Symmetric linear kinetic theory

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Equilibrium time correlation functions are expressed by two Onsager-symmetric quantumlike operators containing equilibrium distribution function. A model of dissipation for smooth interaction potentials is proposed. Approximations leading to the mode coupling formula are clearly stated and the Green-Kubo prescription for the calculation of the transport coefficients is reformulated.

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I. INTRODUCTION

The main problem in the linear kinetic theory is to construct a kinetic equation consistent with Onsager-symmetry relations (OSR) for transport coefficients in nonequilibrium thermodynamics [1]. Although time correlation functions are evidently symmetric, it is by no means obvious whether a given equation is symmetric and obeys OSR. The problem was solved for the Enskog equation [2,3] and it allowed to prove an H theorem for a hard sphere fluid both in linear and nonlinear regime [2,4]. It is possible to obtain a symmetric linear kinetic equation for a one-particle distribution function also for a square-well potential [5,6] and multistep potential [7,8]. A more general linear theory of hard spheres [9] similarly as the Enskog theory consists in fact of two adjoint kinetic equations [9–11]. In the kinetic theory for smooth potentials, no irreversible equation that satisfies OSR is present except a smooth potential with a hard core (square well) [12].

On the other hand, we have a symmetric mode coupling formula for calculation of time correlation functions and transport coefficients [13–16]. It is, however, derived rather intuitively and it is hardly known what is neglected.

We present a different method to construct a linear kinetic theory where OSR are natural. Instead of kinetic equations we rather propose an algebra of operators used to calculate time correlation functions. It algebraically resembles quantum mechanics because of using a Hilbert space and operators developed by Bławzdziewicz and Cichocki [10,11]. We construct the Hilbert space of fluctuations with a standard scalar product. Then two quantumlike operators are defined. The operator Q [10,11] counts equal time equilibrium correlation functions and the operator L [6,17] counts infinitesimal time correlation function. Note that in the standard Mori approach [18], the operator Q was included in the scalar product. It may be convenient for one-particle functions but causes troubles when considering two-particle functions, because correlations do not factorize [16].

Our main result is a symmetric formula for the Laplace transform of a time correlation function. Moreover, we propose a mechanism of dissipation for smooth potentials which can be interpreted as a coarse graining in the phase space. We cut correlations if considered particles are at the distance larger than certain length D. It turns out that this discontinuity is enough to have nonpositive real parts of eigenvalues of L as for hard spheres. Hence our theory includes the H theorem (decay of correlations) for smooth potentials similarly as in the case of hard spheres [19]. We are able to write an Enskog-like equation for smooth potentials. The Green-Kubo expressions for transport coefficients [20] are reformulated using Q and L. Due to the H theorem, the dissipative character of transport is transparent. However, it cannot be proved for smooth potentials that only energy and density modes belong to the kernel of L in the truncated space. We also discuss the derivation of the mode coupling formula, though no H theorem can be proved there.

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 introduced. The structure of the static operator Q and dynamic operator L is described in Sec. IV. The operator L for hard spheres is derived in Sec. V. The mechanism of dissipation for smooth potentials is presented in Sec. VI and the Enskog-like equation is given in Sec. VII. The Green-Kubo formulas are expressed in our formalism in Sec. VIII. The main result of the paper, the formula for time correlation functions, is presented in Sec. IX. An application to mode coupling is presented in Sec. X and Sec. XI is devoted to discussion and conclusions.

II. BASIC CONCEPTS

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

The probability density of finding exactly n particles in the phase space point $\boldsymbol{n}=\{1, \ldots, n\}$ is $\rho(\boldsymbol{n}) \equiv \rho_n$. 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 $\mathcal{A}=\{\mathcal{A}(\boldsymbol{n}); n \geqslant 0\}$ is given by

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

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where $d\boldsymbol{n} \equiv d1, \ldots, dn/n!$ denotes integration over all canonical coordinates of phases, that is

$$\int di = h^{-3} \int d^3\boldsymbol{r}_i \int d^3\boldsymbol{p}_i, \tag{2}$$

where h is the Planck's constant. Arguments of ρ_n and $\mathcal{A}_n$ are omitted whenever it is unambiguous. Reduced distribution functions are defined as

$$f(\boldsymbol{m}) = \sum_{n=0}^{\infty} \int d\boldsymbol{n}\, \rho(\boldsymbol{n}+\boldsymbol{m}). \tag{3}$$

The probability distribution must satisfy the normalization condition

$$f_0 = \sum_{n=0}^{\infty} \int d\boldsymbol{n}\, \rho_n = 1. \tag{4}$$

Functions f are useful in averages of cluster functions,

$$\mathcal{A}(\boldsymbol{n}) = a_0 + \sum_{i \in \boldsymbol{n}} a(i) + \sum_{i>j} a(ij) + \cdots = \sum_{\boldsymbol{m} \subseteq \boldsymbol{n}} a(\boldsymbol{m}), \tag{5}$$

$$\langle \mathcal{A} \rangle = \sum_{m=0}^{\infty} \int d\boldsymbol{m}\, a_m f_m. \tag{6}$$

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.

When considering hard spheres of diameter d, one introduces the overlap function W defined as

$$W(\boldsymbol{n}) = \prod_{\substack{i>j \\ ij \in \boldsymbol{n}}} W(ij), \quad W(ij) = \theta(r_{ij}-d) = \begin{cases} 1 & \text{if } r_{ij} \geqslant d \\ 0 & \text{if } r_{ij} < d, \end{cases} \tag{7}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, $r_{ij} = |\boldsymbol{r}_{ij}|$. The equilibrium probability density ρ of hard spheres of mass M interacting with the pair potential $\phi_2(\boldsymbol{r}_{ij})$ at the temperature T is given by

$$\rho_n = W_n \exp\{(\Omega + n\mu - \mathcal{H}_n)/k_B T\}, \tag{8}$$

where the Hamiltonian $\mathcal{H}$ is defined as

$$\mathcal{H}_n = \sum_{i \in \boldsymbol{n}} p_i^2/2M + \sum_{i>j} \phi_2(\boldsymbol{r}_{ij}) \tag{9}$$

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

$$f(\boldsymbol{m}) = g(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_m) \prod_{i=1}^{m} f(i), \tag{10}$$

where g_m is m-point correlation function and f_1 is a Maxwellian distribution of velocities,

$$f(\boldsymbol{r},\boldsymbol{p}) = nh^3 (2\pi M k_B T)^{-3/2} \exp\{-p^2/2Mk_B T\} \tag{11}$$

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 $|u\rangle \equiv \{u_1, u_2, \ldots\}$ with infinite number of components, where $u_i(\boldsymbol{i})$ is a symmetric function of phases of i particles (similar to Fock space for bosons) [10,11]. The adjoint bra vector is $\langle u| \equiv \{u_1^*, u_2^*, \ldots\}$, where the asterisk denotes complex conjugation. The scalar product of two vectors u and w is defined as

$$\langle u|w\rangle = \sum_{k=1}^{\infty} \int d\boldsymbol{k}\, u_k^* w_k. \tag{12}$$

We define linear operators in such a space. The operator X acting on the vector u gives the vector

$$X|u\rangle = |Xu\rangle \tag{13}$$

with the components

$$(Xu)_k = \sum_{i=1}^{\infty} X_{ki} u_i \tag{14}$$

and

$$X_{ki} u_i = \int d\boldsymbol{i}\, X(\boldsymbol{k}|\boldsymbol{i}) u(\boldsymbol{i}). \tag{15}$$

The product of operators X and Y is defined as

$$(XY)_{ij} = \sum_{k=1}^{\infty} X_{ik} Y_{kj}, \tag{16}$$

where

$$X_{ik} Y_{kj} = \int d\boldsymbol{k}\, X(\boldsymbol{i}|\boldsymbol{k}) Y(\boldsymbol{k}|\boldsymbol{j}). \tag{17}$$

The adjoint of the operator X is then defined by the equality

$$\langle u|X^+|w\rangle^* = \langle w|X|u\rangle \tag{18}$$

and the identity operator I is defined by

$$\langle u|I|w\rangle = \langle u|w\rangle \tag{19}$$

for arbitrary u and w. It can be explicitly written as

$$I(\boldsymbol{k}|\boldsymbol{k}') = \sum_{\sigma} \prod_{i=1}^{k} \delta(i - \sigma(i')), \quad I_{mn} = 0, m \neq n, \tag{20}$$

where

$$\delta(i-j) = h^{-3} \delta(\boldsymbol{r}_i - \boldsymbol{r}_j)\, \delta(\boldsymbol{p}_i - \boldsymbol{p}_j) \tag{21}$$

and the sum is taken over all permutations σ of the set $\boldsymbol{k}'$.

