Omega = -pV$ is the grand thermodynamic potential, and p is the pressure of the fluid in a volume V . The equilibrium distribution functions have always the form $f(\mathbf{m}) = g(\mathbf{r}_1, \dots, \mathbf{r}_m) \prod_{i=1}^m f(i)$, where g_m is the m -point correlation function and $f(i)$ is a Maxwellian distribution of velocities

$$f(\mathbf{r}, \mathbf{p}) = nh^3(2\pi M k_B T)^{-3/2} \exp\{-p^2/2M k_B T\} \quad (6)$$

with density $n = n(\mu, T)$. Functions ρ_m and f_m without any additional indices will represent equilibrium distribution hereafter.

III. LINEAR OPERATORS

It is convenient to work with a Hilbert space of ket vectors $|u\rangle \equiv \{u_1, u_2, \dots\}$ with an infinite number of components, where $u(\mathbf{i})$ is a symmetric function of phases of i particles (similar to Fock space for bosons) [12,13]. The adjoint bra vector is $\langle u| \equiv \{u_1, u_2, \dots\}$. The scalar product of two vectors u and w is defined as

$$\langle u|w\rangle = \sum_{k=1}^{\infty} u_k w_k, \quad u_k w_k = \int d\mathbf{k} u(\mathbf{k}) w(\mathbf{k}). \quad (7)$$

We define linear operators in such a space. The operator X acting on the vector u gives the vector $X|u\rangle = |Xu\rangle$ with the components $(Xu)_k = \sum_{i=1}^{\infty} X_{ki} u_i$ and $X_{ki} u_i = \int d\mathbf{i} X(\mathbf{k}|\mathbf{i}) u(\mathbf{i})$. The product of operators X and Y is defined as $(XY)_{ij} = \sum_{k=1}^{\infty} X_{ik} Y_{kj}$, where $X_{ik} Y_{kj} = \int d\mathbf{k} X(\mathbf{i}|\mathbf{k}) Y(\mathbf{k}|\mathbf{j})$. The adjoint of the operator X is then defined by the equality $\langle u|X^T|w\rangle = \langle w|X|u\rangle$.

A linear nonequilibrium state of the system is described by a small deviation from equilibrium given by a vector b [13]

$$\rho_b(\mathbf{n}) = \rho(\mathbf{n})[1 + \mathcal{B}(\mathbf{n}) - \langle \mathcal{B} \rangle], \quad (8)$$

where $\mathcal{B}(\mathbf{n}) = \sum_{\mathbf{m} \subseteq \mathbf{n}} b(\mathbf{m})$. The average of $\delta\mathcal{A} = \mathcal{A} - \langle \mathcal{A} \rangle$ corresponding to a given quantity a in the nonequilibrium state represented by (8) is written as $\langle \delta\mathcal{A} \rangle_b = \langle \delta\mathcal{A} \delta\mathcal{B} \rangle = \langle a|Q|b\rangle$, where the matrix elements of Q have the form

$$\langle a|Q|b\rangle = \sum_{i,j,k} \int d\mathbf{i} d\mathbf{j} d\mathbf{k} [f_{i+j+k} - \delta_{k,0} f_i f_j] a_{i+k} b_{j+k}. \quad (9)$$

For example,

$$\begin{aligned} a_1 Q_{11} b_1 &= \int d1 a(1) b(1) f(1) \\ &+ \int d1 d2 a(1) b(2) h(12) f(1) f(2), \end{aligned}$$

$$\begin{aligned} a_1 Q_{12} b_2 &= \int d1 d2 a(1) b(12) f(12) \\ &+ \int d2 d3 a(3) b(12) f(12) f(3) h(12,3), \end{aligned}$$

$$\begin{aligned} a_2 Q_{22} b_2 &= \int d2 a(2) b(2) f(2) + \int d1 d2 d3 a(12) b(13) f(3) \\ &+ \int d2_a d2_b a(2_a) b(2_b) f(2_a) f(2_b) h(2_a, 2_b), \quad (10) \end{aligned}$$

where $h(12) = g(12) - 1$, $h(12,3) = g(123) - g(12)$ and

$h(12,34)=g(1234)-g(12)g(34)$. The operator Q is positively definite since $\langle a|Q|a\rangle=\langle(\delta A)^2\rangle>0$. We introduce the Liouville evolution operator for smooth potentials

$$\mathcal{L}_k=\{\cdot,\mathcal{H}_k\}=\sum_{i\in k}\mathbf{v}_i\cdot\frac{\partial}{\partial\mathbf{r}_i}-\sum_{i\neq j}\cdot\frac{\partial\phi(\mathbf{r}_{ij})}{\partial\mathbf{r}_{ij}}\frac{\partial}{\partial\mathbf{p}_i}\quad (11)$$

where $\{\alpha,\beta\}$ is the Poisson bracket defined as

$$\{\alpha,\beta\}=\sum_i\left(\frac{\partial\alpha}{\partial\mathbf{r}_i}\cdot\frac{\partial\beta}{\partial\mathbf{p}_i}-\frac{\partial\alpha}{\partial\mathbf{p}_i}\cdot\frac{\partial\beta}{\partial\mathbf{r}_i}\right)\quad (12)$$

and $\mathbf{v}=\mathbf{p}/M$. We will use the operator \mathcal{L} acting in our Hilbert space defined by $|w\rangle=\mathcal{L}|u\rangle\Leftrightarrow\mathcal{W}=\mathcal{L}\mathcal{U}$, where

$$w_k=\mathcal{L}_k u_k-\sum_{i\neq j}\frac{\partial\phi(\mathbf{r}_{ij})}{\partial\mathbf{r}_{ij}}\cdot\frac{\partial}{\partial\mathbf{p}_i}u(\mathbf{k}-j).\quad (13)$$

The conjugate of \mathcal{L} is defined by equality $|u\rangle=\mathcal{L}^\dagger|w\rangle$, where

$$u_k=-\mathcal{L}_k w_k+\int d(k+1)\sum_{i\in k}\frac{\partial\phi(\mathbf{r}_{i,k+1})}{\partial\mathbf{r}_{i,k+1}}\cdot\frac{\partial}{\partial\mathbf{p}_i}w(\mathbf{k}+1).\quad (14)$$

The evolution of a phase function a is described by the equation $\partial_t\mathcal{A}=\mathcal{L}\mathcal{A}$ or $\partial_t|a\rangle=\mathcal{L}|a\rangle$, while the evolution of probability fluctuation b differs from the above by a minus sign, $\partial_t\mathcal{B}=-\mathcal{L}\mathcal{B}$ or $\partial_t|b\rangle=-\mathcal{L}|b\rangle$. The time evolution of an average $\langle\mathcal{A}(t)\rangle_{b(0)}=\langle\mathcal{A}(0)\rangle_{b(t)}$ is governed by the equation

$$\frac{d\langle\mathcal{A}\rangle_b}{dt}=\langle\mathcal{L}\mathcal{A}\rangle_b=\langle\{\mathcal{A},\mathcal{H}\}\rangle_b=k_B T\langle\{\mathcal{A},\mathcal{B}\}\rangle.\quad (15)$$

The above observation leads to the definition of the operator L [22,23] by its matrix elements

$$\langle a|L|b\rangle=k_B T\langle\{\mathcal{A},\mathcal{B}\}\rangle=k_B T\sum_{m,i,j}\int d\mathbf{i}d\mathbf{j}d\mathbf{m}f_{i+j+m}\{a_{i+m},b_{j+m}\}.\quad (16)$$

Note that $L=-Q\mathcal{L}=\mathcal{L}^\dagger Q$. The evolution of a and b reads now

$$\partial_t Q|a\rangle=-L|a\rangle,\quad \partial_t Q|b\rangle=L|b\rangle.\quad (17)$$

The operator L has purely imaginary eigenvalues of equation $\lambda Q|b\rangle=L|b\rangle$, because it is antisymmetric,

$$\langle a|L|b\rangle=-\langle b|L|a\rangle.\quad (18)$$

The simplest operators can be written down explicitly

$$\begin{aligned} a_1 L_{11} b_1 &= k_B T \int d1 \{a(1), b(1)\} f(1), \\ a_1 L_{12} b_2 &= k_B T \int d1 d2 \{a(1), b(2)\} f(12), \\ a_2 L_{22} b_2 &= k_B T \int d2 \{a(2), b(2)\} f(2) \\ &+ \int d1 d2 d3 \{a(12), b(13)\} f(3). \end{aligned}\quad (19)$$

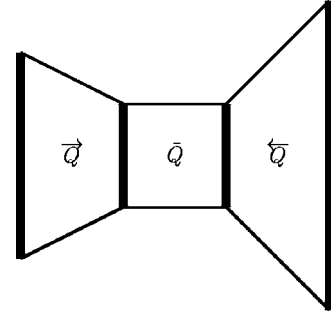


FIG. 1. Decomposition of Q into \vec{Q} , \bar{Q} , and \overleftarrow{Q} .

It is important that L satisfies two relations

$$\langle a(\mathbf{p})|L|b(\mathbf{p})\rangle=\langle b(-\mathbf{p})|L|a(-\mathbf{p})\rangle,$$

$$\langle a(\mathbf{r})|L|b(\mathbf{r})\rangle=\langle b(-\mathbf{r})|L|a(-\mathbf{r})\rangle.\quad (20)$$

They follow from the definition (16) and the Poisson bracket (12). The first one represents time reversal and is related to Onsager symmetry. It leads to the conclusion that certain cross transport coefficients should be pairwise equal [4].

We may ask what kind of vectors b such that $b_k\rightarrow 0$, if $r_{ij}\rightarrow\infty$ for arbitrary $ij\in k$, satisfy $L|b\rangle=0$. Although one can find that $b(1)=Cp_1^2/2M+\mathbf{D}\cdot\mathbf{p}_1+E$, $b_2=C\phi$ is a solution, it is by no means clear that this is the only solution [24].

