

General H -Theorem for Hard Spheres

Adam Bednorz¹ and Bogdan Cichocki¹

Received September 13, 2002; accepted June 10, 2003

The maximum entropy formalism is used to investigate the growth of entropy (H -theorem) for an isolated system of hard spheres in an external potential under general boundary geometry. Assuming that only correlations of a finite number of particles are controlled and the rest maximizes entropy, we obtain an H -theorem for such a system. The limiting cases such as the modified Enskog equation and linear kinetic theory are discussed.

KEY WORDS: H -theorem; entropy; distribution functions.

1. INTRODUCTION

The main problem in the nonequilibrium statistical mechanics is to find an appropriate model of dissipation. Microscopic equations of motion are reversible in time but macroscopic behavior of physical systems is rather irreversible. Therefore we must include dissipation in the microscopic description of systems. To be sure that we have constructed an irreversible dynamics we should have an indicator of irreversibility, a function of the state of the system that is monotonic in time. In the macroscopic description we can use entropy. Due to Gibbs⁽¹⁾ and Shannon⁽²⁾ we can also define entropy in the statistical description. The reversible microscopic dynamics makes Shannon–Gibbs entropy constant in time^(3,4) unless we break the reversibility. We shall present such a broken dynamics that leads to the monotonic growth of entropy warranted by H -theorem.⁽⁵⁾ We shall apply the most natural maximum entropy formalism (MEF) presented in refs. 4–7 to a system of identical hard spheres.

The mechanism of the growth of entropy is outlined in refs. 6 and 10. We assume that the evolution of l first reduced distribution functions is

¹Institute of Theoretical Physics, Warsaw University, 00-681 Warszawa, Hoza 69, Poland; e-mail: abednorz@fuw.edu.pl

governed by Bogolubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy equations.⁽¹¹⁾ Due to MEF the distribution functions F_{l+1}, F_{l+2}, \dots are determined by $F_1 \cdots F_l$. Note that this procedure has been already used for some kinetic variational theories.⁽⁶⁾ The case $l=1$ —the Enskog equation—was analyzed by Resibois⁽¹²⁾ and the linear kinetic theory (LKT) of hard spheres was investigated by Bławdziewicz *et al.*⁽¹³⁾ Smooth potentials were investigated in ref. 8 but positive entropy production there is only due to the hard core. In addition to the Enskog equation and LKT we construct a set of kinetic equations describing the evolution of correlations ($l=2$). The H -theorems presented here contains two novel features besides arbitrary l . The global theorem allows arbitrary boundary conditions and external field. The local entropy density is well defined for systems with phase transitions contrary to standard definition.⁽¹⁴⁾

In Section 2 basic definitions are given. Section 3 contains evolution equations for hard spheres. In Sections 4 and 5 global and local H -theorems for hard spheres are presented, respectively. Limiting cases like revised Enskog equation and LKT are explained in Sections 6 and 7, respectively. New kinetic equations including correlations are given in Section 8. Section 9 is devoted to discussion and conclusions.

2. 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 a 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 \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. Similarly, $\mathbf{i} + j$ denotes a set of phases \mathbf{i} and one phase j and $\mathbf{i} - j$ denotes a set of phases \mathbf{i} without one phase j .

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

$$\langle \mathcal{A} \rangle = \sum_{n=0}^{\infty} \int d\mathbf{n} \rho(\mathbf{n}) \mathcal{A}(\mathbf{n}) \equiv \sum_{n=0}^{\infty} \int d\mathbf{n} \rho_n \mathcal{A}_n \quad (2.1)$$

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

$$\int d\mathbf{i} = h^{-3} \int d^3 \mathbf{r}_i \int d^3 \mathbf{p}_i, \quad (2.2)$$

where h is the Planck's constant. We shall write ρ_n and \mathcal{A}_n instead of $\rho(\mathbf{n})$ and $\mathcal{A}(\mathbf{n})$ whenever it is unambiguous. The probability distribution must satisfy normalization

$$\sum_{n=0}^{\infty} \int d\mathbf{n} \rho_n = 1. \tag{2.3}$$

Reduced distribution functions are defined as

$$F(\mathbf{m}) = \sum_{n=0}^{\infty} \int d\mathbf{n} \rho(\mathbf{n} + \mathbf{m}). \tag{2.4}$$