IV. OPERATORS *Q* AND *L*

A linear nonequilibrium state of the system is described by a small deviation from equilibrium given by a vector b [11],

$$\rho_b(\boldsymbol{n})=\rho(\boldsymbol{n})[1+\mathcal{B}(\boldsymbol{n})-\langle\mathcal{B}\rangle], \tag{22}$$

where

$$\mathcal{B}(\boldsymbol{n})=\sum_{\boldsymbol{m}\subseteq\boldsymbol{n}} b(\boldsymbol{m}). \tag{23}$$

The average of $\delta\mathcal{A}^*=\mathcal{A}^*-\langle\mathcal{A}^*\rangle$ corresponding to a given quantity a in the nonequilibrium state represented by Eq. (22) is written as

$$\langle\delta\mathcal{A}^*\rangle_b=\langle\delta\mathcal{A}^*\delta\mathcal{B}\rangle=\langle a|Q|b\rangle, \tag{24}$$

where the matrix elements of Q have the form

$$\langle a|Q|b\rangle=\sum_{i,j,k}\int d\boldsymbol{i}\,d\boldsymbol{j}\,d\boldsymbol{k}[f_{i+j+k}-\delta_{k,0}f_if_j]a^*_{i+k}b_{j+k}. \tag{25}$$

The operator Q is positive definite since

$$\langle a|Q|a\rangle=\langle|\delta\mathcal{A}|^2\rangle>0. \tag{26}$$

We introduce Liouville evolution operator for smooth potentials,

$$\mathcal{L}_k=\{\cdot,\mathcal{H}\}=\sum_{i\in\boldsymbol{k}}\boldsymbol{v}_i\cdot\frac{\partial}{\partial\boldsymbol{r}_i}-\sum_{i\neq j}\frac{\partial\phi_2(\boldsymbol{r}_{ij})}{\partial\boldsymbol{r}_{ij}}\cdot\frac{\partial}{\partial\boldsymbol{p}_i}, \tag{27}$$

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

$$\{\alpha,\beta\}=\sum_i\left(\frac{\partial\alpha}{\partial\boldsymbol{r}_i}\cdot\frac{\partial\beta}{\partial\boldsymbol{p}_i}-\frac{\partial\alpha}{\partial\boldsymbol{p}_i}\cdot\frac{\partial\beta}{\partial\boldsymbol{r}_i}\right) \tag{28}$$

and $\boldsymbol{v}=\boldsymbol{p}/M$. We will use the operator $\mathcal{L}$ acting in our Hilbert space defined by

$$|w\rangle=\mathcal{L}|u\rangle\Leftrightarrow\mathcal{W}=\mathcal{L}\mathcal{U}, \tag{29}$$

where

$$w_k=\mathcal{L}_ku_k-\sum_{i\neq j}\frac{\partial\phi_2(\boldsymbol{r}_{ij})}{\partial\boldsymbol{r}_{ij}}\cdot\frac{\partial}{\partial\boldsymbol{p}_i}u(\boldsymbol{k}-j). \tag{30}$$

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

$$u_k=-\mathcal{L}_kw_k+\int d(k+1)\sum_{i\in\boldsymbol{k}}\frac{\partial\phi_2(\boldsymbol{r}_{i,k+1})}{\partial\boldsymbol{r}_{i,k+1}}\cdot\frac{\partial}{\partial\boldsymbol{p}_i}w(\boldsymbol{k}+\boldsymbol{1}). \tag{31}$$

The evolution of a phase function a is described by the equation

$$\partial_t\mathcal{A}=\mathcal{L}\mathcal{A}\ \text{ or }\ \partial_t|a\rangle=\mathcal{L}|a\rangle. \tag{32}$$

The evolution of probability fluctuation b differs from the above by a minus sign,

$$\partial_t\mathcal{B}=-\mathcal{L}\mathcal{B}\ \text{ or }\ \partial_t|b\rangle=-\mathcal{L}|b\rangle. \tag{33}$$

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

$$\frac{d\langle\mathcal{A}\rangle_b}{dt}=\langle\mathcal{L}\mathcal{A}\rangle_b=\langle\{\mathcal{A},\mathcal{H}\}\rangle_b=k_BT\langle\{\mathcal{A},\mathcal{B}\}\rangle. \tag{34}$$

The above observation leads to the definition of the operator L [6,17] by its matrix elements,

$$\langle a|L|b\rangle=k_BT\langle\{\mathcal{A}^*,\mathcal{B}\}\rangle=k_BT\sum_{m,i,j}\int d\boldsymbol{i}\,d\boldsymbol{j}\,d\boldsymbol{m}\,f_{i+j+m}\{a^*_{i+m},b_{j+m}\}. \tag{35}$$

Note that $L=-Q\mathcal{L}=\mathcal{L}^\dagger Q$.

If we introduce a functional

$$H=\langle|\delta\mathcal{B}|^2\rangle=\langle b|Q|b\rangle, \tag{36}$$

then

$$dH/dt=2k_BT\,\mathrm{Re}\langle\{\mathcal{B}^*,\mathcal{B}\}\rangle=2\,\mathrm{Re}\langle b|L|b\rangle=0 \tag{37}$$

so that there is no dissipation (H theorem) in this picture.

V. HARD SPHERES

The operator $\mathcal{L}$ must be defined in a slightly different way for hard spheres because of singular interactions. It is a pseudo-operator [21,22] depending on where the overlap function W in Eq. (7) is placed,

$$\overline{\mathcal{L}}_{k\pm}=\mathcal{L}_k\pm\sum_{i>j=1}^{k}\overline{T}_\pm(ij),$$

$$\mathcal{L}_{k\pm}=\mathcal{L}_k\pm\sum_{i>j=1}^{k}T_\pm(ij), \tag{38}$$

where

$$T_\pm(ij)=\delta(r_{ij}-d^+)|\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij}|\,\theta(\mp\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij})(g_{ij}-1), \tag{39}$$

$$\overline{T}_\pm(ij)=T^\dagger_\mp=\delta(r_{ij}-d^+)|\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij}|\{\theta(\mp\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij})g_{ij}-\theta(\pm\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij})\} \tag{40}$$

and $\boldsymbol{v}_{ij}=\boldsymbol{v}_i-\boldsymbol{v}_j$, $\hat{\boldsymbol{r}}_{ij}=\boldsymbol{r}_{ij}/r_{ij}$, $d^+=d+|\epsilon|$ with $\epsilon\to0$. The operator g_{ij} turns velocities,

$$g_{ij}\varphi(\ldots,\boldsymbol{v}_i,\ldots,\boldsymbol{v}_j,\ldots)=\varphi(\ldots,\boldsymbol{v}'_i,\ldots,\boldsymbol{v}'_j,\ldots),$$

$$\boldsymbol{v}_i' = \boldsymbol{v}_i - (\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij})\hat{\boldsymbol{r}}_{ij},$$
$$\boldsymbol{v}_j' = \boldsymbol{v}_j + (\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij})\hat{\boldsymbol{r}}_{ij}, \tag{41}$$