IV. ENSKOG-LIKE RENORMALIZATION

Let us introduce irreducible operators \vec{Q} , \bar{Q} , and \overleftarrow{Q} [12,13] defined uniquely by $Q=\vec{Q}\bar{Q}\overleftarrow{Q}$ and $\bar{Q}_{ij}=0$, if $i\neq j$ with \bar{Q}_{ij} equal to I_{ii} (identity operator) if $i=j$ and 0 if $i>j$, $\vec{Q}=\overleftarrow{Q}^\dagger$. The operator \bar{Q} is nonzero only if its left phases are close to its right phases. In particular [12,13],

$$\bar{Q}(12|34)\rightarrow Q(1|3)Q(2|4)+Q(1|4)Q(2|3),\quad (21)$$

if $r_{ij}\rightarrow\infty$ for any pair $i\in\{12\}$ and $j\in\{34\}$.

The graphical illustration of this decomposition is presented in Fig. 1. For example, $\bar{Q}_{11}=Q_{11}$, $\bar{Q}_{21}=Q_{21}\bar{Q}_{11}^{-1}$, $\bar{Q}_{22}=Q_{22}-Q_{21}\bar{Q}_{11}^{-1}Q_{12}$. Some of these operators are expressed by well-known correlation functions

$$(\bar{Q}_{11}a_1)(1)=f(1)a(1)+f(1)\int d2f(2)h(12)a(2),\quad (22)$$

$$(\bar{Q}_{11}^{-1}a_1)(1)=a(1)/f(1)-\int d2c(12)a(2),\quad (23)$$

where $h_2=g_2-1$ is the pair correlation and Eq. (23) defines the direct correlation function c_2 [25]. For more detailed analysis of these operators, see Ref. [13]. We also define \bar{L} by $L=\vec{Q}\bar{L}\overleftarrow{Q}$. The operator \bar{L} is antisymmetric and has imaginary eigenvalues similarly as L in Eq. (18). It can be represented in the form $\bar{L}=-\vec{Q}\overleftarrow{Q}^{-1}\mathcal{L}\overleftarrow{Q}$. Since \vec{Q}_{ij} and $\overleftarrow{Q}_{ij}^{-1}$ are zero for $i>j$ and $\mathcal{L}_{ij}=0$ for $i>j+1$, we have $\bar{L}_{ij}=0$ for $|i-j|$

> 1 . We define capital vectors as $|U\rangle = \bar{Q}|u\rangle$ so that the evolution equation (17) reads

$$\partial_t \bar{Q}|B\rangle = \bar{L}|B\rangle. \quad (24)$$

The explicit form of some operators \bar{L} is

$$A_1 \bar{L}_{11} B_1 = A_1 L_{11} B_1 = k_B T \int d1 f(1) \{A(1), B(1)\},$$

$$\begin{aligned} A_1 \bar{L}_{12} B_2 &= -k_B T \int d1 d2 f(1) f(2) \{A(1), g(12)\} B(12) \\ &\quad - k_B T \int d2 d3 f(1) f(2) f(3) \{A(3), c(3|12)\} B(12), \end{aligned}$$

$$\begin{aligned} A_2 \bar{L}_{22} B_2 &= k_B T \int d2 f(12) \{A(12), B(12)\} \\ &\quad + \int d1 d2 d3 f(1) f(2) f(3) [g(123) - g(12)g(13)] \\ &\quad \times \{A(12), B(13)\}, \end{aligned} \quad (25)$$

where the conditional direct correlation function is defined as

$$\begin{aligned} c(1|23) &= g(123) - [1 + c(12) + c(13)]g(23) - \int d4 c(14) f(4) \\ &\quad \times [g(423) - g(23)]. \end{aligned} \quad (26)$$

The function $c(1|23)$ vanishes whenever r_{12} , r_{23} , or r_{31} is large. It is clear when 1 is far from 23 since then $g(123) \rightarrow g(23)$ and $c_2 \rightarrow 0$. If 3 is far from 12 then $g_3 \rightarrow g(12)$, $g(23) \rightarrow 1$, $c(13) \rightarrow 0$, so $c(1|23)$ reduces to $h(12) - c(12) - \int d4 c(14) f(4) h(42)$, which is 0 from the definition of c_2 .

Hence, the operators \bar{L}_{12} and \bar{L}_{22} have the important asymptotic property,

$$\bar{L}(1|23) \rightarrow 0, \text{ if } r_{ij} \rightarrow \infty \text{ for any pair } ij \in \mathbf{3},$$

$$\begin{aligned} \bar{L}(12|34) &\rightarrow \bar{L}(1|3) \bar{Q}(2|4) + \bar{L}(1|4) \bar{Q}(2|3) + \bar{L}(2|3) \bar{Q}(1|4) \\ &\quad + \bar{L}(2|4) \bar{Q}(1|3), \end{aligned} \quad (27)$$

if $r_{ij} \rightarrow 0$ for any pair $i \in \{12\}$ and $j \in \{34\}$.

The above observation leads to the conclusion that the motion of correlation outside the correlation sphere is just the free independent mean-field motion

$$B(12, t) \rightarrow \int d3 d4 S(1|3; t) S(2|4; t) B(34, 0), \quad (28)$$

where $S_{11}(t) = \exp(t \bar{Q}_{11}^{-1} \bar{L}_{11})$.

We present a counterpart of the linearized Enskog equation for smooth interactions by truncation of the Hilbert space, taking $b_k \equiv 0$ for $k=3, 4, \dots$ in (8). The counterpart of the Enskog equation [7,8] consists then of two equations,

$$\partial_t \bar{Q}_{11} b_1 + \partial_t \bar{Q}_{12} b_2 = L_{11} b_1 + L_{12} b_2,$$

$$\partial_t \bar{Q}_{21} b_1 + \partial_t \bar{Q}_{22} b_2 = L_{21} b_1 + L_{22} b_2. \quad (29)$$

Note that, due to the fact that \bar{Q}_{ij} vanishes for $i > j$, the truncation of vectors denoted by small letters is equivalent to the truncation of capital vectors. The Enskog-like equation (29) can be rewritten in the form

$$\begin{aligned} \partial_t \bar{Q}_{11} B_1 &= \bar{L}_{11} B_1 + \bar{L}_{12} B_2, \\ \partial_t \bar{Q}_{22} B_2 &= \bar{L}_{21} B_1 + \bar{L}_{22} B_2. \end{aligned} \quad (30)$$

The important case is when the volume of interaction is much smaller than the average space occupied by one particle—the Grad limit. We achieve this limit by reducing density at constant temperature.

In particular, we get in Grad limit,

$$f(12) \rightarrow f(1) f(2) \exp\left(-\frac{\phi(\mathbf{r}_{12})}{k_B T}\right),$$

$$\bar{Q}_{11} \rightarrow f(1), \quad \bar{Q}_{22} \rightarrow f(12),$$

$$\bar{Q}_{21} a_1 \rightarrow f(12) [a(1) + a(2)], \quad \bar{L}_{11} \rightarrow -f(1) \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1},$$

$$\bar{L}_{21} B_1 \rightarrow f(12) \frac{\partial \phi}{\partial \mathbf{r}_{12}} \cdot \left(\frac{\partial B(1)}{\partial \mathbf{p}_1} - \frac{\partial B(2)}{\partial \mathbf{p}_2} \right),$$

$$\bar{L}_{22} \rightarrow f(12) \left(\frac{\partial \phi}{\partial \mathbf{r}_{12}} \cdot \frac{\partial}{\partial \mathbf{p}_1} - \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + 1 \leftrightarrow 2 \right). \quad (31)$$

The evolution is governed by the following set of equations:

$$\begin{aligned} \partial_t B_1 &= \bar{Q}_{11}^{-1} (\bar{L}_{11} B_1 + \bar{L}_{12} B_2) \\ &= -\mathbf{v}_1 \cdot \frac{\partial B(1)}{\partial \mathbf{r}_1} + f^{-1}(1) \int d2 \frac{\partial \phi}{\partial \mathbf{r}_{12}} \cdot \frac{\partial [f(12) B(12)]}{\partial \mathbf{p}_1}, \\ \partial_t B_2 &= \bar{Q}_{22}^{-1} (\bar{L}_{22} B_2 + \bar{L}_{21} B_1) \\ &= \left(\frac{\partial \phi}{\partial \mathbf{r}_{12}} \cdot \frac{\partial [B(12) + B(1)]}{\partial \mathbf{p}_1} - \mathbf{v}_1 \cdot \frac{\partial B(12)}{\partial \mathbf{r}_1} + 1 \leftrightarrow 2 \right). \end{aligned} \quad (32)$$

In the Grad limit it corresponds to the linear Boltzmann equation as we show in Appendix A.

The Boltzmann equation implies the H theorem for the function $H(t) = -B_1 \bar{Q}_{11} B_1$, namely, $\pm H'(t) \geq 0$ for $\pm t > 0$. Note, however, that total entropy $\delta S = -\langle B | \bar{Q} | B \rangle$ remains constant, leaving us with the conclusion that one-particle entropy grows by decreasing two-particle entropy. Indeed, two-particle correlations, once created, escape to infinity due to the property (28) of evolution operator and the escape rate is related to one-particle entropy production.

For higher densities, the potential ϕ in Eqs. (32) should be replaced by effective potential $\phi^{\text{eff}}(r) = -k_B T \ln g(r)$. However, it may lead to the appearance of an effectively attractive potential (even for hard spheres), which allows the

existence of bound states. The bound states can be destroyed by three-particle corrections which are absent in our picture. This leads to linear dependence on density for bulk viscosity [26].

The problem of the H theorem in the truncated space reduces then rather to the question: what functions ψ satisfy $\bar{L}|\psi\rangle = i\lambda\bar{Q}|\psi\rangle$ and $\langle\psi^*|\bar{Q}|\psi\rangle < \infty$. For an attractive potential, bound states are such functions at the two-particle level. Thus, shifting of the truncation level may be necessary in some cases.