Due to the normalization condition (2.3) we have

$$F_0 = 1. \tag{2.5}$$

One may interpret the distribution function $F(\mathbf{m})$ as average

$$F(\mathbf{m}) = \langle f(\mathbf{m}) \rangle \tag{2.6}$$

of the microscopic density $f(\mathbf{m})$ which for n particle phase space point \mathbf{n} is given as

$$f(\mathbf{m} | \mathbf{n}) = \sum_{\mathbf{m}' \subseteq \mathbf{n}} \delta(\mathbf{m} - \mathbf{m}') \tag{2.7}$$

where the summation runs over all different m -particle sequences. The expansion of multidelta is

$$\delta(\mathbf{m} - \mathbf{m}') = \delta(1 - 1') \cdots \delta(m - m'), \quad \delta(i - i') = h^3 \delta(\mathbf{r}_i - \mathbf{r}_{i'}) \delta(\mathbf{p}_i - \mathbf{p}_{i'}). \tag{2.8}$$

The relation between ρ and F can be inverted

$$\rho(\mathbf{n}) = \sum_{m=0}^{\infty} (-1)^m \int d\mathbf{m} F(\mathbf{n} + \mathbf{m}). \tag{2.9}$$

However not all systems of functions F_n are allowed since they must give a nonnegative probability distribution. Averages of cluster functions

$$\mathcal{A}(\mathbf{n}) = a_0 + \sum_{i \in \mathbf{n}} a(i) + \sum_{i > j} a(ij) + \cdots = \sum_{\mathbf{m} \subseteq \mathbf{n}} a(\mathbf{m}) \tag{2.10}$$

are expressed by distribution functions

$$\langle \mathcal{A} \rangle = \sum_{m=0}^{\infty} \int \mathbf{d}\mathbf{m} a_m F_m. \quad (2.11)$$

We will consider hard spheres of diameter d . The probability density of an overlapping of the hard spheres is zero, and we shall take this into account by introducing the overlap function W_n defined as

$$W(\mathbf{n}) = \prod_{\substack{i>j \\ ij \in \mathbf{n}}} W(ij), \quad W(ij) = \theta(r_{ij} - d) = \begin{cases} 1 & \text{if } r_{ij} \geq d \\ 0 & \text{if } r_{ij} < d \end{cases} \quad (2.12)$$

and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$. Now we can introduce a smooth continuation of ρ to the overlap configurations $\tilde{\rho}$ defined by

$$\rho_n = W_n \tilde{\rho}_n. \quad (2.13)$$

We define functions $\gamma(\mathbf{n})$ for $n > 0$ and a number $\psi \equiv \gamma_0$ by the system of relations

$$\ln \tilde{\rho}(\mathbf{n}) = -\psi - \sum_{\mathbf{m} \subseteq \mathbf{n}} \gamma(\mathbf{m}), \quad (2.14)$$

for example

$$\begin{aligned} \ln \tilde{\rho}_0 &= -\psi, \\ \ln \tilde{\rho}(1) &= -\psi - \gamma(1), \\ \ln \tilde{\rho}(12) &= -\psi - \gamma(1) - \gamma(2) - \gamma(12). \end{aligned} \quad (2.15)$$

The quantity ψ is a functional of γ_i due to the normalization condition (2.3)

$$\psi = \psi[\gamma_i; i > 0]. \quad (2.16)$$

The Shannon–Gibbs entropy is defined as^(1,2)

$$S = - \sum_{n=0}^{\infty} \int \mathbf{d}\mathbf{n} \rho_n \ln \rho_n \quad (2.17)$$

where we set $k_B = 1$ to have entropy dimensionless and in agreement with Boltzmann function $H = -S$. However, to avoid singular terms $0 \ln 0$ for

overlapping configurations, the entropy of hard spheres is better expressed as

$$S = - \sum_{n=0}^{\infty} \int d\mathbf{n} \rho_n \ln \tilde{\rho}_n \quad (2.18)$$

due to Eq. (2.13). The above relation can be rewritten in the form containing the distribution functions, the group functions γ_i , $i > 0$ and the functional ψ , using Eq. (2.11)

$$S = \psi + \sum_{m=1}^{\infty} \int d\mathbf{m} F_m \gamma_m. \quad (2.19)$$

The equilibrium state is described by grand canonical distribution. It is such a probability distribution that at fixed average energy U and average number of particles N