Due to the relation

$$\overline{T}_{\pm}(ij) - T_{\pm}(ij) = \mp \boldsymbol{v}_{ij}\cdot\frac{\partial W_2(ij)}{\partial \boldsymbol{r}_{ij}} = \mp \boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{r}}_{ij}\delta(d^+ - r_{ij}), \tag{42}$$

we have $\overline{\mathcal{L}}_{\pm} W = W\mathcal{L}_{\pm}$. The operator $\mathcal{L}_{\pm}$ is now defined by

$$|w\rangle = \mathcal{L}_{\pm}|u\rangle \Leftrightarrow \mathcal{W} = \mathcal{L}_{\pm}\mathcal{U}, \tag{43}$$

where

$$w_k = \mathcal{L}_{k\pm}u_k \pm \sum_{i\neq j} T_{\pm}(ij)u(\boldsymbol{k}-j) - \sum_{i\neq j}\frac{\partial\phi_2(\boldsymbol{r}_{ij})}{\partial \boldsymbol{r}_{ij}}\cdot\frac{\partial}{\partial \boldsymbol{p}_i}u(\boldsymbol{k}-j) \tag{44}$$

and the conjugate operator $\mathcal{L}_{\pm}^{\dagger}$ is defined by $|u\rangle = \mathcal{L}_{\pm}^{\dagger}|w\rangle$,

$$u_k = -\overline{\mathcal{L}}_{k\mp}w_k + \int d(k+1)\sum_{i\in\boldsymbol{k}}\left(\frac{\partial\phi_2(\boldsymbol{r}_{i,k+1})}{\partial \boldsymbol{r}_{i,k+1}}\cdot\frac{\partial}{\partial \boldsymbol{p}_i} \pm \overline{T}_{\mp}(i,k+1)\right)w(\boldsymbol{k}+\boldsymbol{1}). \tag{45}$$

The time evolution of phase functions $\mathcal{A}$ and probability fluctuation $\mathcal{B}$ are given for $t>0$ by

$$\partial_t\mathcal{A} = \mathcal{L}_+\mathcal{A} \quad \text{or} \quad \partial_t|a\rangle = \mathcal{L}_+|a\rangle, \tag{46}$$

$$\partial_t\mathcal{B} = -\mathcal{L}_-\mathcal{B} \quad \text{or} \quad \partial_t|b\rangle = -\mathcal{L}_-|b\rangle. \tag{47}$$

We define

$$L = -Q\mathcal{L}_- = \mathcal{L}_+^{\dagger}Q. \tag{48}$$

We shall evaluate $\langle a|L|b\rangle$ assuming that a and b are *continuous* when spheres overlap,

$$\langle a|L|b\rangle = -\langle\mathcal{A}^*\mathcal{L}_-\mathcal{B}\rangle = k_BT\langle\{\mathcal{A}^*,\mathcal{B}\}\rangle + k_BT\left\langle\sum_{i>j}\frac{\mathcal{A}^*\partial\mathcal{B} - \mathcal{B}\partial\mathcal{A}^*}{\partial \boldsymbol{p}_{ij}}\cdot\hat{\boldsymbol{r}}_{ij}\delta(r_{ij}-d^+)\right\rangle - \frac{1}{2}\left\langle\sum_{i>j}\delta(r_{ij}-d^+)\hat{\boldsymbol{r}}_{ij}\cdot\boldsymbol{v}_{ij}\theta(\boldsymbol{r}_{ij}\cdot\boldsymbol{v}_{ij})\times(\mathcal{A}^*\mathcal{B} - 2\mathcal{A}^*\mathcal{B}' + \mathcal{A}^{*\prime}\mathcal{B}')\right\rangle, \tag{49}$$

where

$$\frac{\partial}{\partial \boldsymbol{p}_{ij}} = \frac{1}{2}\left(\frac{\partial}{\partial \boldsymbol{p}_i} - \frac{\partial}{\partial \boldsymbol{p}_j}\right) \tag{50}$$

and $\mathcal{U}' = g_{ij}\mathcal{U}$. The operator L can be divided into three parts

$$L = L_A + L_B + L_C, \tag{51}$$

where L_A, L_B, and L_C are Poisson term, hard core and entropy production term, respectively, where

$$\langle a|L_A|b\rangle = k_BT\sum_{k,m,n}\int d\boldsymbol{k}\,d\boldsymbol{m}\,d\boldsymbol{n}\,f_{k+m+n}\{a_{k+m}^*, b_{k+n}\}, \tag{52}$$

$$\langle a|L_B|b\rangle = k_BT\sum_{k,m,n}\int d\boldsymbol{k}\,d\boldsymbol{m}\,d\boldsymbol{n}\,f_{k+m+n}\sum_{\substack{i\in\boldsymbol{k}+\boldsymbol{m}\\ j\in\boldsymbol{k}+\boldsymbol{n}}}^{i>j}\times\delta(r_{ij}-d^+)\hat{\boldsymbol{r}}_{ij}\cdot\left(a_{k+m}^*\frac{\partial b_{k+n}}{\partial \boldsymbol{p}_{ij}} - b_{k+n}\frac{\partial a_{k+m}^*}{\partial \boldsymbol{p}_{ij}}\right) + k_BT\sum_{k,m,n}\int d\boldsymbol{1}\,d\boldsymbol{k}\,d\boldsymbol{m}\,d\boldsymbol{n}\,f_{1+k+m+n}\sum_{i\in\boldsymbol{k}}\times\delta(r_{i1}-d^+)\hat{\boldsymbol{r}}_{i1}\cdot\left(a_{k+m}^*\frac{\partial b_{k+n}}{2\partial \boldsymbol{p}_i} - b_{k+n}\frac{\partial a_{k+m}^*}{2\partial \boldsymbol{p}_i}\right), \tag{53}$$

$$\langle a|L_C|b\rangle = -\frac{1}{2}\sum_{k,m,n}\int d\boldsymbol{k}\,d\boldsymbol{m}\,d\boldsymbol{n}\,f_{k+m+n}\sum_{\substack{i\in\boldsymbol{k}+\boldsymbol{m}\\ j\in\boldsymbol{k}+\boldsymbol{n}}}^{i>j}\delta(r_{ij}-d^+)\times\hat{\boldsymbol{r}}_{ij}\cdot\boldsymbol{v}_{ij}\theta(\boldsymbol{r}_{ij}\cdot\boldsymbol{v}_{ij})(a_{k+m}^*b_{k+n} - 2a_{k+m}^*b_{k+n}' + a^{*\prime}_{k+m}b_{k+n}') - \frac{1}{2}\sum_{k,m,n}\int d\boldsymbol{1}\,d\boldsymbol{k}\,d\boldsymbol{m}\,d\boldsymbol{n}\times f_{1+k+m+n}\sum_{i\in\boldsymbol{k}}\delta(r_{1i}-d^+)\hat{\boldsymbol{r}}_{1i}\cdot\boldsymbol{v}_{1i}\theta(\boldsymbol{r}_{1i}\cdot\boldsymbol{v}_{1i})\times(a_{k+m}^*b_{l+m} - 2a_{k+m}^*b_{k+n}' + a^{*\prime}_{k+m}b_{k+n}'). \tag{54}$$

It is important that Eq. (37) holds for hard spheres if

$$\mathcal{B}_n(ij) = \mathcal{B}_n(i'j') \quad \text{for} \quad r_{ij} = d, \tag{55}$$

where other phases are omitted and only nonoverlapping configurations are considered. This is generally true if the dynamics is let for a period of time but not for a single time point.

VI. DISSIPATION

Our purpose is to change the action of the operator L in such a way that we get the H theorem

$$dH/dt = 2\,\mathrm{Re}\langle b|L|b\rangle \leqslant 0. \tag{56}$$

In the case of hard spheres it is enough to cut the Hilbert space of vectors u so that $u_k = 0$ for $k>l$. Equation (32) is then no longer valid. Instead, the evolution of phase functions a and probability b is given by equations

$$\partial_t Q|a\rangle = Q\partial_t|a\rangle = -L|a\rangle, \tag{57}$$

$$\partial_t Q|b\rangle = Q\partial_t|b\rangle = L|b\rangle. \tag{58}$$

The operator Q commutes with time derivative because equilibrium distribution is invariant in time. The operators Q_{mn} and L_{mn} are both truncated to $m,n \leqslant l$. Such a general description leads to the H theorem (56) as shown in Ref. [19]. The H theorem follows immediately from the last term in Eq. (49). Note that we can reverse the inequality (56) by changing $\mathcal{L}_-$ to $\mathcal{L}_+$ in Eq. (48), but then time must be reversed too.