V. TRANSPORT COEFFICIENTS

The Green-Kubo formulas for transport coefficients can be reformulated in terms of our reduced Hilbert space, Q and L . Let us consider a set of five hydrodynamic modes \tilde{n} , $\tilde{\mathbf{v}}$, and \tilde{e} , depending on a wave vector \mathbf{q} , corresponding to density, velocity, and energy fluctuations, defined $\tilde{n}_1 = e^{i\mathbf{q}\cdot\mathbf{r}_1}$, $\tilde{\mathbf{v}}_1 = e^{i\mathbf{q}\cdot\mathbf{r}_1}\mathbf{v}_1$, $\tilde{e}_1 = e^{i\mathbf{q}\cdot\mathbf{r}_1}Mv_1^2/2$, $\tilde{e}_2 = e^{i\mathbf{q}\cdot(\mathbf{r}_1+\mathbf{r}_2)/2}\phi(r_{12})$. It is useful to replace the energy mode by the temperature mode $|\tilde{t}\rangle = |\tilde{e}\rangle - (\partial n/\partial n)_T|\tilde{n}\rangle$, where $(\partial n/\partial n)_T = e + p/n - T(\partial p/\partial T)_n/n$. We have fluctuation formulas to the first order in \mathbf{q} : $\langle\tilde{n}^*|Q|\tilde{n}\rangle \approx Vnk_B T(\partial n/\partial p)_T$, $\langle\tilde{t}^*|Q|\tilde{t}\rangle \approx Vnk_B T^2 c_V$, $\langle\tilde{\mathbf{v}}^*|Q|\tilde{\mathbf{v}}\rangle \approx \hat{V}Vnk_B T/M$, where V , n , T , p , c_V , and e denote volume, concentration, temperature, pressure, specific heat per particle at constant volume, and energy per particle, respectively. The matrix elements of our dynamic operator L are to the second order in \mathbf{q}

$$\langle\tilde{n}^*|L|\tilde{\mathbf{v}}\rangle = -\langle\tilde{\mathbf{v}}|L|\tilde{n}^*\rangle \approx -i\mathbf{q}Vnk_B T/M,$$

$$\langle\tilde{\mathbf{v}}^*|L|\tilde{t}\rangle = -\langle\tilde{t}|L|\tilde{\mathbf{v}}^*\rangle \approx -i\mathbf{q}Vnk_B T^2 \left(\frac{\partial p}{\partial T}\right)_n / M. \quad (33)$$

To find transport coefficients, we assume that in the limit $\mathbf{q} \rightarrow 0$, only five eigenfunctions corresponding to hydrodynamic modes give eigenvalues tending to 0 [2]. In this limit, we have our modes corrected by a nonhydrodynamical part proportional to \mathbf{q} , $|a'\rangle = |\tilde{a}\rangle + |a^\perp\rangle$, where $\langle\tilde{a}|Q|b^\perp\rangle = 0$ for $a, b = n, \mathbf{v}, t$. These modes must obey linearized Navier-Stokes equations to the second order in \mathbf{q} ,

$$\frac{d|n'\rangle}{dt} = -i\mathbf{q} \cdot |\mathbf{v}'\rangle,$$

$$\frac{d|\mathbf{v}'\rangle}{dt} \approx -\left(\frac{\partial p}{\partial n}\right)_T \frac{i\mathbf{q}|n'\rangle}{M} - \frac{i\mathbf{q}|T'\rangle}{Mnc_V} \left(\frac{\partial p}{\partial T}\right)_n - \nu q^2|\mathbf{v}'\rangle - (\xi + \nu/3)\mathbf{q}(\mathbf{q} \cdot |\mathbf{v}'\rangle),$$

$$\frac{d|T'\rangle}{dt} \approx -T \left(\frac{\partial p}{\partial T}\right)_n i\mathbf{q} \cdot |\mathbf{v}'\rangle/n - \kappa q^2|T'\rangle/c_V, \quad (34)$$

where ν , ξ , and κ denote kinematic shear viscosity, bulk viscosity, and thermal conductivity, respectively.

We first find expressions for currents up to the first order in \mathbf{q} ,

$$\mathcal{L}\tilde{\mathcal{N}} = i\mathbf{q} \cdot \mathcal{J}_n, \quad \mathcal{L}\tilde{\mathcal{V}} \approx i\mathbf{q} \cdot \hat{\mathcal{J}}_v, \quad \mathcal{L}\tilde{\mathcal{E}} \approx i\mathbf{q} \cdot \mathcal{J}_e \quad (35)$$

and $|\mathbf{j}_t\rangle = |\mathbf{j}_e\rangle - (\partial n/\partial n)_T|\mathbf{j}_n\rangle$. We denote by j_a , the current corresponding to a hydrodynamic mode a . Due to Eq. (11) we have

$$\begin{aligned} \mathbf{j}_n &= \tilde{\mathbf{v}}, & \hat{j}_{v,1} &= \mathbf{v}_1\mathbf{v}_1, & \hat{j}_{v,2} &= -\frac{\mathbf{r}_{12}}{M} \frac{\partial\phi(r_{12})}{\partial\mathbf{r}_{12}}, \\ \mathbf{j}_{e,1} &= \frac{Mv_1^2}{2}\mathbf{v}_1, & \mathbf{j}_{e,2} &= -\mathbf{r}_{12} \frac{\partial\phi(r_{12})}{\partial\mathbf{r}_{12}} \cdot \mathbf{u}_{12} + \mathbf{u}_{12}\phi(r_{12}), \end{aligned} \quad (36)$$

where $\mathbf{u}_{12} = (\mathbf{v}_1 + \mathbf{v}_2)/2$.

The final Green-Kubo expressions for transport coefficients are

$$\begin{aligned} \nu &= -\frac{3\langle\check{J}_v|:\bar{Q}\bar{L}^{-1}\bar{Q}|\check{J}_v\rangle}{10\langle\tilde{\mathbf{v}}|:Q|\tilde{\mathbf{v}}\rangle_{q=0}} = -\frac{\langle J_v^{xy}|\bar{Q}\bar{L}^{-1}\bar{Q}|J_v^{xy}\rangle}{Vnk_B Tn/M}, \\ \xi &= -\frac{3\langle J_v^\perp|\bar{Q}\bar{L}^{-1}\bar{Q}|J_v^\perp\rangle}{\langle\tilde{\mathbf{v}}|:Q|\tilde{\mathbf{v}}\rangle_{q=0}} = -\frac{\langle J_v^\perp|\bar{Q}\bar{L}^{-1}\bar{Q}|J_v^\perp\rangle}{Vnk_B Tn/M}, \\ \kappa &= -\frac{c_V\langle J_t^\perp|\bar{Q}\bar{L}^{-1}\bar{Q}|J_t^\perp\rangle}{3\langle\tilde{t}|Q|\tilde{t}\rangle_{q=0}} = -\frac{\langle J_t^{\perp x}|\bar{Q}\bar{L}^{-1}\bar{Q}|J_t^{\perp x}\rangle}{Vnk_B T^2}. \end{aligned} \quad (37)$$

The perpendicular currents are defined as

$$\begin{aligned} |\check{J}_v\rangle &= |\hat{J}_v\rangle - \hat{1}|J_v\rangle, & |J_v\rangle &= \frac{1}{3}\text{tr}|\hat{J}_v\rangle, \\ |J_v^\perp\rangle &= |J_v\rangle - \frac{1}{Mnc_V} \left(\frac{\partial p}{\partial T}\right)_n |\tilde{t}\rangle - \left(\frac{\partial p}{\partial n}\right)_T |\tilde{n}\rangle/M, \\ |J_t^\perp\rangle &= |J_t\rangle - \frac{T}{n} \left(\frac{\partial p}{\partial T}\right)_n |\tilde{\mathbf{v}}\rangle. \end{aligned} \quad (38)$$

We stress that \bar{L} is inverted in the reduced Hilbert space. Moreover, due to Eq. (18) the spectrum of \bar{L} is imaginary and includes zero. In order to get positive transport coefficients and more generally—to get dissipation for positive times—it is necessary to put a pole-shifting rule into \bar{L}^{-1} . Namely, $\bar{L}^{-1} \rightarrow (\bar{L} - \epsilon\bar{Q})^{-1}$ with $\epsilon \rightarrow 0_+$. A simple example that it really leads to proper values of transport coefficients is given in Appendix B.

The main difference between this and former Green-Kubo relations is that classical derivations lead to an infinite ladder of equations. Therefore, those relations can be checked only by computer simulations. In our approach, it is also possible to carry out calculations more analytically, i.e., using the Enskog-like approximation from Sec. IV. We need two-point and three-point equilibrium correlation functions then so the problem is much more complicated than hard spheres.

We also remember that to calculate ξ , we need scalar base, κ —vector base, and ν —traceless tensor base for elements of \bar{L} and \bar{Q} .

VI. SUTHERLAND FORMULA

At first, we shall consider a system of elastic, but nearly hard balls. Namely, the interaction will be repulsive and changing rapidly within the distance $\Delta \ll d$, where d is the diameter of the core, that is $\phi'(r) < 0$, $\phi(r \rightarrow d) \rightarrow +\infty$, $\phi(r \geq d + \Delta) = 0$.

In this case, the perpendicular currents are as follows:

$$J_{v,1}^\perp = \left(\frac{v_1^2}{3} - \frac{k_B T}{M} \right) \frac{n}{6} \int d^3 r g(r) r \frac{d\phi}{dr}, \quad J_{v,2}^\perp = -\frac{r_{12}}{3M} \frac{d\phi}{dr_{12}},$$

$$\check{J}_{v,1}^{ij} = v_1^i v_1^j - \frac{\delta^{ij}}{3} v_1^2, \quad \check{J}_{v,2}^{ij} = -\frac{3r_{12}^i r_{12}^j - \delta^{ij} r_{12}^2}{3Mr} \frac{d\phi}{dr_{12}},$$

$$J_{t,1}^\perp = \mathbf{v}_1 (M v_1^2 - 5k_B T)/2, \quad J_{t,2}^\perp = -\mathbf{r}_{12} (\mathbf{u}_{12} \cdot \mathbf{r}_{12}) r_{12}^{-1} \frac{d\phi}{dr_{12}}. \quad (39)$$

We will calculate transport coefficients using approximations for the Boltzmann-Grad limit, Eqs. (31), but the results will be extensible to moderate densities.