$$U = \int d1 (p_1^2/2M + \phi(\mathbf{r}_1)) F(1), \quad (2.20)$$

$$N = \int d1 F(1) \quad (2.21)$$

gives maximal possible entropy.⁽¹⁵⁾ It is then fully described by (see Appendix A)

$$k_B T \gamma(\mathbf{r}, \mathbf{v}) = \phi(\mathbf{r}) + Mv^2/2 - \mu, \quad \gamma_i = 0 \quad \text{for } i > 1 \quad (2.22)$$

where T is the temperature and μ is the chemical potential. If the particles interact by a pair potential $\phi_2(\mathbf{r}_{ij})$ or more generally a many-body potential ϕ_n then we add $k_B T \gamma_2 = \phi_2$ or $k_B T \gamma_n = \phi_n$, respectively.

Finally, in the equilibrium

$$S - \frac{U}{k_B T} + \frac{\mu N}{k_B T} = \psi = \frac{pV}{k_B T}, \quad (2.23)$$

where p is the pressure and V is the volume of the system. The entropy $S(U, V, N)$ is finite.⁽¹⁶⁾

The many-body potentials have a *group property*, i.e., $\phi(\mathbf{n})$ tends to zero if $r_{ij} \rightarrow \infty$ for any pair $i, j \in \mathbf{n}$. We shall assume that the group property is preserved for γ_n also in nonequilibrium states.

3. DYNAMICS OF HARD SPHERES

We shall analyze the dynamics of hard spheres of diameter d and mass M . The evolution consists of elastic collisions and smooth movements between collisions. A set of n particles at time t is described by phases $\mathbf{n}(t; \mathbf{n}_0)$ where \mathbf{n}_0 denotes the initial phases at time 0. Between collisions the phases change according to Newton's laws

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial\phi(\mathbf{r}_i)}{\partial\mathbf{r}_i} \quad (3.1)$$

where $\mathbf{v} = \mathbf{p}/M$ is a velocity. When spheres i and j collide then the velocities \mathbf{v}_i and \mathbf{v}_j turn into \mathbf{v}'_i and \mathbf{v}'_j , respectively according to the elastic collision law

$$\begin{aligned} \mathbf{v}'_i &= \mathbf{v}_i - (\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) \hat{\mathbf{r}}_{ij}, \\ \mathbf{v}'_j &= \mathbf{v}_j + (\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) \hat{\mathbf{r}}_{ij}, \end{aligned} \quad (3.2)$$

where $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$. The same relation holds if \mathbf{v}'_i and \mathbf{v}'_j are the velocities of colliding particles turning into \mathbf{v}_i and \mathbf{v}_j , respectively, with fixed $\hat{\mathbf{r}}_{ij}$.

Averages given by Eq. (2.1) change in time according to the evolution of particles

$$\langle \mathcal{A}(t) \rangle = \sum_{\mathbf{n}_0} \int d\mathbf{n}_0 \mathcal{A}(\mathbf{n}(t; \mathbf{n}_0)) \rho(\mathbf{n}_0) = \sum_{\mathbf{n}_0} \int d\mathbf{n} \mathcal{A}(\mathbf{n}) \rho(\mathbf{n}(-t; \mathbf{n}_0)). \quad (3.3)$$

We define the evolution operator $\bar{\mathcal{F}}$ acting on functions vanishing for overlapping spheres by

$$\bar{\mathcal{F}}(t) f(\mathbf{n}_0) = f(\mathbf{n}(t; \mathbf{n}_0)). \quad (3.4)$$

The evolution of the probability distribution ρ is given by

$$\rho(\mathbf{n}; t) = \bar{\mathcal{F}}(-t) \rho(\mathbf{n}, 0). \quad (3.5)$$

The pseudo-Liouville equation for ρ is

$$\partial_t \rho = -\bar{L}_\pm \rho \quad \text{for } \mp t > 0 \quad (3.6)$$

where \bar{L}_\pm is defined by

$$\frac{d}{dt} \bar{\mathcal{F}}(\pm t) = \pm \bar{L}_\pm \bar{\mathcal{F}}(\pm t), \quad t > 0. \quad (3.7)$$