Unfortunately, such a truncation is useless in the case of smooth potentials since we still obtain Eq. (37). The truncation must be carried out more carefully. We introduce another arbitrary parameter: the length D, which is larger than the range of the potential. The components u_k are equal to 0 for $k>l$ and u_l is equal to zero if $r_{ij}>D$ for every pair $\{i,j\}\subseteq \boldsymbol{l}$. We can define the characteristic function $\mathcal{W}$ as

$$\mathcal{W}=1-\prod_{ij}\ \theta(r_{ij}-D) \tag{59}$$

so that $u_l=\mathcal{W}\tilde{u}_l$, where $\tilde{u}_l$ is a continuous function. In the case $l=2$, the truncation means that $u_2(12)=0$ for $r_{12}>D$. However, for $l=3$ we have $u_3(123)=0$ if $r_{12}>D$, $r_{23}>D$ and $r_{31}>D$ simultaneously. It is important to take properly into account the discontinuity of functions u_l at $r_{ij}=D$. We introduce shifted functions u_l^+ and u_l^- defined as

$$u_l^{\pm}=\mathcal{W}^{\pm}\,\tilde{u}_l, \tag{60}$$

where

$$\mathcal{W}^{\pm}=\begin{cases}1 & \text{if} \quad r_{ij}<D_{ij}^{\pm} \ \text{ and for any pair } \ (ij)\\ 0 & \text{otherwise,}\end{cases} \tag{61}$$

and $D_{ij}^{\pm}=D\pm|\epsilon|\boldsymbol{r}_{ij}\cdot\boldsymbol{v}_{ij}$ with $\epsilon\to 0$. The function u_l^+ is slightly stretched for $\boldsymbol{r}_{ij}\cdot\boldsymbol{v}_{ij}>0$ and squeezed for $\boldsymbol{r}_{ij}\cdot\boldsymbol{v}_{ij}<0$ and vice versa for u_l^-. All functions u_k for $k<l$ are not affected by $\mathcal{W}$.

The matrix elements of Q are independent of the choice of signs since

$$\langle a^{\pm}|Q|b^{\pm}\rangle=\langle a^{\mp}|Q|b^{\pm}\rangle=\langle a|Q|b\rangle. \tag{62}$$

The key point of our construction is a proper choice of signs in L, because it contains derivatives. The choice that leads to the H theorem for $t>0$ is the following:

$$\langle a|L|b\rangle=\langle a^-|L|b^+\rangle=k_BT\langle\{\mathcal{A}^{*-},\mathcal{B}^+\}\rangle \tag{63}$$

for every a and b. It can be written also in terms of distribution functions

$$\langle a|L|b\rangle=k_BT\sum_{mij}\int d\boldsymbol{i}\,d\boldsymbol{j}\,d\boldsymbol{m}\,f_{i+j+m}\{a_{i+m}^{-*},b_{j+m}^{+}\}. \tag{64}$$

However, the derivatives should be carried out very carefully since they act upon $\mathcal{W}^{\pm}$. In the case $m+i\neq l\neq m+j$ we have

$$\int d\boldsymbol{i}\,d\boldsymbol{j}\,d\boldsymbol{m}\,f_{i+j+m}\{a_{i+m}^{-*},b_{j+m}^{+}\}=\int d\boldsymbol{i}\,d\boldsymbol{j}\,d\boldsymbol{m}\,f_{i+j+m}\{a_{i+m}^{*},b_{j+m}\}, \tag{65}$$

but $m+i=m+j=l$ and is a tricky term. We show in Appendix A that we obtain for $n=k=l-m$,

$$\begin{aligned}
&k_BT\int d\boldsymbol{m}\,d\boldsymbol{k}\,d\boldsymbol{n}\,f_{m+k+n}\{a_{m+k}^{-*},b_{m+n}^{+}\}\\
&=k_BT\int d\boldsymbol{m}\,d\boldsymbol{n}\,d\boldsymbol{k}\,f_{m+k+n}\left[\prod_{\substack{i>j\\ ij\in\boldsymbol{m}}}[1-\tilde{\mathcal{W}}(ij)\,\theta(D-r_{ij})]\right]\\
&\times\{a_{m+k}^{*},b_{m+n}\}+k_BT\int d\boldsymbol{m}\,d\boldsymbol{k}\,d\boldsymbol{n}\,f_{m+k+n}\\
&\times\sum_{\substack{i>j\\ ij\in\boldsymbol{m}}}\tilde{\mathcal{W}}(ij)\,\theta(D-r_{ij})\{\tilde{a}_{m+k}^{*},\tilde{b}_{m+n}\}+k_BT\\
&\times\int d\boldsymbol{m}\,d\boldsymbol{k}\,d\boldsymbol{n}\,f_{m+k+n}\sum_{i>j}\tilde{\mathcal{W}}(ij)\,\delta(r_{ij}-D)\\
&\times\hat{\boldsymbol{r}}_{ij}\cdot\frac{\tilde{b}_{m+n}\partial\tilde{a}_{m+k}^{*}-\tilde{a}_{m+k}^{*}\partial\tilde{b}_{m+n}}{\partial\boldsymbol{p}_{ij}}-\frac{1}{2}\int d\boldsymbol{m}\,d\boldsymbol{k}\,d\boldsymbol{n}\\
&\times f_{m+k+n}\sum_{i>j}\tilde{\mathcal{W}}(ij)\,\delta(r_{ij}-D)|\hat{\boldsymbol{r}}_{ij}\cdot\boldsymbol{v}_{ij}|\tilde{a}_{m+k}^{*}\tilde{b}_{m+n},
\end{aligned} \tag{66}$$

where

$$\tilde{\mathcal{W}}(ij)=\prod_{\substack{(pq)\neq(ij)\\ pq\in\boldsymbol{m}+\boldsymbol{k}}}\theta(r_{pq}-D)\prod_{\substack{(pq)\neq(ij)\\ pq\in\boldsymbol{m}+\boldsymbol{n}}}\theta(r_{pq}-D) \tag{67}$$

and $\partial/\partial\boldsymbol{p}_{ij}$ is defined by Eq. (50). It is apparent that the two first, the third, and the fourth term correspond to L_A, L_B, and L_C for hard spheres, respectively. The H theorem (56) follows from the last, dissipative term for $a=b$. The equal sign holds for $b_l=0$ at the boundary of the region of $\mathcal{W}=1$. Hence, it is the discontinuity of vector component that gives the H theorem just like the discontinuity of the potential in the case of hard spheres.

We may ask what kind of vectors b with the group property, i.e., $b_k\to 0$ for $r_{ij}\to\infty$ and $i,j\in\boldsymbol{k}$ satisfy

$$\mathcal{L}|b\rangle=0. \tag{68}$$

In the case of hard spheres, it can be proved that b must be an invariant of motion [19], namely,

$$\begin{aligned}
&b_1(1)=C_1p_1^2/2M+\mathbf{C}_2\cdot\boldsymbol{p}_1+C_3, \quad b_2=C_1\phi_2,\\
&b_k=0 \quad \text{for} \quad k>2.
\end{aligned} \tag{69}$$

We present the proof for hard spheres with a smooth tail in Appendix B. Although one can find that Eq. (69) satisfies Eq. (68) in the case of smooth potentials, it is by no means clear

that this is the only solution. The reason why it cannot be simply proved is explained in Appendix B. Thus, we are left with an intriguing hypothesis that there may be other solutions of Eq. (68) than just Eq. (69).

VII. ENSKOG-LIKE RENORMALIZATION

The linearized Enskog equation for hard spheres is obtained by cutting the Hilbert space at $l=1$. From Eq. (57), it reads in our formalism

$$\partial_t Q_{11} b_1 = Q_{11}\partial_t b_1 = L_{11} b_1 . \tag{70}$$

We present a counterpart of linearized Enskog equation for smooth interactions. We truncate the Hilbert space at $l=2$ and take D sufficiently larger than the range of interaction. The Enskog-like equation is then consisted of two equations,

$$\begin{aligned} &\partial_t Q_{11} b_1 + \partial_t Q_{12} b_2 = L_{11} b_1 + L_{12} b_2 , \\ &\partial_t Q_{21} b_1 + \partial_t Q_{22} b_2 = L_{21} b_1 + L_{22} b_2 . \end{aligned} \tag{71}$$

The second equation is valid only for $r_{12} < D^+$ and all operations involving L must be carried out using Eq. (64). If the potential ϕ_2 contains a tail that should not be cut (e.g., to keep energy strictly conserved), the definition of $u^{\pm}$ may be modified as

$$|u^{\pm}\rangle = P|u\rangle + \mathcal{W}^{\pm}(I-P)|u\rangle, \tag{72}$$

where P is a Zwanzig projection operator [23] onto the energy space

$$P = \int \frac{d^3\boldsymbol{q}}{(2\pi)^3} \frac{|\tilde{e}_{\boldsymbol{q}}\rangle\langle\tilde{e}_{\boldsymbol{q}}|Q}{\langle\tilde{e}_{\boldsymbol{q}}|Q|\tilde{e}_{\boldsymbol{q}}\rangle} \tag{73}$$

and

$$\tilde{e}_{n,\boldsymbol{q}} = \begin{cases} \exp\{i\boldsymbol{q}\cdot\boldsymbol{r}_1\} p_1^2/2M & \text{if } n=1 \\ \exp\{i\boldsymbol{q}\cdot(\boldsymbol{r}_1+\boldsymbol{r}_2)/2\}\phi_2(\boldsymbol{r}_{12}) & \text{if } n=2 \\ 0 \quad \text{otherwise.} \end{cases} \tag{74}$$

The matrix elements Q_{11}, Q_{12}, Q_{22}, L_{11}, L_{12}, and L_{22} contain up to four-point correlation functions. Therefore, calculations are much more complicated than in the hard sphere case.