We start with the easiest coefficient, bulk viscosity ξ and leave calculation of ν and κ for Appendix C. For low fraction of volume occupied by particles, we have $J_{v,1}^\perp = -2\pi n d^3 (v_1^2/3 - k_B T/M)/3$. We look for the function ψ , such that

$$(\bar{L} - \epsilon \bar{Q})|\psi\rangle = \bar{Q}|J_v^\perp\rangle, \quad (40)$$

where \bar{L} and \bar{Q} are given by (31). The solution is $\psi_1 = 0$ and

$$\psi_2 = \frac{d}{6} (\mathbf{v}'_{12} - \mathbf{v}_{12}) \cdot \boldsymbol{\sigma} \exp[-\epsilon (\mathbf{r}_{12} \cdot \mathbf{v}_{12})/v_{12}^2], \quad (41)$$

where \mathbf{v}'_{12} is the relative velocity before entering the collision, namely

$$\mathbf{v}'_{12} \cdot \boldsymbol{\sigma} = -\sqrt{(\mathbf{v}_{12} \cdot \boldsymbol{\sigma})^2 + 4\phi(r_{12})/M} \quad (42)$$

and $\boldsymbol{\sigma} = (\mathbf{r}_{12} - \mathbf{v}_{12} t_c)/d$ denotes the direction of collision, where t_c is the collision time defined by

$$v_{12}^2 t_c = \mathbf{r}_{12} \cdot \mathbf{v}_{12} - s \sqrt{(\mathbf{r}_{12} \cdot \mathbf{v}_{12})^2 - (r_{12}^2 - d^2) v_{12}^2}, \quad (43)$$

with $s = \pm 1$ for $\pm \mathbf{r}_{12} \cdot \mathbf{v}_{12} > v_{12} \sqrt{r_{12}^2 - d^2}$ and 0 otherwise. Note that in the case $s = 0$, we have $\mathbf{v}_{12} \cdot \boldsymbol{\sigma} = 0$. The function ψ_2 vanishes for $\mathbf{r}_{12} \rightarrow \infty$, because we have $\mathbf{v}'_{12} = \mathbf{v}_{12}$ for $\mathbf{r}_{12} \cdot \mathbf{v}_{12} < 0$. To see that ψ is the solution of Eq. (40), it is enough to approximate $\boldsymbol{\sigma} \approx \mathbf{r}_{12}/d$ for $r_{12} < d + \Delta$ and neglect all terms containing $\partial \boldsymbol{\sigma} / \partial r_{12}$ in this region because they are finite on the set of a very small measure.

The bulk viscosity ξ is then equal

$$\xi = -\frac{J_{v,2}^\perp \bar{Q}_{22} \psi_2}{V k_B T n / M}$$

$$= -\frac{nd \sqrt{\pi M}}{18 (k_B T)^{3/2}} \int_{-\infty}^{+\infty} dv \int_0^\infty dr \exp\left(-\frac{Mv^2 + 4\phi}{4k_B T}\right)$$

$$\times r^3 \frac{d\phi}{dr} \sqrt{v^2 + 4\phi/M}. \quad (44)$$

We use the approximation $r^3 \approx d^3$ and substitute new variables k and α such that $v = (4k_B T/M)^{1/2} \sqrt{k} \cos \alpha$ and $\phi(r) = k_B T k \sin^2 \alpha$. In our new variables, ξ reads

$$\xi = \frac{2nd^4 \sqrt{\pi k_B T/M}}{9} \int_0^\infty dk \int_0^\pi d\alpha e^{-k} k \sin \alpha = \frac{4nd^4 \sqrt{\pi k_B T/M}}{9}. \quad (45)$$

Let us consider expansion of transport coefficients of hard cores with a smooth tail $\phi^s = -k_B T \ln g$ in powers of nd^3 and $\beta = 1/k_B T$ around hard-sphere results, namely,

$$\lambda = \lambda_0 (1 + A nd^3 + \beta S + B \beta nd^3 + C \ln(nd^3)(nd^3)^2 + D \beta^2 \dots) \quad (46)$$

for $\lambda = \xi, \nu, \kappa$, where S, A, B, C, D are independent of n and T . The expansion is not analytic because of long-range dynamical three-particle correlations [6]. Both ν_0 and κ_0 behave $\sim (k_B T)^{1/2}/nd^2$, but $\xi_0 \sim (nd^3)^2 \sqrt{k_B T}/nd^2$. The bulk viscosity for attractive interaction has also a term $\sim (nd^3)/nd^2$. It comes from the fact that particles are sometimes in a bound state which lasts up to the collision with a third particle [26]. In this case, the expansion has the form

$$\xi = \xi_0 (1 + A nd^3 + S/k_B T + \dots) + \xi_1 (1 + D nd^3 + \dots), \quad (47)$$

where $\xi_1 \sim nd^3 (k_B T)^{-3}/nd^2$. The Sutherland formula [2,3] is the expression for S .

Taking into account that we consider only the low-density limit, one can neglect all terms \bar{L}_{ij} with $i > 2$ or $j > 2$, since they have contribution to higher density corrections—from collisions with at least a third particle.

It is convenient to divide the interaction of the core and the smooth tail, $\phi(r) = \phi^c(r) + \phi^s(r)$, $|J\rangle = |J^c\rangle + |J^s\rangle$, $\bar{Q} = \bar{Q}^c + \bar{Q}^s$, $\bar{L} = \bar{L}^c + \bar{L}^s$. The Green-Kubo expressions can be expanded to the first order in β as follows:

$$\langle J | \bar{Q} (\bar{L} - \epsilon \bar{Q})^{-1} \bar{Q} | J \rangle$$

$$\approx \langle J^c | \bar{Q}^c (\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{Q}^c | J^c \rangle + 2 \langle J^s | \bar{Q}^c (\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{Q}^c | J^c \rangle$$

$$+ 2 \langle J^c | \bar{Q}^s (\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{Q}^c | J^c \rangle - \langle J^c | \bar{Q}^c (\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{L}^s$$

$$\times (\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{Q}^c | J^c \rangle. \quad (48)$$

Taking into account that

$$J_{v,2}^\perp = -\frac{r_{12}}{3M} \frac{d\phi^s}{dr_{12}} - \frac{2}{3M} \phi^s, \quad \bar{Q}_{22}^s = -f^c(12) \beta \phi^s,$$

$$A_2 \bar{L}_{21}^s B_1 = \int d1 d2 f(1) f(2) A(12) \{g^c(12) \phi^s, B(1)\},$$

$$A_2 \bar{L}_{22}^s B_2 = -\int d2 f^c(12) \phi^s \{A(12), B(12)\}, \quad (49)$$

we arrive at

$$\begin{aligned} & \langle J_v^\perp | \bar{Q}(\bar{L} - \epsilon \bar{Q})^{-1} \bar{Q} | J_v^\perp \rangle \\ & \approx [1 - \beta \phi(d_+)] \langle J_v^\perp | \bar{Q}^c(\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{Q}^c | J_v^\perp \rangle + 2J_{v,2}^{s\perp} \bar{Q}_{22} \psi_2. \end{aligned} \quad (50)$$

In the above expression, we used the fact that

$$\langle J^c | \bar{Q}^c(\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{L}^s(\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{Q}^c | J^c \rangle = \psi_2(-\mathbf{v}) \bar{L}_{22}^s \psi_2(\mathbf{v}), \quad (51)$$

which is nonzero only for $r_{12} \approx d$. Note the use of Onsager symmetry (20) in the last equality. Hence, in this case, we can make approximations $\phi^s \approx \phi^s(d^+)$ and $\bar{L}_{22}^s = -\phi^s(d^+) \bar{L}_{22}^c / k_B T$. In the case of hard spheres, we can perform the calculation on the straight lines with constant σ and \mathbf{v}_{12} , namely,

$$\begin{aligned} 2J_{v,2}^{s\perp} \bar{Q}_{22} \psi_2 &= -\frac{Vn^2 d}{6} \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 f(1) f(2) \int d^3 \mathbf{r} (gJ_v^{s\perp})(\mathbf{r}) \\ & \quad \times |\mathbf{v}_{12} \cdot \sigma| \\ &= -\frac{Vn^2 d \sqrt{k_B T / M \pi^3}}{6} \int d^2 \hat{\mathbf{v}} \int d^2 \sigma \int_{xd}^\infty dl (gJ_v^{s\perp})(\mathbf{r}) \\ & \quad \times |\hat{\mathbf{v}}_{12} \cdot \sigma| \\ &= -\frac{8Vn^2 d^4 \sqrt{\pi k_B T / M}}{3} \int_0^1 dx \int_1^\infty dy \frac{yx^2 (gJ_v^{s\perp})(yd)}{\sqrt{y^2 - 1 + x^2}} \\ &= -\frac{2Vn^2 d^4 \sqrt{\pi k_B T / M}}{3} \int_d^\infty dy (gJ_v^{s\perp})(yd) y \\ & \quad \times \left[2y + (1 - y^2) \ln \left(\frac{y+1}{y-1} \right) \right], \end{aligned} \quad (52)$$

where $l^2 = r^2 - d^2 + d^2 x^2$ and $x = |\hat{\mathbf{v}}_{12} \cdot \sigma|$.