The explicit form of \bar{L}_\pm is

$$\bar{L}_\pm(\mathbf{n}) = \sum_{i \in \mathbf{n}} \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} - \sum_{i \in \mathbf{n}} \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \pm \sum_{i > j} \bar{T}_\pm(ij) \tag{3.8}$$

where the pseudo-operator $\bar{T}_\pm(ij)$ is defined as⁽²²⁻²⁵⁾

$$\bar{T}_\pm(ij) = \delta(r_{ij} - d^+) |\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}| \{ \theta(\mp \mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) b_{ij} - \theta(\pm \mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) \}, \tag{3.9}$$

and the operator b_{ij} turns i th and j th velocities in a function on its right according to the elastic collision law (3.2)

$$b_{ij} f(\dots, \mathbf{r}_i, \mathbf{v}_i, \dots, \mathbf{r}_j, \mathbf{v}_j, \dots) = f(\dots, \mathbf{r}_i, \mathbf{v}'_i, \dots, \mathbf{r}_j, \mathbf{v}'_j, \dots). \tag{3.10}$$

The Dirac δ -function is taken at $r_{ij} = d^+$, where $d^+ = d + |\epsilon|$, $\epsilon \rightarrow 0$.

It is more convenient to work with the evolution equations for the distribution functions, namely the BBGKY hierarchy for hard spheres.⁽²⁵⁾ It follows from the definition (2.4) of F and Liouville equation (3.6) and for $t > 0$ has the form

$$\{ \partial_t + \bar{L}_-(\mathbf{m}) \} F(\mathbf{m}) = \sum_{i \in \mathbf{m}} \int d(m+1) \bar{T}_-(i, m+1) F(\mathbf{m}+1), \quad m = 1, 2, \dots \tag{3.11}$$

We define also an operator \mathcal{S} acting on functions continuous at overlapping configurations by

$$\bar{\mathcal{S}}W = W\mathcal{S}. \tag{3.12}$$

We can write then the evolution equation for $\tilde{\rho}$ as

$$\tilde{\rho}(\mathbf{n}; t) = \mathcal{S}(-t) \tilde{\rho}(\mathbf{n}, 0) \tag{3.13}$$

valid only for non-overlapping configurations that lead to the equation

$$\partial_t \tilde{\rho} = -L_\pm \tilde{\rho} \quad \text{for} \quad \mp t > 0 \tag{3.14}$$

where L_\pm is defined as

$$\frac{d}{dt} \mathcal{S}(\pm t) = \pm L_\pm \mathcal{S}(\pm t), \quad t > 0 \tag{3.15}$$

and has the property

$$\bar{L}_\pm W = W L_\pm. \tag{3.16}$$

Its explicit form is

$$L_{\pm}(\mathbf{n}) = \sum_{i \in \mathbf{n}} \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} - \sum_{i \in \mathbf{n}} \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \pm \sum_{i > j} T_{\pm}(ij), \quad (3.17)$$

where

$$T_{\pm}(ij) = \delta(r_{ij} - d^+) |\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}| \theta(\mp \mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij})(b_{ij} - 1). \quad (3.18)$$

Operators T and \bar{T} are also related by the following property

$$\int di dj u(i, j) T_{\pm}(ij) w(i, j) = \int di dj w(i, j) \bar{T}_{\mp}(ij) u(i, j) \quad (3.19)$$

for arbitrary functions u and w . To prove the above one should use the exchange of integration variables $\mathbf{v}_i, \mathbf{v}_j \leftrightarrow \mathbf{v}'_i, \mathbf{v}'_j$, and properties following from the collision law (3.2): $\mathbf{v}''_i = \mathbf{v}_i, \mathbf{v}''_j = \mathbf{v}_j, d\mathbf{v}_i d\mathbf{v}_j = d\mathbf{v}'_i d\mathbf{v}'_j$, and $\mathbf{r}_{ij} \cdot \mathbf{v}'_{ij} = -\mathbf{r}_{ij} \cdot \mathbf{v}_{ij}$. The last leads to

$$\cdots \theta(\pm \mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) b_{ij} \cdots = \cdots b_{ij} \theta(\mp \mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) \cdots \quad (3.20)$$

at fixed $\mathbf{r}_i, \mathbf{r}_j$ (see also refs. 23 and 24).