VIII. TRANSPORT COEFFICIENTS

The Green-Kubo formulas for transport coefficients can be reformulated in terms of our Hilbert space, Q and L. We briefly outline the well-known derivation of the formulas for kinematic shear viscosity ν, kinematic bulk viscosity ξ, and kinematic heat conductivity κ. For details see, e.g., Ref. [20].

Let us consider a set of five hydrodynamic modes $|\tilde{n}\rangle$, $|\tilde{\boldsymbol{v}}\rangle$, and $|\tilde{e}\rangle$, depending on a wave vector $\boldsymbol{q}$, corresponding to density, velocity, and energy fluctuations with components

$$\begin{aligned} \tilde{n}_1 &= e^{i\boldsymbol{q}\cdot\boldsymbol{r}_1}, \\ \tilde{\boldsymbol{v}}_1 &= e^{i\boldsymbol{q}\cdot\boldsymbol{r}_1}\boldsymbol{v}_1, \\ \tilde{e}_1 &= e^{i\boldsymbol{q}\cdot\boldsymbol{r}_1} M v_1^2/2, \\ \tilde{e}_2 &= e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_1+\boldsymbol{r}_2)/2}\phi_2(r_{12}). \end{aligned} \tag{75}$$

It is useful to replace the energy mode by the heat mode:

$$|\tilde{t}\rangle = |\tilde{e}\rangle - \left(\frac{\partial e}{\partial n}\right)_T |\tilde{n}\rangle, \tag{76}$$

where

$$\left(\frac{\partial e}{\partial n}\right)_T = e + \frac{p}{n} - \frac{T}{n}\left(\frac{\partial p}{\partial T}\right)_n , \tag{77}$$

and e, p, T, n denote energy per particle, pressure, concentration, and temperature, respectively.

The following analysis applies both to hard spheres and smooth potentials. In the case of smooth potentials, one may just omit terms with diameter of spheres d. We first find expressions for currents up to the first order in $\boldsymbol{q}$,

$$\begin{aligned} &\mathcal{L}_{\pm}|\tilde{n}\rangle = i\boldsymbol{q}\cdot|\boldsymbol{j}_n\rangle = i\boldsymbol{q}\cdot|\tilde{\boldsymbol{v}}\rangle, \\ &\mathcal{L}_-|\tilde{\boldsymbol{v}}\rangle \simeq i\boldsymbol{q}\cdot|\hat{j}_{\boldsymbol{v}+}\rangle, \quad -\langle\tilde{\boldsymbol{v}}|\mathcal{L}_+^{\dagger} \simeq \langle\hat{j}_{\boldsymbol{v}-}|\cdot i\boldsymbol{q}, \\ &\mathcal{L}_-|\tilde{e}\rangle \simeq i\boldsymbol{q}\cdot|\boldsymbol{j}_{e+}\rangle, \quad -\langle\tilde{e}|\mathcal{L}_+^{\dagger} \simeq \langle\boldsymbol{j}_{e-}|\cdot i\boldsymbol{q}, \end{aligned} \tag{78}$$

and

$$|\boldsymbol{j}_t\rangle = |\boldsymbol{j}_e\rangle - \left(\frac{\partial e}{\partial n}\right)_T |\tilde{\boldsymbol{v}}\rangle_{q=0}. \tag{79}$$

Due to Eqs. (27) and (38), the explicit expressions for currents are

$$\begin{aligned} \hat{j}_{\boldsymbol{v},1} &= \boldsymbol{v}_1\boldsymbol{v}_1, \\ \hat{j}_{\boldsymbol{v},2\pm} &= d\hat{\boldsymbol{r}}_{12}\hat{\boldsymbol{r}}_{12}(\hat{\boldsymbol{r}}_{12}\cdot\boldsymbol{v}_{12})^2\delta(r_{12}-d^+)\theta(\pm\boldsymbol{r}_{12}\cdot\boldsymbol{v}_{12}) \\ &\quad - \frac{\boldsymbol{r}_{12}}{M}\cdot\frac{\partial\phi_2(r_{12})}{\partial\boldsymbol{r}_{12}}, \\ \boldsymbol{j}_{e,1} &= \frac{M v_1^2}{2}\boldsymbol{v}_1, \\ \boldsymbol{j}_{e,2\pm} &= Md\hat{\boldsymbol{r}}_{12}(\boldsymbol{u}_{12}\cdot\hat{\boldsymbol{r}}_{12})(\hat{\boldsymbol{r}}_{12}\cdot\boldsymbol{v}_{12})^2\delta(r_{12}-d^+)\theta(\pm\boldsymbol{r}_{12}\cdot\boldsymbol{v}_{12}) \\ &\quad - \boldsymbol{r}_{12}\frac{\partial\phi_2(r_{12})}{\partial\boldsymbol{r}_{12}}\cdot\boldsymbol{u}_{12} + \boldsymbol{u}_{12}\phi_2(r_{12}), \end{aligned} \tag{80}$$

where $\mathbf{u}_{12} = (\boldsymbol{v}_1+\boldsymbol{v}_2)/2$ and we take the sign $+$ or $-$ in $\pm$ in ket or bra vector, respectively.

The Green-Kubo expressions for transport coefficients are

$$\nu = \nu_{GK} + \nu_0, \quad \xi = \xi_{GK} + \xi_0, \quad \kappa = \kappa_{GK} + \kappa_0, \tag{81}$$

where

$$\nu_{GK}=-\frac{3\langle\check{j}_{\boldsymbol{v}-}|:QL^{-1}Q|\check{j}_{\boldsymbol{v}+}\rangle}{10\langle\tilde{\boldsymbol{v}}|\cdot Q|\tilde{\boldsymbol{v}}\rangle_{q=0}}=-\frac{\langle j^{xy}_{\boldsymbol{v}-}|QL^{-1}Q|j^{xy}_{\boldsymbol{v}+}\rangle}{Vk_BTn/M},$$

$$\xi_{GK}=-\frac{3\langle j^{\perp}_{\boldsymbol{v}-}|QL^{-1}Q|j^{\perp}_{\boldsymbol{v}+}\rangle}{\langle\tilde{\boldsymbol{v}}|\cdot Q|\tilde{\boldsymbol{v}}\rangle_{q=0}}=-\frac{\langle j^{\perp}_{\boldsymbol{v}-}|QL^{-1}Q|j^{\perp}_{\boldsymbol{v}+}\rangle}{Vk_BTn/M},$$

$$\kappa_{GK}=-\frac{c_V\langle\boldsymbol{j}^{\perp}_{t-}|\cdot QL^{-1}Q|\boldsymbol{j}^{\perp}_{t+}\rangle}{3\langle\tilde{t}|Q|\tilde{t}\rangle_{q=0}}=-\frac{\langle j^{\perp x}_{t-}|QL^{-1}Q|j^{\perp x}_{t+}\rangle}{Vnk_BT^2}, \tag{82}$$

where c_V is specific heat per particle and V is volume of the system. The perpendicular currents are defined as

$$|\check{j}_{\boldsymbol{v}}\rangle=|\hat{j}_{\boldsymbol{v}}\rangle-\hat{\mathrm{I}}|j_{\boldsymbol{v}}\rangle,$$

$$j_{\boldsymbol{v}}\rangle=\frac{1}{3}\mathrm{tr}|\hat{j}_{\boldsymbol{v}}\rangle,$$

$$|\boldsymbol{j}^{\perp}_{\boldsymbol{v}}\rangle=|\boldsymbol{j}_{\boldsymbol{v}}\rangle-\frac{1}{nc_V}\left(\frac{\partial p}{\partial T}\right)_n|\tilde{t}\rangle_{q=0}-\left(\frac{\partial p}{\partial n}\right)_T|\tilde{n}\rangle_{q=0}/M,$$

$$|\boldsymbol{j}^{\perp}_{t}\rangle=|\boldsymbol{j}_{t}\rangle-\frac{T}{n}\left(\frac{\partial p}{\partial T}\right)_n|\tilde{\boldsymbol{v}}\rangle_{q=0}. \tag{83}$$