Hence, bulk viscosity has the form

$$\begin{aligned} \xi &= \xi_0 \left[G(1_+) + \frac{1}{2} \int_{1_+}^\infty dy (yG' + 2G \ln G) \right. \\ & \quad \left. \times [2y^2 + y(1 - y^2)] \ln \left(\frac{y+1}{y-1} \right) \right], \end{aligned} \quad (53)$$

where ξ_0 is bulk viscosity for dilute hard spheres and $G(y) = g(yd)$. For low densities, we obtain

$$S = \int_1^\infty dy \left[2y^2 - y^3 \ln \left(\frac{y+1}{y-1} \right) \right] \phi^s(yd). \quad (54)$$

In particular, for the square well of depth E and radius R , we have

$$S = -\frac{E(q^2 - 1)}{4} \left[2q - (q^2 + 1) \ln \left(\frac{q+1}{q-1} \right) \right], \quad (55)$$

where $q = R/d$. For large q , we have $S \rightarrow 2qE/3$. It is quite opposite to the theory of Davis, Rice, and Sengers (DRS) [17] and van Beijeren, Karkheck, and Sengers [27,28], where $S_{DRS} = E$, $\xi_{vBKS} = \xi_0(1 + \pi/2q^2)$.

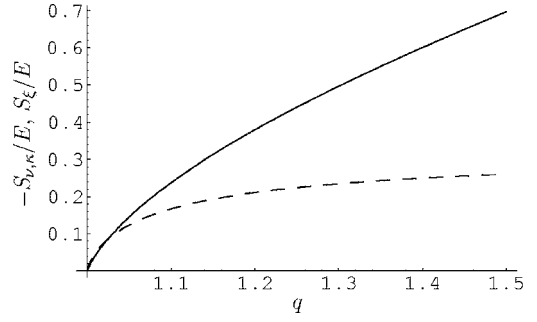


FIG. 2. Plots of S_ξ/E (solid line) and $-S_{\nu,\kappa}/E$ (dashed line) for a square-well fluid in function of q .

We stress that the Sutherland correction for bulk viscosity in the case of an attractive well is dominant in the range of parameters $(nd^3)^{2/5} \gg E/k_B T \gg nd^3$.

In the case of shear viscosity and thermal conductivity at low densities, the problem reduces to corrections predicted by the Boltzmann equation—the standard Sutherland formula [2,3].

The calculation using our method is performed in Appendix D and gives the same result as by the Boltzmann equation, namely

$$S = \int_1^\infty dy \left[\frac{15y^5 - 12y^3 + y}{2} \ln \left(\frac{y+1}{y-1} \right) + y^2(7 - 15y^2) \right] \phi^s(yd) \quad (56)$$

for both ν and κ . For the square well with $q = R/d$ and depth E , we get

$$S = -E \left[\frac{q^2(q^2 - 1)(5q^2 - 1)}{4} \ln \left(\frac{q+1}{q-1} \right) + \frac{2 + 13q^3 - 15q^5}{6} \right]. \quad (57)$$

Note that for $q \rightarrow \infty$, we have $S \rightarrow -E/3$, while $S_{DRS} = -E$. The results are summarized in Fig. 2.

VII. DISCUSSION

We have obtained a set of closed, symmetric, reversible kinetic equations (30) by simple truncation of a general equation (24) on a two-particle level. Moreover, it is possible to include further corrections to the evolution symmetrically by truncation of (24) on a higher level, e.g., including three-particle motion. Although we cannot prove an H theorem like for the Boltzmann equation, the separation property (28) of the evolution operator is an equivalent argument for irreversibility. Our approach allows to get proper values of transport coefficients. We have compared our results to some existing kinetic equations, like DRS theory [17], by computing high temperature corrections for transport coefficients—Sutherland formula, especially in the case of square-well fluid.

Many existing theories, including DRS, try to reduce the description of fluid to a one-particle distribution function and assume molecular chaos on many particle distributions. This is incorrect in the low-density limit because correlations in

finite-time collisions cannot be represented by a simple product of distributions. The most evident discrepancy occurs between the Boltzmann equation and DRS theory in the low-volume fraction limit. The values of transport coefficients are different from those predicted by DRS, as we have shown by comparing their high temperature corrections to Boltzmann values.

Moreover, our description allows us to find such a correction to bulk viscosity, which is impossible to get from the Boltzmann equation as it vanishes in the Grad limit. Once again, our result is different from DRS, because we allow propagation of dynamical correlations.

We have considered only very simple models, but the presented method is more general. It permits us to recover density corrections for transport coefficients predicted by Senegers [9] if we add \bar{L}_{23} , \bar{L}_{32} , and \bar{L}_{33} to our set of equations, since the dynamics of three particles is then necessary. The method is especially interesting for the calculation of bulk viscosity. Continuous potentials are certainly more difficult than simple hard spheres, but it should be possible numeri-

cally. We hope to investigate these issues in future papers.

The last problem worth analysis is the contribution of bound states to bulk viscosity (47). Although there exist some results concerning shear viscosity and thermal conductivity [29], the full answer remains to be found.

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APPENDIX A

We shall find global solution $B(1, t)$ and $B(12, t)$ of Eqs. (32) with the initial condition $B(12, 0)=0$. To achieve this goal, we need some auxiliary definitions. Let d denote a certain length greater than the range of ϕ . Let t_c denote the collision time [given, e.g., by Eq. (43)]. Our solution is

$$B(12, t) = \begin{cases} B(1_{\mp}, t') + B(2_{\mp}, t') - B(1, t') - B(2, t') & \text{for } t' > 0 \text{ and } \pm t_c > 0, \\ B(1_{\mp}, t) + B(2_{\mp}, t) - B(1, t) - B(2, t) & \text{for } \pm t > 0 \text{ and } r < d, \\ 0 & \text{otherwise,} \end{cases} \quad (\text{A1})$$

where 1_{\pm} and 2_{\pm} denote coordinates of particles 1 and 2 at $r_{12}=d$ after/before collision and $t'=t-t_c$ unless it means evolution of collision trajectory (to 12_{\pm}) through the time point $t=0$. In the latter case, 1_{\pm} and 2_{\pm} correspond to phase points at $t=0$ according to the standard free Liouville evolution. The function $B(1)$ changes at times and lengths much greater than the characteristic times and lengths of collisions. The second of Eqs. (32), which is important only inside the collision sphere, takes hence the form

$$\left(\frac{\partial \phi}{\partial \mathbf{r}_{12}} \cdot \frac{\partial}{\partial \mathbf{p}_{12}} - \mathbf{v}_{12} \cdot \frac{\partial}{\partial \mathbf{r}_{12}} \right) [B(1_{\pm}) + B(2_{\pm})] = 0. \quad (\text{A2})$$

Since $f(12)$ contains only invariants of motion, we have also

$$\left(\frac{\partial \phi}{\partial \mathbf{r}_{12}} \cdot \frac{\partial}{\partial \mathbf{p}_{12}} - \mathbf{v}_{12} \cdot \frac{\partial}{\partial \mathbf{r}_{12}} \right) f(12) [B(1_{\pm}) + B(2_{\pm})] = 0. \quad (\text{A3})$$

After integration of the above expression with $\int d^2 \theta(d-r_{12})$, the last term in the first of Eqs. (32) is equal to

$$d^2 \int d^3 \mathbf{p}_2 d^2 \hat{\mathbf{r}}_{12} \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} f(1) f(2) [B(1_{\pm}) + B(2_{\pm})]. \quad (\text{A4})$$

If $\pm \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} > 0$, then $B(1_{\pm}) + B(2_{\pm}) = B(1) + B(2)$ and we have

$$d^2 \int d^3 \mathbf{p}_2 d^2 \hat{\mathbf{r}}_{12} \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} f(1) f(2) [\theta(\mp \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}) (B(1_{\pm}) + B(2_{\pm})) + \theta(\pm \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}) (B(1) + B(2))]. \quad (\text{A5})$$

Taking into account that $B(2) \simeq B(\mathbf{r}_1, \mathbf{v}_2)$, $B(1_{\pm}) \simeq B(\mathbf{r}_1, \mathbf{v}_{1\pm})$, and $B(2_{\pm}) \simeq B(\mathbf{r}_1, \mathbf{v}_{2\pm})$, we arrive at

$$d^2 \int d^3 \mathbf{p}_2 d^2 \hat{\mathbf{r}}_{12} \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} f(1) f(2) [B(\mathbf{r}_1, \mathbf{v}_{1\pm}) + B(\mathbf{r}_1, \mathbf{v}_{2\pm})], \quad (\text{A6})$$

which is equivalent to

$$(C_{11}^{\pm} B_1) = d^2 \int d^3 \mathbf{p}_2 d^2 \hat{\mathbf{r}}_{12} \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} f(1) f(2) [\theta(\mp \mathbf{v}_{12} \cdot \hat{\mathbf{r}}) (B(\mathbf{r}_1, \mathbf{v}_{1\pm}) + B(\mathbf{r}_1, \mathbf{v}_{2\pm})) + \theta(\pm \mathbf{v}_{12} \cdot \hat{\mathbf{r}}) (B(\mathbf{r}_1, \mathbf{v}_1) + B(\mathbf{r}_1, \mathbf{v}_2))]. \quad (\text{A7})$$

This is exactly the Boltzmann collision term [1,2]. Hence, $B(1, t)$ must be the solution of Boltzmann equation for $\pm t > |t_0|$, namely,

$$\partial_t B(1, t) = -\mathbf{v}_1 \cdot \frac{\partial B(1, t)}{\partial \mathbf{r}_1} + f^{-1}(1) (C_{11}^{\mp} B_1)(1, t) \quad \text{for } \pm t > |t_0|, \quad (\text{A8})$$

where t_0 denotes maximal time of duration of a collision.