4. GLOBAL H-THEOREM

Let us consider only l first equations in the hierarchy (3.11). To close the set of equation we express F_{l+1} functionally by $F_1 \cdots F_l$ by construction of such a probability distribution that at fixed $F_1 \cdots F_l$ has maximum possible entropy (see Appendix A). The result is that the probability distribution ρ as well as distribution functions F are described either by $F_1 \cdots F_l$ or by $\gamma_1 \cdots \gamma_l$ and

$$\gamma_m = 0 \quad \text{for } m = l+1, l+2, \dots \quad (4.1)$$

Hence distribution functions $F_m, m > l$ are not arbitrary and must depend functionally on $F_1 \cdots F_l$. The above relations, though formal, have a graphical interpretation by (generalized) Mayer graphs as shown in refs. 19–21. We shall assume that the considered system is isolated.

The expression for the change of entropy is

$$\frac{dS}{dt} = - \sum_{n=0}^{\infty} \int d\mathbf{n} (\rho_n \partial_t \ln \tilde{\rho}_n + \ln \tilde{\rho}_n \partial_t \rho_n). \quad (4.2)$$

The first term vanishes from the normalization condition (2.3) and the rest can be collected similarly as in Eq. (2.19)

$$\frac{dS}{dt} = \sum_{m=1}^l \int d\mathbf{m} \gamma_m \partial_t F_m. \quad (4.3)$$

We obtain from BBGKY hierarchy (3.11)

$$\begin{aligned} \frac{dS}{dt} = & - \sum_{m=1}^l \int d\mathbf{m} \gamma_m \sum_{i \in \mathbf{m}} \mathbf{v}_i \cdot \frac{\partial F_m}{\partial \mathbf{r}_i} + \sum_{m=1}^l \int d\mathbf{m} \gamma_m \sum_{i \in \mathbf{m}} \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial F_m}{\partial \mathbf{p}_i} \\ & + \sum_{m=2}^l \int d\mathbf{m} \gamma_m \sum_{i>j} \bar{T}_-(ij) F_m + \sum_{m=1}^l \int d\mathbf{m} d\mathbf{l} \gamma_m \sum_{i \in \mathbf{m}} \bar{T}_-(i1) F_{m+1}. \end{aligned} \quad (4.4)$$

Firstly, let us consider the first term on the right hand side in the above equation (free streaming). As shown in Appendix B it is equal

$$- \sum_{m=1}^l \int d\mathbf{m} \gamma_m \sum_{i \in \mathbf{m}} \mathbf{v}_i \cdot \frac{\partial F_m}{\partial \mathbf{r}_i} = \int d\mathbf{2} \delta(r_{12} - d^+) \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} F_2. \quad (4.5)$$

The next term in Eq. (4.4) (potential term) is

$$\sum_{m=1}^l \int d\mathbf{m} \gamma_m \sum_{i \in \mathbf{m}} \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial F_m}{\partial \mathbf{p}_i} = 0, \quad (4.6)$$

because contrary to the free streaming there are no boundary terms in momentum. The last two terms in Eq. (4.4) can be written with help of Eq. (3.19) as

$$\begin{aligned} & \sum_{m=2}^l \int d\mathbf{m} \gamma_m \sum_{i>j} \bar{T}_-(ij) F_m + \sum_{m=1}^l \int d\mathbf{m} d\mathbf{l} \gamma_m \sum_{i \in \mathbf{m}} \bar{T}_-(i1) F_{m+1} \\ & = \sum_{m=2}^{l+1} \int d\mathbf{m} F(\mathbf{m}) \sum_{i>j} T_+(ij) \{ \gamma(\mathbf{m}) + \gamma(\mathbf{m}-i) + \gamma(\mathbf{m}-j) \} \end{aligned} \quad (4.7)$$

where $\gamma_{l+1} = 0$.