If the tail of the potential is not cut, then formulas (82) are still valid since

$$L|\tilde{e}_{\boldsymbol{q}}\rangle\simeq-i\boldsymbol{q}\cdot Q|\boldsymbol{j}_{e+}\rangle,\quad\langle\tilde{e}_{\boldsymbol{q}}|L\simeq-i\boldsymbol{q}\cdot\langle\boldsymbol{j}_{e-}|Q,$$

$$L|\tilde{\boldsymbol{v}}_{\boldsymbol{q}}\rangle\simeq-i\boldsymbol{q}\cdot Q|\hat{j}_{\boldsymbol{v}+}\rangle,\quad\langle\tilde{\boldsymbol{v}}_{\boldsymbol{q}}|L\simeq-i\boldsymbol{q}\cdot\langle\hat{j}_{\boldsymbol{v}-}|Q, \tag{84}$$

where energy modes $\tilde{e}_{\boldsymbol{q}}$ are included in the truncated space by Eq. (73).

The bare coefficients ν_0, ξ_0, and κ_0 are equal to zero for smooth potentials. However, they occur in the case of hard spheres due to the hard core and they are obtained from the second order terms of $\langle\tilde{a}|L|\tilde{a}\rangle$ [20],

$$\frac{3\langle\tilde{\boldsymbol{v}}|L|\tilde{\boldsymbol{v}}\rangle}{\langle\tilde{\boldsymbol{v}}|\cdot Q|\tilde{\boldsymbol{v}}\rangle}\simeq-\nu_0(\hat{\mathrm{I}}q^2+\boldsymbol{qq}/3)-\xi_0\boldsymbol{qq},$$

$$\frac{\langle\tilde{t}|L|\tilde{t}\rangle}{\langle\tilde{t}|Q|\tilde{t}\rangle}\simeq-\frac{\kappa_0}{c_V}q^2. \tag{85}$$

We stress that L is inverted in the reduced Hilbert space so the truncation of the space not only leaves the Green-Kubo formulas unchanged but also includes dissipation.

IX. TIME CORRELATION FUNCTIONS

It is important that L satisfies two OSR [1] even if the Hilbert space is truncated:

$$\langle a(\boldsymbol{p})|L|b(\boldsymbol{p})\rangle=\langle b(-\boldsymbol{p})|L|a(-\boldsymbol{p})\rangle^*,$$
$$\langle a(\boldsymbol{r})|L|b(\boldsymbol{r})\rangle=\langle b(-\boldsymbol{r})|L|a(-\boldsymbol{r})\rangle^*. \tag{86}$$

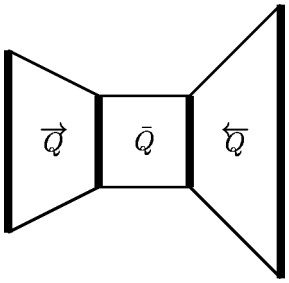

FIG. 1. Decomposition of Q into $\vec{Q}$, $\bar{Q}$ and $\overleftarrow{Q}$.

It follows from the fact that under transformation $\boldsymbol{r}\to-\boldsymbol{r}$ or $\boldsymbol{v}\to-\boldsymbol{v}$ we have

$$\boldsymbol{v}_i\cdot\frac{\partial}{\partial\boldsymbol{r}_i}\to-\boldsymbol{v}_i\cdot\frac{\partial}{\partial\boldsymbol{r}_i},\quad T_+\to T_-,\quad\mathcal{W}^+\to\mathcal{W}^-. \tag{87}$$

Suppose we would like to find the time correlation function of two vectors a and b (or $\delta\mathcal{A}$ and $\delta\mathcal{B}$),

$$\langle\delta\mathcal{A}^*(0)\,\delta\mathcal{B}(t)\rangle=\langle a|Q\exp(tQ^{-1}L)|b\rangle. \tag{88}$$

The Laplace transform of the time correlation function has a little simpler form,

$$\langle a|G(z)|b\rangle=\int_0^\infty e^{-zt}\langle\delta\mathcal{A}^*(0)\,\delta\mathcal{B}(t)\rangle dt$$
$$=\langle a|Q(zQ-L)^{-1}Q|b\rangle \tag{89}$$

or

$$G(z)=Q(zQ-L)^{-1}Q. \tag{90}$$

The difference between this and Mori's method [18] is that there the operator Q is hidden in the scalar product. Here the symmetry of time correlation functions, even with dissipation included, is transparent.

Let us introduce irreducible operators $\vec{Q}$, $\bar{Q}$, and $\overleftarrow{Q}$ [10,11] defined uniquely by

$$Q=\vec{Q}\bar{Q}\overleftarrow{Q} \tag{91}$$

and

$$\bar{Q}_{ij}=0\quad\text{if}\quad i\neq j, \tag{92}$$

$$\overleftarrow{Q}_{ij}=\begin{cases}I_{ii} & \text{if}\quad i=j\\ 0 & \text{if}\quad i>j,\end{cases} \tag{93}$$

and $\vec{Q}=\overleftarrow{Q}^{\dagger}$. The operator $\bar{Q}$ is nonzero only if its left phases are close to right phases. The graphical illustration of this decomposition is presented in Fig. 1. For example,

$$\bar{Q}_{11}=Q_{11},$$

$$\vec{Q}_{21}=Q_{21}\bar{Q}_{11}^{-1},$$

$$\bar{Q}_{22}=Q_{22}-Q_{21}\bar{Q}_{11}^{-1}Q_{12}. \tag{94}$$

Some of these operators are expressed by well-known correlation functions,

$$(\overline{Q}_{11}a_1)(1)=f_1(1)a_1(1)+f_1(1)\int d2\, f_1(2)h_2(12)a_1(2), \tag{95}$$

$$(\overline{Q}_{11}^{-1}a_1)(1)=\frac{a_1(1)}{f_1(1)}-\int d2\, c_2(12)a_1(2), \tag{96}$$

where $h_2=g_2-1$ and c_2 represent the pair correlation and the direct correlation function, respectively [24]. For more detailed analysis of these operators, see Ref. [11]. We also define $\overline{L}$ by

$$L=\vec{Q}\overline{L}\tilde{Q}. \tag{97}$$

We remember from Eqs. (30) and (44) that $\mathcal{L}_{ij-}$ is equal to 0 if $i>j+1$. Such a situation takes place whenever there is only pair interaction. We have

$$\overline{L}=-\overline{Q}\tilde{Q}\mathcal{L}_-\tilde{Q}^{-1} \tag{98}$$

and due to the definition (93) $\overline{L}_{ij}=0$ if $i>j+1$ similarly as $\mathcal{L}_-$. Taking into account the Onsager symmetry (86) we have

$$\overline{L}_{ij}=0 \quad \text{for} \quad |i-j|>1. \tag{99}$$

The formula (90) can be rewritten in the form containing A, B, $\overline{Q}$, and $\overline{L}$:

$$\langle a|G(z)|b\rangle=\langle A|\overline{G}(z)|B\rangle, \tag{100}$$

where capital vectors are defined as

$$|U\rangle=\tilde{Q}|u\rangle \tag{101}$$

and

$$\overline{G}(z)=\overline{Q}(z\overline{Q}-\overline{L})^{-1}\overline{Q}. \tag{102}$$

Note that due to Eq. (93) truncation of vectors denoted by small letters is equivalent to the truncation of capital vectors. The Enskog-like equation (71) can be written in the form

$$\begin{aligned}\partial_t\overline{Q}_{11}B_1&=\overline{L}_{11}B_1+\overline{L}_{12}B_2,\\ \partial_t\overline{Q}_{22}B_2&=\overline{L}_{21}B_1+\overline{L}_{22}B_2.\end{aligned} \tag{103}$$