APPENDIX B

Our expressions for transport coefficients (37) can be related to time integrals

$$\begin{aligned} -\langle J|\bar{Q}(\bar{L}-\epsilon\bar{Q})^{-1}\bar{Q}|J\rangle &= \int_0^\infty dt \langle J(0)|\bar{Q}|J(t)\rangle \\ &= \int_0^\infty dt \langle J(0)|\bar{Q}|J(-t)\rangle \\ &= \int_{-\infty}^{+\infty} dt \langle J(t)|\bar{Q}|J(-t)\rangle, \end{aligned} \quad (\text{B1})$$

where $J(0)=J$ and $\partial_t \bar{Q}|J(t)\rangle = -\bar{L}|J(t)\rangle$. As a very simple example that the Green-Kubo integral can really have positive value if \bar{L} has only imaginary eigenvalues, let us consider the following model. The operators \bar{Q} and \bar{L} will be defined $\langle f|\bar{Q}|g\rangle = \int_{-\infty}^{+\infty} dx f(x)g(x)$ and $\langle f|\bar{L}|g\rangle = \int_{-\infty}^{+\infty} dx f(x)g'(x)$, respectively, with $J(t) = \theta(1-|x-t|)$ and $J=J(0)$. Then

$$\psi = (\bar{L} - \epsilon\bar{Q})^{-1}\bar{Q}J = \begin{cases} 0 & \text{for } x > 1, \\ \epsilon^{-1}(e^{\epsilon(x-1)} - 1) & \text{for } |x| < 1, \\ \epsilon^{-1}(e^{-\epsilon} - e^\epsilon)e^{\epsilon x} & \text{for } x < -1. \end{cases} \quad (\text{B2})$$

In the limit $\epsilon \rightarrow 0$, we get

$$\psi = \begin{cases} 0 & \text{for } x > 1, \\ x-1 & \text{for } |x| < 1, \\ -2 & \text{for } x < -1. \end{cases} \quad (\text{B3})$$

It is easy to check that Eq. (B1) holds.

Another point of view is Fourier transform $\tilde{J}(k) = \sqrt{2/\pi} \sin k/k$. Then we have the integral

$$\begin{aligned} \langle J|\bar{Q}(\epsilon\bar{Q}-\bar{L})^{-1}\bar{Q}|J\rangle &= \frac{2}{\pi} \int_{-\infty}^{+\infty} dk \frac{\sin^2 k}{k^2(\epsilon+ik)} \\ &= \frac{e^{-2\epsilon} + 2\epsilon - 1}{\epsilon^2} \rightarrow 2. \end{aligned} \quad (\text{B4})$$

Moreover, if we introduce periodic boundary conditions, $-\Lambda/2 \leftrightarrow \Lambda/2$, then $\psi_\Lambda = \psi - \epsilon^{-1}(e^\epsilon - e^{-\epsilon})(e^{\epsilon\Lambda} - 1)^{-1}e^{\epsilon x}$ and

$$\langle J|\bar{Q}(\epsilon\bar{Q}-\bar{L})^{-1}\bar{Q}|J\rangle = \frac{e^{-2\epsilon} + 2\epsilon - 1}{\epsilon^2} + \left(\frac{e^\epsilon - e^{-\epsilon}}{\epsilon}\right)^2 (e^{\epsilon\Lambda} - 1)^{-1}, \quad (\text{B5})$$

which tends to $(\epsilon\Lambda)^{-1}$ for small ϵ . Thus, one must first take the limit $\Lambda \rightarrow \infty$ and then $\epsilon \rightarrow 0$. In other words, the thermodynamic limit must be performed first

$$(\text{correct}) \lim_{\epsilon \rightarrow 0} \lim_{\infty} \neq \lim_{\infty} \lim_{\epsilon \rightarrow 0} (\text{incorrect}). \quad (\text{B6})$$

For a fluid in finite volume V , we must keep $\epsilon \gg \sqrt{k_B T / M d^2} / V$.

APPENDIX C

In order to calculate ν and κ , it is convenient to introduce the dimensionless Boltzmann collision operator B defined for functions of $\bar{\mathbf{v}}_1$,

$$(Bf)(\bar{\mathbf{v}}_1) = \frac{1}{2(2\pi)^{3/2}} \int d^3\bar{\mathbf{v}}_2 d^2\boldsymbol{\sigma} e^{-\bar{v}_2^2/2} |\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12}| [f(\bar{\mathbf{v}}_1^c) + f(\bar{\mathbf{v}}_2^c) - f(\bar{\mathbf{v}}_1) - f(\bar{\mathbf{v}}_2)], \quad (\text{C1})$$

where $\bar{\mathbf{v}}_1^c = \bar{\mathbf{v}}_1 - \boldsymbol{\sigma}(\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})$ and $\bar{\mathbf{v}}_2^c = \bar{\mathbf{v}}_2 + \boldsymbol{\sigma}(\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})$. Now, let Π^{ij} satisfy the equation

$$B\Pi^{ij} = \bar{v}_1^i \bar{v}_1^j - \delta^{ij} \bar{v}_1^2 / 3. \quad (\text{C2})$$

The solution of the equation $(\bar{L} - \epsilon\bar{Q})|G^{ij}\rangle = \bar{Q}|J_v^{ij}\rangle$ is

$$|G^{ij}\rangle = (1 + 4\pi n d^3 / 15)(n d^2)^{-1} (k_B T / M)^{1/2} |R^{ij}\rangle + |\psi^{ij}\rangle,$$

$$R_1^{ij} = \Pi^{ij}(\bar{\mathbf{v}}_1), \quad \psi_1^{ij} = 0,$$

$$\begin{aligned} R_2^{ij} &= [\Pi^{ij}(\bar{\mathbf{v}}_1') + \Pi^{ij}(\bar{\mathbf{v}}_2') - \Pi^{ij}(\bar{\mathbf{v}}_1) - \Pi^{ij}(\bar{\mathbf{v}}_2)] \\ &\quad \times \exp[-\epsilon(\mathbf{r}_{12} \cdot \mathbf{v}_{12}) / v_{12}^2], \end{aligned}$$

$$\psi_2^{ij} = \frac{d}{2} (\sigma^i \sigma^j - \delta^{ij} / 3) \boldsymbol{\sigma} \cdot (\mathbf{v}'_{12} - \mathbf{v}_{12}) \exp[-\epsilon(\mathbf{r}_{12} \cdot \mathbf{v}_{12}) / v_{12}^2], \quad (\text{C3})$$

where $\bar{\mathbf{v}} = \mathbf{v} \sqrt{M / k_B T}$ and

$$\mathbf{v}'_1 = \mathbf{v}_1 + \boldsymbol{\sigma}[(\mathbf{v}'_{12} - \mathbf{v}_{12}) \cdot \boldsymbol{\sigma}] / 2,$$

$$\mathbf{v}'_2 = \mathbf{v}_2 - \boldsymbol{\sigma}[(\mathbf{v}'_{12} - \mathbf{v}_{12}) \cdot \boldsymbol{\sigma}] / 2. \quad (\text{C4})$$

We shall use the following property,

$$\left[\frac{\partial \phi}{\partial \mathbf{r}_{12}} \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) - \mathbf{v}_{12} \frac{\partial}{\partial \mathbf{r}_{12}} \right] F(Mv_1^2 + Mv_2^2 + 2\phi, \mathbf{v}'_1, \mathbf{v}'_2) = 0 \quad (\text{C5})$$

for arbitrary function F .

We have, therefore,

$$\begin{aligned} \bar{L}_{12} \psi_2^{ij} &= f^{-1}(1) \int_{r_{12} \leq d+\Delta} d^3 \mathbf{r}_{12} d^3 \mathbf{p}_2 \mathbf{v}_{12} \cdot \frac{\partial}{\partial \mathbf{r}_{12}} [f(12) \psi_2^{ij}] \\ &= -d^3 \int d^2 \boldsymbol{\sigma} d^3 \mathbf{p}_2 \theta(\boldsymbol{\sigma} \cdot \mathbf{v}_{12}) f(2) (\mathbf{v}_{12} \cdot \boldsymbol{\sigma})^2 (\sigma^i \sigma^j - \delta^{ij} / 3) \\ &= -\frac{4nd^3 \pi}{15} (v_1^i v_1^j - \delta^{ij} v_1^2 / 3) \end{aligned} \quad (\text{C6})$$

and

$$\begin{aligned} \bar{L}_{12} R_2^{ij} &= f^{-1}(1) \int_{r_{12} \leq d+\Delta} d^3 \mathbf{r}_{12} d^3 \mathbf{p}_2 \mathbf{v}_{12} \cdot \frac{\partial}{\partial \mathbf{r}_{12}} [f(12) R_2^{ij}] \\ &= nd^2 (k_B T / M)^{1/2} (B\Pi^{ij})(\bar{\mathbf{v}}_1). \end{aligned} \quad (\text{C7})$$

The shear viscosity ν will be evaluated by

$$-\frac{\check{J}_1^{ij}\Pi_1^{ij}}{10Vnk_B T/M} = \bar{\nu}_B, \quad (\text{C8})$$

where the dimensionless Boltzmann viscosity is equal to

$$\bar{\nu}_B = -\frac{1}{10(2\pi)^{3/2}} \int d^3\bar{\mathbf{v}}_1 (\bar{v}_1^i \bar{v}_1^j - \delta^{ij} \bar{v}_1^2/3) e^{-\bar{v}_1^2/2} \Pi^{ij}(\bar{\mathbf{v}}_1). \quad (\text{C9})$$