We are ready to prove the announced *H*-theorem. As shown in Appendix B, the right hand side of Eq. (4.7) can be written in the form

$$- \sum_{n=2}^{\infty} \int d\mathbf{n} \sum_{i>j} \delta(r_{ij} - d^+) |\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}| \theta(-\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) W_n \tilde{\rho}(\mathbf{n}) \ln \frac{\tilde{\rho}(\mathbf{n}')}{\tilde{\rho}(\mathbf{n})}, \quad (4.8)$$

where $\mathbf{n}' = \{1 \cdots i' \cdots j' \cdots n\}$ with \mathbf{v}'_i and \mathbf{v}'_j given by the collision law (3.2). We apply the inequality

$$x \ln \frac{y}{x} \leq y - x \quad (4.9)$$

to $x = \tilde{\rho}(\mathbf{n})$ and $y = \tilde{\rho}(\mathbf{n}')$. Finally we get

$$\begin{aligned} & - \sum_{n=2}^{\infty} \int d\mathbf{n} \rho_n \sum_{i>j} T_+(ij) \ln \tilde{\rho}_n \\ & \geq \sum_{n=2}^{\infty} \int d\mathbf{n} \sum_{i>j} \delta(r_{ij} - d^+) |\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}| \theta(-\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) (\rho(\mathbf{n}) - \rho(\mathbf{n}')) \\ & = - \int d\mathbf{2} \delta(r_{12} - d^+) \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} F_2. \end{aligned} \quad (4.10)$$

The term on the right hand side in the above equation cancels exactly the right hand side in Eq. (4.5) so that

$$\frac{dS}{dt} \geq 0. \quad (4.11)$$

In the isolated system the average number of particles and energy (see Eqs. (2.20) and (2.21)) are conserved since from BBGKY hierarchy (3.11) we have

$$\frac{dN}{dt} = \int d\mathbf{1} \frac{\partial}{\partial \mathbf{r}_1} \cdot (\mathbf{v}_1 F_1) \quad (4.12)$$

$$\frac{dU}{dt} = \int d\mathbf{1} \frac{\partial}{\partial \mathbf{r}_1} \cdot (F(1) \mathbf{v}_1 p_1^2 / 2M) + \int d\mathbf{2} F(12) T_+(12) M v_1^2 / 2. \quad (4.13)$$

Due to symmetry, we can exchange $1 \leftrightarrow 2$ in the latter equation and the last term vanishes because $T_+(12)(v_1^2 + v_2^2) = 0$. The boundary terms vanish because $F(v_{\perp}) = F(-v_{\perp})$ for component v_{\perp} perpendicular to the boundary of the isolated system. Hence, N and U are constant and the entropy must reach the maximum which does not exceed the entropy of the Gibbs state (2.22).

Let us find a condition for equilibrium states. Such states are characterized by the condition

$$\frac{dS}{dt} = 0 \quad (4.14)$$

and

$$\frac{\partial F_m}{\partial t} = 0, \quad m \leq l. \quad (4.15)$$

It follows from the inequality (4.9) that (4.14) holds only if

$$\ln \tilde{\rho}(\mathbf{n}) = \ln \tilde{\rho}(\mathbf{n}') \quad \text{for } r_{ij} = d, \quad (4.16)$$

or equivalently, using the expansion (2.14)

$$\begin{aligned} & \gamma(\mathbf{m} + i' + j') + \gamma(\mathbf{m} + i') + \gamma(\mathbf{m} + j') \\ & = \gamma(\mathbf{m} + i + j) + \gamma(\mathbf{m} + i) + \gamma(\mathbf{m} + j) \quad \text{for } r_{ij} = d, \quad m < l \end{aligned} \quad (4.17)$$

for all non-overlapping configurations. The time derivatives of F are related to the time derivatives of γ by

$$\partial_t F_k = - \sum_{m>0} \int \mathbf{d}\mathbf{m} \mathcal{Q}_{km} \partial_t \gamma_m \quad (4.18)$$

where the operator \mathcal{Q} is defined by functional derivatives of F or $\psi^{(17,18)}$ (see also Appendix A)

$$\mathcal{Q}_{km} = - \frac{\delta F_k}{\delta \gamma_m} = \frac{\delta^2 \psi}{\delta \gamma_k \delta \gamma_m}. \quad (4.19)$$

It is proved in Appendix C that due to Eq. (4.17) we can rewrite BBGKY hierarchy (3.11) in the form

$$\partial_t F_k = \sum_m \int \mathbf{d}\mathbf{m} \mathcal{Q}_{km} L_{0,m} \gamma_m \quad \text{for } 0 < k \leq l \quad (4.20)$$

where

$$L_0(\mathbf{m}) = \sum_{i \in \mathbf{m}} \left(\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right). \quad (4.21)$$