X. MODE COUPLING

We can construct one-particle Enskog propagator for hard spheres or hard spheres with a smooth tail using $\overline{Q}_{11}$ and $\overline{L}_{11}$:

$$S_{11}^E(t)=\exp\{t\overline{Q}_{11}^{-1}\overline{L}_{11}\}\overline{Q}_{11}^{-1} \tag{104}$$

or its Laplace transform

$$\tilde{S}_{11}^E(z)=(z\overline{Q}_{11}-\overline{L}_{11})^{-1}. \tag{105}$$

We define operators $\dot{X}$ and $\tilde{X}$ by

$$\begin{aligned}\overline{L}_{22}&=\dot{L}_{22}+\tilde{L}_{22},\\ \overline{Q}_{22}&=\dot{Q}_{22}+\tilde{Q}_{22},\\ \overline{Q}_{22}^{-1}&=\dot{Q}_{22}^{-1}+K_{22},\end{aligned} \tag{106}$$

where

$$\begin{aligned}\dot{Q}_{22}(12|1'2')&=\overline{Q}_{11}(1|1')\overline{Q}_{11}(2|2')\\ &\quad+\overline{Q}_{11}(1|2')\overline{Q}_{11}(2|1'),\\ \dot{Q}_{22}^{-1}(12|1'2')&=\overline{Q}_{11}^{-1}(1|1')\overline{Q}_{11}^{-1}(2|2')\\ &\quad+\overline{Q}_{11}^{-1}(1|2')\overline{Q}_{11}^{-1}(2|1'),\end{aligned} \tag{107}$$

$$\dot{L}_{22}(12|1'2')=\overline{L}_{11}(1|1')\overline{Q}_{11}(2|2')+\overline{L}_{11}(2|2')\overline{Q}_{11}(1|1')+1\leftrightarrow 2.$$

Due to the property

$$\langle a|L|b\rangle=0 \tag{108}$$

for a and b independent of velocities, that is, for density modes and since $\overline{Q}$ stands at z, one may neglect operators $\tilde{L}$ and K for small z in the mode coupling formula [25]. The most trivial self-consistent ring approximation for the full propagator $\overline{G}$ is based on the ring operator

$$R_{11}^{MC}(t)=\overline{L}_{12}S_{22}^R(t)\overline{L}_{21}, \tag{109}$$

where

$$\begin{aligned}S_{22}^R(12|1'2';t)&=S_{11}^R(1|1';t)S_{11}^R(2|2';t)\\ &\quad+S_{11}^R(1|2';t)S_{11}^R(2|1';t)\end{aligned} \tag{110}$$

and the propagator S_{11}^R is defined by

$$\tilde{S}_{11}^R(z)=[z\overline{Q}_{11}-\overline{L}_{11}-\tilde{R}_{11}^{MC}(z)]^{-1}. \tag{111}$$

The celebrated mode coupling formula [13–16] is recovered for

$$\overline{G}_{11}(z)\simeq\overline{Q}_{11}\tilde{S}_{11}^R(z)\overline{Q}_{11}. \tag{112}$$

In the case of hard spheres interaction is taken into account by $\overline{L}_{11}$, while in the case of smooth tail $\overline{L}_{22}$ can be needed. Therefore, the mode coupling formula for hard spheres with smooth tails should be corrected by interaction. The correction is based on the full two-particle propagator

$$S_{22}(t)=\exp\{t\overline{Q}_{22}^{-1}\overline{L}_{22}\}\overline{Q}_{22}^{-1}. \tag{113}$$

As shown in Appendix C the *repeated ring correction* has the form

$$R_{22}^{MCR}(t)=\int_0^t ds\,\overline{L}_{12}S_{22}^R(s)\widetilde{L}_{22}S_{22}^R(t-s)\overline{L}_{21}+\frac{d}{dt}\int_0^t ds\,\overline{L}_{12}S_{22}^R(s)\dot{Q}_{22}K_{22}\dot{Q}_{22}S_{22}^R(t-s)\overline{L}_{21}. \tag{114}$$

Finally, we have

$$\widetilde{S}_{11}^R(z)=[z\overline{Q}_{11}-\overline{L}_{11}-\widetilde{R}_{11}^{MC}(z)-\widetilde{R}_{11}^{MCR}(z)]^{-1}. \tag{115}$$

This formula is solved by recurrence. One can take Enskog approximation $S^R\simeq S^E$ and $R_{11}^{MC}=R_{11}^{MCR}=0$ to the first iteration. We emphasize that there is no H theorem proven for mode coupling formulas. Therefore, the formula may not work in some cases, especially at very high densities.

XI. CONCLUSIONS

We have presented an algebraic approach to the linear kinetic theory by introducing well defined Hilbert space and two quantumlike operators. Only equilibrium distribution functions are necessary to calculate matrix elements of operators Q and L. Therefore, using standard techniques to determine distribution functions [26–29], it is possible in principle to find transport coefficients and arbitrary time correlation functions either for hard spheres or smooth potentials. The discontinuity of the Hilbert space plays the same role in dissipation as a hard core interaction. However, contrary to hard spheres, it is much harder to prove that only energy and density modes do not decay in the smooth case. We have constructed an extension of Enskog theory to smooth potentials, whereas OSR are natural consequences of our symmetric procedure. The Green-Kubo formulas are reformulated with dissipation included and a correction to the mode coupling formula is found for interactions with a hard core. The symmetric, algebraic approach may be helpful in further analysis of linear kinetic theory.

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APPENDIX A

We shall analyze only the case $l=2$. From the definitions (61) and (28), we get

$$\{a_2^{-}*,b_2^{+}\}=\mathcal{W}\{\widetilde{a}_2^*,\widetilde{b}_2\}+\sum_{i\in\mathbf{2}}\left(\widetilde{a}_2^*\mathcal{W}^{+}\frac{\partial\mathcal{W}^{-}}{\partial\boldsymbol{r}_i}\cdot\frac{\partial\widetilde{b}_2}{\partial\boldsymbol{p}_i}-\widetilde{b}_2\mathcal{W}^{-}\frac{\partial\mathcal{W}^{+}}{\partial\boldsymbol{r}_i}\cdot\frac{\partial\widetilde{a}_2^*}{\partial\boldsymbol{p}_i}\right). \tag{A1}$$

We have

$$\mathcal{W}^{\pm}(12)=\theta(D^{\pm}-r_{12}) \tag{A2}$$

and

$$\frac{\partial\mathcal{W}^{\pm}(12)}{\partial\boldsymbol{r}_{12}}=-\hat{\boldsymbol{r}}_{12}\delta(D^{\pm}-r_{12}). \tag{A3}$$

Hence, the second term on the right hand side of Eq. (A1) can be written in the form

$$-\hat{\boldsymbol{r}}_{12}\cdot\left[2\,\delta(D^{-}-r_{12})\,\theta(D^{+}-r_{12})\widetilde{a}_2^*\frac{\partial\widetilde{b}_2}{\partial\boldsymbol{p}_{12}}-2\,\delta(D^{+}-r_{12})\times\theta(D^{-}-r_{12})\widetilde{b}_2\frac{\partial\widetilde{a}_2^*}{\partial\boldsymbol{p}_{12}}\right], \tag{A4}$$

where

$$\frac{\partial}{\partial\boldsymbol{p}_{12}}=\frac{1}{2}\left(\frac{\partial}{\partial\boldsymbol{p}_1}-\frac{\partial}{\partial\boldsymbol{p}_2}\right). \tag{A5}$$

We use the identity

$$x\,\partial y=[\partial(xy)+x\,\partial y-y\,\partial x]/2 \tag{A6}$$

and

$$\delta(D^{-}-r_{12})\,\theta(D^{+}-r_{12})+\delta(D^{+}-r_{12})\,\theta(D^{-}-r_{12})=\delta(D-r_{12}) \tag{A7}$$

in order to get

$$[\delta(D^{+}-r_{12})\,\theta(D^{-}-r_{12})-\delta(D^{-}-r_{12})\,\theta(D^{+}-r_{12})]\times\hat{\boldsymbol{r}}_{12}\cdot\frac{\partial(\widetilde{a}_2^*\widetilde{b}_2)}{\partial\boldsymbol{p}_{12}}-\delta(D-r_{12})\hat{\boldsymbol{r}}_{12}\cdot\frac{\widetilde{a}_2^*\partial\widetilde{b}_2-\widetilde{b}_2\partial\widetilde{a}_2^*}{\partial\boldsymbol{p}_{12}}. \tag{A8}$$