We have

$$\begin{aligned} -\check{J}_{v,2}^{ij} \bar{Q}_{22} R_2^{ij} &= \frac{Vd^3}{M} \int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^2\boldsymbol{\sigma} \int_0^\infty dr f(12) (\sigma^i \sigma^j \\ &\quad - \delta^{ij}/3) \phi'(r) \Pi^{ij}(\bar{\mathbf{v}}_1) \\ &= -\frac{Vd^3}{M} \int d^3\mathbf{p}'_1 d^3\mathbf{p}'_2 d^2\boldsymbol{\sigma} (\sigma^i \sigma^j - \delta^{ij}/3) \\ &\quad \times \int_0^{M(v'_{12} \cdot \boldsymbol{\sigma})^2/4} d\phi \frac{|\mathbf{v}'_{12} \cdot \boldsymbol{\sigma}| f(\mathbf{v}'_1) f(\mathbf{v}'_2) \Pi^{ij}(\bar{\mathbf{v}}_1)}{\sqrt{(\mathbf{v}'_{12} \cdot \boldsymbol{\sigma})^2 - 4\phi/M}} \\ &= -\frac{Vd^3}{2} \int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^2\boldsymbol{\sigma} (\sigma^i \sigma^j - \delta^{ij}/3) (\mathbf{v}'_{12} \cdot \boldsymbol{\sigma})^2 \\ &\quad \times f(\mathbf{v}'_1) f(\mathbf{v}'_2) \Pi^{ij}(\bar{\mathbf{v}}_1) \\ &= \frac{4\pi V n^2 d^3}{15} (k_B T/M)^2 10 \bar{\nu}_B \end{aligned} \quad (\text{C10})$$

and

$$\begin{aligned} \check{J}_2^{ij} \psi_2^{ij} &= \frac{Vd^4}{4M} \int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^2\boldsymbol{\sigma} \int_0^\infty dr f(12) (\sigma^i \sigma^j - \delta^{ij}/3) \phi'(r) \\ &\quad \times (\sigma^i \sigma^j - \delta^{ij}/3) \sqrt{(\mathbf{v}_{12} \cdot \boldsymbol{\sigma})^2 + 4\phi/M} \\ &= \frac{2Vd^4}{3M} \int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^2\boldsymbol{\sigma} \int_0^\infty dr f(12) \phi'(r) \\ &\quad \times \sqrt{(\mathbf{v}_{12} \cdot \boldsymbol{\sigma})^2 + 4\phi/M} \\ &= -\frac{8Vn^2 d^4 \sqrt{\pi} (k_B T/M)^{3/2}}{3}. \end{aligned} \quad (\text{C11})$$

Hence,

$$\nu = \left(1 + \frac{4\pi n d^3}{15}\right) \frac{\sqrt{k_B T/M}}{nd^2} \bar{\nu}_B + \frac{4nd^4 \sqrt{\pi k_B T/M}}{15}. \quad (\text{C12})$$

Similarly, we can calculate thermal conductivity κ . Let Π^i be the solution of equation

$$(B\Pi^i)(\bar{\mathbf{v}}_1) = \bar{v}_1^i (\bar{v}_1^2 - 5)/2. \quad (\text{C13})$$

The solution of the equation $(\bar{L} - \epsilon\bar{Q})|G^i\rangle = \bar{Q}|J_i^{\perp i}\rangle$ is

$$|G^i\rangle = (1 + 2\pi n d^3/5)(nd^2)^{-1} (k_B T/M) M |R^i\rangle + |\psi^i\rangle,$$

$$R_1^i = \Pi^i(\bar{\mathbf{v}}_1), \quad \psi_1^i = 0,$$

$$\begin{aligned} R_2^i &= [\Pi^i(\bar{\mathbf{v}}_1) + \Pi^i(\bar{\mathbf{v}}_2) - \Pi^i(\bar{\mathbf{v}}_1) - \Pi^i(\bar{\mathbf{v}}_2)] \\ &\quad \times \exp[-\epsilon(\mathbf{r}_{12} \cdot \mathbf{v}_{12})/v_{12}^2], \end{aligned}$$

$$\psi_2^i = \frac{Md}{4} \sigma^i (v_1'^2 - v_2'^2 - v_1^2 + v_2^2) \exp[-\epsilon(\mathbf{r}_{12} \cdot \mathbf{v}_{12})/v_{12}^2]. \quad (\text{C14})$$

We have

$$\begin{aligned} \bar{L}_{12} \psi_2^i &= -\frac{Md^3}{2f(1)} \int d^2\boldsymbol{\sigma} d^3\mathbf{p}_2 \int_0^\infty dr \phi'(r) \sigma^i \sigma^k \frac{\partial}{\partial p_1^k} \\ &\quad \times [f(12)(\mathbf{u}_{12} \cdot \mathbf{v}_{12})] + \frac{Md}{2f(1)} \\ &\quad \times \int_{r_{12} \leq d+\Delta} d^3\mathbf{p}_2 d^3\mathbf{r}_{12} v_{12}^k \sigma^i \frac{\partial}{\partial r_{12}^k} [f(12)(\mathbf{u}_{12} \cdot \mathbf{v}'_{12})] \\ &= -\frac{Md^3 \pi}{3} v_1^i (v_1^2 - 5k_B T/M) + \frac{Md^3}{2} \int d^2\boldsymbol{\sigma} d^3\mathbf{p}_2 f(2) \\ &\quad \times (\mathbf{v}_{12} \cdot \boldsymbol{\sigma}) \sigma^i (\mathbf{u}_{12} \cdot [\mathbf{v}_{12} - \boldsymbol{\sigma}(\mathbf{v}_{12} \cdot \boldsymbol{\sigma})]) \\ &= -\frac{2nd^3 \pi}{5} M v_1^i (v_1^2 - 5k_B T/M)/2 \end{aligned} \quad (\text{C15})$$

and

$$\begin{aligned} \bar{L}_{12} R_2^i &= f^{-1}(1) \int_{r_{12} \leq d+L} d^3\mathbf{r}_{12} d^3\mathbf{p}_2 v_{12} \frac{\partial}{\partial r_{12}} [f(12) R_2^i] \\ &= nd^2 (k_B T/M)^{1/2} (B\Pi^i)(\bar{\mathbf{v}}_1). \end{aligned} \quad (\text{C16})$$

The thermal conductivity will be evaluated by

$$-\frac{J_1^{\perp i} \Pi_1^i}{3Vn k_B T^2} = (k_B T/M)^{1/2} T^{-1} \bar{\kappa}_B, \quad (\text{C17})$$

where the dimensionless Boltzmann thermal conductivity is equal to

$$\bar{\kappa}_B = -\frac{1}{6(2\pi)^{3/2}} \int d^3\bar{\mathbf{v}}_1 \bar{v}_1^i (\bar{v}_1^2 - 5) e^{-\bar{v}_1^2/2} \Pi^i(\bar{\mathbf{v}}_1). \quad (\text{C18})$$

We have

$$\begin{aligned}
-J_{i,2}^{\perp} \bar{Q}_{22} R_2^i &= \frac{Vd^3}{M} \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 d^2 \boldsymbol{\sigma} \int_0^\infty dr f(12) \sigma^i (\mathbf{u}_{12} \cdot \boldsymbol{\sigma}) \phi'(r) [\Pi^i(\bar{\mathbf{v}}_1') - \Pi(\bar{\mathbf{v}}_1)] \\
&= -\frac{Vd^3}{M} \int d^3 \mathbf{p}_1' d^3 \mathbf{p}_2' d^2 \boldsymbol{\sigma} \sigma^i (\mathbf{u}_{12} \cdot \boldsymbol{\sigma}) \int_0^{M(\mathbf{v}_{12}' \cdot \boldsymbol{\sigma})^{2/4}} d\phi \frac{|\mathbf{v}_{12}' \cdot \boldsymbol{\sigma}| f(\mathbf{v}_1') f(\mathbf{v}_2') \Pi^i(\bar{\mathbf{v}}_1')}{\sqrt{(\mathbf{v}_{12}' \cdot \boldsymbol{\sigma})^2 - 4\phi/M}} \\
&\quad + \frac{Vd^3 k_B T}{M} \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 d^2 \boldsymbol{\sigma} f(1) f(2) \sigma^i (\mathbf{u}_{12} \cdot \boldsymbol{\sigma}) \Pi(\bar{\mathbf{v}}_1) \\
&= -\frac{Vd^3}{2} \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 d^2 \boldsymbol{\sigma} \sigma^i (\mathbf{u}_{12} \cdot \boldsymbol{\sigma}) [(\mathbf{v}_{12}' \cdot \boldsymbol{\sigma})^2 - 2k_B T/M] f(\mathbf{v}_1') f(\mathbf{v}_2') \Pi^i(\bar{\mathbf{v}}_1') \\
&= \frac{2\pi V n^2 d^3}{5} (k_B T/M)^{3/2} 3\bar{\kappa}_B
\end{aligned} \tag{C19}$$

and

$$\begin{aligned}
J_2^{\perp i} \psi_2^i &= \frac{MVd^4}{4} \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 d^2 \boldsymbol{\sigma} \int_0^\infty dr f(12) \\
&\quad \times (\mathbf{u}_{12} \cdot \boldsymbol{\sigma})^2 \phi'(r) \sqrt{(\mathbf{v}_{12} \cdot \boldsymbol{\sigma})^2 + 4\phi/M} \\
&= -2VM^2 n^2 d^4 \sqrt{\pi} (k_B T/M)^{5/2}.
\end{aligned} \tag{C20}$$

Hence,

$$\frac{\kappa}{k_B} = \left(1 + \frac{2\pi n d^3}{5}\right)^2 \frac{\sqrt{k_B T/M}}{n d^2} \bar{\kappa}_B + \frac{2n d^4 \sqrt{\pi k_B T/M}}{3}. \tag{C21}$$

APPENDIX D

We shall calculate the Sutherland correction appearing in Eq. (46) for ν and κ using the expansion (48). It is enough to compute the term,

$$I = \langle J^c | \bar{Q}^c (\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{L}^s (\bar{L}^c - \epsilon \bar{Q}^c)^{-1} \bar{Q}^c | J^c \rangle, \tag{D1}$$

where $J_{c,2}=0$. We know already the normal solution $|G\rangle$. It is convenient to distinguish between the right and left solutions, $|G^-\rangle$ and $\langle G^+|$, respectively. They are solutions of equations

$$\langle G^+ | (\bar{L}^c - \epsilon \bar{Q}^c) = \langle J^c | \bar{Q}^c, \quad (\bar{L}^c - \epsilon \bar{Q}^c) | G^-\rangle = \bar{Q}^c | J^c \rangle. \tag{D2}$$

We use the notation $G^{\pm ij} = (nd^2)^{-1} (k_B T/M)^{1/2} R^{\pm ij}$ and $G^{\pm i} = (nd^2)^{-1} (k_B T/M)^{1/2} M R^{\pm i}$. The vector $|R^-\rangle$ corresponds to $|R\rangle$, but $\langle R^+|$ differs a little, namely,

$$\begin{aligned}
R_1^\pm &= \Pi(\bar{\mathbf{v}}_1), \\
R_2^\pm &= [\Pi(\bar{\mathbf{v}}_1^\pm) + \Pi(\bar{\mathbf{v}}_2^\pm) - \Pi(\bar{\mathbf{v}}_1) - \Pi(\bar{\mathbf{v}}_2)] \exp[\pm \epsilon (\mathbf{r}_{12} \cdot \mathbf{v}_{12}) / v_{12}^2],
\end{aligned} \tag{D3}$$

where

$$\mathbf{v}_1^\pm = \mathbf{v}_1 \mp \boldsymbol{\sigma} [(\mathbf{v}_{12}' \pm \mathbf{v}_{12}) \cdot \boldsymbol{\sigma}] / 2,$$

$$\mathbf{v}_2^\pm = \mathbf{v}_2 \pm \boldsymbol{\sigma} [(\mathbf{v}_{12}' \pm \mathbf{v}_{12}) \cdot \boldsymbol{\sigma}] / 2, \tag{D4}$$

and we used Onsager symmetry (20). We have to calculate the quantity $\bar{I} = \langle R^+ | \bar{L}^s | R^- \rangle$. By using the relations (49), we arrive at

$$\bar{I} = - \int d\mathbf{2} f^c(12) \phi^s \{ \Pi(\bar{\mathbf{v}}_1^+) + \Pi(\bar{\mathbf{v}}_2^+), \Pi(\bar{\mathbf{v}}_1^-) + \Pi(\bar{\mathbf{v}}_2^-) \}. \tag{D5}$$

Note that \mathbf{v}^\pm are constants at the collision. Hence, the Poisson bracket is also constant along the collision trajectory. Thus, there is no singular contribution to the integral proportional to $\phi^s(d^\pm)$ as claimed by the Enskog theory. We have an integral involving ϕ^s instead, namely,

$$\begin{aligned}
\bar{I} &= 2 \int d\mathbf{2} f^c(12) \phi^s \theta(\mathbf{p}_{12} \cdot \boldsymbol{\sigma}) \left[\frac{\partial \Pi(\bar{\mathbf{v}}_1)}{\partial p_1^a} \right. \\
&\quad \left. - \frac{\partial \Pi(\bar{\mathbf{v}}_2)}{\partial p_2^a} \right] \frac{\partial p_1^{b-}}{\partial r_{12}^a} \left[\frac{\partial \Pi(\bar{\mathbf{v}}_1)}{\partial p_1^{b-}} - \frac{\partial \Pi(\bar{\mathbf{v}}_2)}{\partial p_2^{b-}} \right],
\end{aligned} \tag{D6}$$

where the second term from Poisson bracket is incorporated by the factor 2. Taking into account that

$$d \frac{\partial p_1^{b-}}{\partial r_{12}^a} = (\boldsymbol{\sigma} \cdot \mathbf{p}_{12}) \delta^{ab} - p_{12}^b \sigma^a + p_{12}^a \sigma^b - \frac{p_{12}^2 \sigma^a \sigma^b}{(\boldsymbol{\sigma} \cdot \mathbf{p}_{12})} \tag{D7}$$

and

$$\int d^3 \mathbf{r}_{12} \theta(\boldsymbol{\sigma} \cdot \mathbf{p}_{12}) = 2\pi d^3 \int_1^\infty dy \int_0^1 dx \frac{xy}{\sqrt{y^2 + x^2 - 1}}, \tag{D8}$$

where $r=yd$ and $x=\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}_{12}$, we obtain

$$\begin{aligned} \bar{I} = & 2\pi d^2 V \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 f(1) f(2) \int_1^\infty dy \phi^s(yd) \\ & \times \int_0^1 dx \frac{xy}{\sqrt{y^2 + x^2 - 1}} \times \left[\frac{\partial \Pi(\bar{\mathbf{v}}_1)}{\partial p_1^a} - \frac{\partial \Pi(\bar{\mathbf{v}}_2)}{\partial p_2^a} \right] \left[\frac{\partial \Pi(\bar{\mathbf{v}}_1)}{\partial p_1^b} \right. \\ & \left. - \frac{\partial \Pi(\bar{\mathbf{v}}_2)}{\partial p_2^b} \right] \left[(\boldsymbol{\sigma} \cdot \mathbf{p}_{12}) \delta^{ab} - p_{12}^b \sigma^a + p_{12}^a \sigma^b - \frac{p_{12}^a \sigma^a \sigma^b}{(\boldsymbol{\sigma} \cdot \mathbf{p}_{12})} \right]. \end{aligned} \quad (\text{D9})$$

We shall calculate the correction to shear viscosity, using the first Sonine approximation. Namely, we postulate Π^{ij} to have the form

$$\Pi^{ij}(\bar{\mathbf{v}}) = \alpha(\bar{v}^i \bar{v}^j - \delta^{ij} \bar{v}^2/3). \quad (\text{D10})$$

and integrate Eq. (C2) with $e^{-\bar{v}^2/2} \Pi^{ij}(\bar{\mathbf{v}}_1)$. We get $10 = -32\sqrt{\pi}\alpha$. Hence, $\alpha = -5/16\sqrt{\pi}$ and $\bar{v}_B = -\alpha$. By substituting the form (D10) into (D9), we get

$$\begin{aligned} \bar{I} = & \frac{4\pi d^2 V \alpha^2}{\sqrt{Mk_B T}} \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 f(1) f(2) \int_1^\infty dy \phi^s(yd) \\ & \times \int_0^1 dx \frac{xy}{\sqrt{y^2 + x^2 - 1}} [9(\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12}) \bar{v}_{12}^2 - 10(\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})^3 \\ & - \bar{v}_{12}^4 / (\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})]. \end{aligned} \quad (\text{D11})$$

Using the fact that

$$\begin{aligned} \bar{I} = & \frac{4\pi d^2 V \alpha^2}{\sqrt{Mk_B T}} \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 f(1) f(2) \int_1^\infty dy \phi^s(yd) \int_0^1 dx \frac{xy}{\sqrt{y^2 + x^2 - 1}} \times [\bar{u}_{12}^2 \bar{v}_{12}^2 (\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12}) - 2\bar{u}_{12}^2 (\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})^3 + 7(\mathbf{v}_{12} \cdot \bar{\mathbf{u}}_{12})^2 (\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12}) \\ & - 14(\boldsymbol{\sigma} \cdot \bar{\mathbf{u}}_{12})(\bar{\mathbf{v}}_{12} \cdot \bar{\mathbf{u}}_{12})(\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})^2 + 6(\boldsymbol{\sigma} \cdot \bar{\mathbf{u}}_{12})^2 (\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12}) \bar{v}_{12}^2 + 2(\boldsymbol{\sigma} \cdot \bar{\mathbf{u}}_{12})(\bar{\mathbf{u}}_{12} \cdot \bar{\mathbf{v}}_{12}) \bar{v}_{12}^2 - [(\boldsymbol{\sigma} \cdot \bar{\mathbf{u}}_{12})^2 \bar{v}_{12}^4 \\ & + (\bar{\mathbf{u}}_{12} \cdot \bar{\mathbf{v}}_{12})^2 \bar{v}_{12}^2] / (\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})]. \end{aligned} \quad (\text{D15})$$

By integrating out $\bar{\mathbf{u}}_{12}$, we get

$$\bar{I} = \frac{2\pi d^2 V \alpha^2}{\sqrt{Mk_B T}} \int d^3 \mathbf{p}_1 d^3 \mathbf{p}_2 f(1) f(2) \int_1^\infty dy \phi^s(yd) \int_0^1 dx \frac{xy}{\sqrt{y^2 + x^2 - 1}} [9(\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12}) \bar{v}_{12}^2 - 10(\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})^3 - \bar{v}_{12}^4 / (\boldsymbol{\sigma} \cdot \bar{\mathbf{v}}_{12})], \quad (\text{D16})$$

which means that thermal conductivity changes in the same way as shear viscosity, namely, S is given by Eq. (56).

$$\begin{aligned} & \int_0^1 dx \frac{9x^2 - 10x^4 - 1}{\sqrt{y^2 + x^2 - 1}} \\ & = -\frac{15y^4 - 12y^2 + 1}{8} \ln\left(\frac{y+1}{y-1}\right) - \frac{y(7-15y^2)}{4} \end{aligned} \quad (\text{D12})$$

and $(4\pi)^{-3/2} \int d^3 \bar{\mathbf{v}} e^{-\bar{v}^2/4} \bar{v}^3 = 32/\sqrt{\pi}$, we get finally

$$\begin{aligned} \bar{I} = & -\frac{16\pi V n^2 d^2 \alpha^2}{\sqrt{Mk_B T}} \int_1^\infty dy \left[(15y^5 - 12y^3 + y) \ln\left(\frac{y+1}{y-1}\right) \right. \\ & \left. + y^2(14 - 30y^2) \right] \phi^s(yd) \end{aligned} \quad (\text{D13})$$

that gives the result (56).

The calculation of thermal conductivity will be done similarly. In the first Sonine approximation,

$$\Pi(\bar{\mathbf{v}}) = \frac{\alpha}{2} (\bar{v}^2 - 5) \bar{v}^i. \quad (\text{D14})$$

Taking into account Eq. (C15), we get $15/2 = -16\alpha\sqrt{\pi}$. Hence, $\alpha = -15/32\sqrt{\pi}$ and $\bar{\kappa}_B = -5\alpha/2 = 75/64\sqrt{\pi}$.

By substituting (D14) to (D9), we obtain

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