Due to the Maxwell's distribution of velocities (11), we get

$$-k_BT\int d\mathbf{2}\,f_2[\,\delta(D^{-}-r_{12})\,\theta(D^{+}-r_{12})-\delta(D^{+}-r_{12})\times\theta(D^{-}-r_{12})]\hat{\boldsymbol{r}}_{12}\cdot\frac{\partial(\widetilde{a}_2^*\widetilde{b}_2)}{\partial\boldsymbol{p}_{12}}=-\frac{1}{2}\int d\mathbf{2}\,f_2\,\delta(D-r_{12})|\hat{\boldsymbol{r}}_{12}\cdot\boldsymbol{v}_{12}|\widetilde{a}_2^*\widetilde{b}_2. \tag{A9}$$

This generalizes easily to the case $l>2$. Only the domain $\mathcal{W}=1$ is affected by other particles. The result is Eq. (66).

APPENDIX B

For hard spheres the condition $\langle u|L|u\rangle=0$ implies from Eq. (55)

$$u(\boldsymbol{k})+u(\boldsymbol{k}-i)+u(\boldsymbol{k}-j)=u(\boldsymbol{k})+u(\boldsymbol{k}-i')+u(\boldsymbol{k}-j') \tag{B1}$$

for $k\leqslant l+1$. Here, primes denote velocities after collision given by Eq. (41). It is proven [19] that for u satisfying the group property $u_n=u_n(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n)$ for $n>1$ and

$$u(\boldsymbol{r},\boldsymbol{v})=av^2+\mathbf{b}\cdot\boldsymbol{v}+f(\boldsymbol{r}), \tag{B2}$$

where a and $\mathbf{b}$ are constants and $f(\boldsymbol{r})$ is an arbitrary function. Due to Eq. (44) and

$$T_{\pm}(ij)[a(v_1^2+v_2^2)+\mathbf{b}\cdot(\boldsymbol{v}_1+\boldsymbol{v}_2)+c]=0, \tag{B3}$$

where c may depend on positions of all particles, a vector $|w\rangle=\mathcal{L}_-|u\rangle$ belongs to the same truncated Hilbert space like u. Hence

$$\langle w|Q|w\rangle=\langle w|L|u\rangle=0. \tag{B4}$$

From the positive definiteness of Q we obtain

$$\mathcal{L}_-|u\rangle=\mathcal{L}|u\rangle=0. \tag{B5}$$

For $n>2$, u_n must be zero or otherwise free streaming will spread it all over the space. For $n=2$ we have

$$\boldsymbol{v}_1\cdot\frac{\partial u_2}{\partial \boldsymbol{r}_1}+\boldsymbol{v}_2\cdot\frac{\partial u_2}{\partial \boldsymbol{r}_2}=2a\boldsymbol{v}_{12}\cdot\frac{\partial\phi(\boldsymbol{r}_{12})}{\partial \boldsymbol{r}_{12}}. \tag{B6}$$

From the arbitrariness of $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ we get

$$\frac{\partial u_2}{\partial \boldsymbol{r}_1}=\frac{\partial\phi(\boldsymbol{r}_{12})}{\partial \boldsymbol{r}_{12}} \tag{B7}$$

and finally $u_2=2\phi_2$ from the fact that $u_2\to\infty$ when $\boldsymbol{r}_{12}\to\infty$. Similarly, for $n=1$ we obtain

$$\boldsymbol{v}\cdot\frac{\partial f(\boldsymbol{r})}{\partial \boldsymbol{r}}=0 \tag{B8}$$

and $f=$const. The result is Eq. (69).

We consider such vectors u that u_l vanish at the boundary of the domain $\mathcal{W}=1$ and

$$\langle a|L|u\rangle=0 \quad \text{for every } a. \tag{B9}$$

Vector a must be the vector truncated in the way described in Sec. VI. We can write the above equation in the form

$$\langle a|Q|\mathcal{L}u\rangle=0. \tag{B10}$$

Note that $\mathcal{L}$ contains elements pushing beyond our truncation, e.g., $\mathcal{L}_{l+1,l}$. Let us define vectors v and w by

$$v_k=\sum_{i=k-1}^{k}\mathcal{L}_{ki}u_i \quad \text{for } k<l,$$

$$v_l=\mathcal{W}\sum_{i=l-1}^{l}\mathcal{L}_{ki}u_i,\ v_k=0 \quad \text{for } k>l, \tag{B11}$$

$$w_l=(1-\mathcal{W})\sum_{i=l-1}^{l}\mathcal{L}_{li}b_i,$$

$$w_{l+1}=\mathcal{L}_{l+1,l}u_i,\quad w_k=0 \quad \text{for } k>l+1. \tag{B12}$$

We take $a=v$ and get

$$\langle v|Q|w\rangle+\langle v|Q|w\rangle=0. \tag{B13}$$

From the positive definiteness of Q we obtain

$$\langle w|Q|w\rangle-\langle v|Q|v\rangle>0. \tag{B14}$$

If u_l does not depend on velocities then $w=0$ and $|v\rangle=\mathcal{L}|u\rangle=0$ and the rest of the proof can be found in Ref. [30]. However, there is no reason for that and a non-Gibbsian solution is in principle possible.

APPENDIX C

Let us expand the propagator (113) in a Taylor series around the free propagator

$$S_{22}^0=\exp\{t\dot{Q}_{22}^{-1}\dot{L}_{22}\}\dot{Q}_{22}^{-1} \tag{C1}$$

with K_{22} or $\tilde{L}_{22}$ appearing only once. We obtain

$$\begin{aligned}S_{22}\simeq S_{22}^0&+\sum_{n=0}^{\infty}\frac{t^n}{n!}\sum_{m=0}^{n-1}(\dot{Q}_{22}^{-1}\dot{L}_{22})^m\dot{Q}_{22}^{-1}\tilde{L}_{22}\\&\times(\dot{Q}_{22}^{-1}\dot{L}_{22})^{n-m-1}\dot{Q}_{22}^{-1}\\&+\sum_{n=0}^{\infty}\frac{t^n}{n!}\sum_{m=0}^{n-1}(\dot{Q}_{22}^{-1}\dot{L}_{22})^m K_{22}\dot{L}_{22}\\&\times(\dot{Q}_{22}^{-1}\dot{L}_{22})^{n-m-1}\dot{Q}_{22}^{-1}+S_{22}^0\dot{Q}_{22}K_{22}.\end{aligned} \tag{C2}$$

Due to the identity

$$\int_0^t ds\, s^m(t-s)^k=\frac{m!k!}{(m+k+1)!}t^{m+k+1}, \tag{C3}$$

we have

$$\begin{aligned}\sum_{n=0}^{\infty}\frac{t^n}{n!}\sum_{m=0}^{n-1}(\dot{Q}_{22}^{-1}\dot{L}_{22})^m\dot{Q}_{22}^{-1}\tilde{L}_{22}(\dot{Q}_{22}^{-1}\dot{L}_{22})^{n-m-1}\dot{Q}_{22}^{-1}\\=\int ds\, S_{22}^0(s)\tilde{L}_{22}S_{22}^0(t-s).\end{aligned} \tag{C4}$$

Similarly,

$$\begin{aligned}\sum_{n=0}^{\infty}\frac{t^n}{n!}\sum_{m=0}^{n-1}(\dot{Q}_{22}^{-1}\dot{L}_{22})^m K_{22}\dot{L}_{22}(\dot{Q}_{22}^{-1}\dot{L}_{22})^{n-m-1}\dot{Q}_{22}^{-1}\\+S_{22}^0\dot{Q}_{22}K_{22}=\frac{d}{dt}\int_0^t ds\, S_{22}^0(s)\dot{Q}_{22}K_{22}\dot{Q}_{22}S_{22}^0(t-s).\end{aligned} \tag{C5}$$

The formula (114) is obtained by replacing S^0 by S^R.

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