We subtract Eq. (4.18) from (4.20) and integrate with $(\partial_t + L_{0,k}) \gamma_k$. The result is

$$\sum_{k,m} \int \mathbf{d}\mathbf{k} \mathbf{d}\mathbf{m} (\partial_t \gamma_k + L_{0,k} \gamma_k) \mathcal{Q}_{km} (\partial_t \gamma_m + L_{0,m} \gamma_m) = 0. \quad (4.22)$$

Since Q is a positive definite operator (see Appendix A) γ_m must satisfy Liouville equation, namely

$$\partial_i \gamma_m + L_{0,m} \gamma_m = 0 \quad \text{for } 0 < m \leq l. \quad (4.23)$$

Due the condition

$$\partial_i F_k = 0 \quad \text{for } 0 < k \leq l \quad (4.24)$$

and positive definiteness of Q we arrive at stationary Liouville equation

$$L_{0,m} \gamma_m = 0 \quad \text{for } 0 < m \leq l. \quad (4.25)$$

We consider the case $m = 0$ and $l = 1$ in Eq. (4.17), i.e.,

$$\gamma(1) + \gamma(2) = \gamma(1') + \gamma(2'), \quad r_{12} = d. \quad (4.26)$$

It is shown in Appendix C that the above equality implies

$$k_B T \gamma(\mathbf{r}, \mathbf{v}) = M v^2 / 2 + M \mathbf{b} \cdot \mathbf{v} + M (\mathbf{c} \times \mathbf{r}) \cdot \mathbf{v} - \mu(\mathbf{r}) \quad (4.27)$$

where T is a constant kinetic temperature ($k_B T = \langle M v^2 / 2 \rangle$), \mathbf{b} and \mathbf{c} are constants and μ is an *intrinsic chemical potential*⁽¹⁴⁾ depending on the position only. Due to Eqs. (2.4) and (2.14) there exists a functional relation between $\mu(\mathbf{r})$ and density profile $n(\mathbf{r})$ defined as

$$n(\mathbf{r}) = h^{-3} \int d^3 \mathbf{p} F(\mathbf{r}, \mathbf{p}). \quad (4.28)$$

In the case $m = 1$ Eq. (4.25) reads

$$\mathbf{v} \cdot \frac{\partial \mu}{\partial \mathbf{r}} = \frac{\partial \phi}{\partial \mathbf{r}} \cdot (\mathbf{v} + \mathbf{b} + \mathbf{c} \times \mathbf{r}). \quad (4.29)$$

Since \mathbf{v} is an independent vector we obtain $\mathbf{b} = \mathbf{c} = 0$ if $\phi \neq \text{const}$ and

$$k_B T \gamma(\mathbf{r}, \mathbf{v}) = \phi(\mathbf{r}) + M v^2 / 2 - \mu \quad \text{or} \quad \mu(\mathbf{r} | n) + \phi(\mathbf{r}) = \text{const}. \quad (4.30)$$

If ϕ is invariant under some translation or rotation then the momentum term $\mathbf{b} \cdot \mathbf{v}$ or the angular momentum term $(\mathbf{c} \times \mathbf{r}) \cdot \mathbf{v}$ need not be zero. However, we can always take another reference system where they are equal to 0.

We take $m = l - 1$ in a general case so that Eq. (4.17) gives

$$\gamma(\mathbf{m} + i) + \gamma(\mathbf{m} + j) = \gamma(\mathbf{m} + i') + \gamma(\mathbf{m} + j'), \quad r_{ij} = d. \quad (4.31)$$

We can use the result (C.25) keeping the phases \mathbf{m} constant.⁽¹³⁾ Then a , \mathbf{b} , and \mathbf{c} depend only on the phases \mathbf{m} . Hence, they must be zero from the group property and $\gamma(\mathbf{m}+i)$ is a function of the position of i and by symmetry a function of positions of all phases only. Then Eq. (4.31) can be used for $m = l-2$ and so on. The conclusion is that $\gamma(\mathbf{m}) = \gamma(\mathbf{r}_1, \dots, \mathbf{r}_m)$ for $m > 1$. It follows from the Liouville equation (4.25) that γ_m is a constant and finally $\gamma_m = 0$ for $m > 1$ from the group property.

We stress that obtained Gibbs states are described by a constant chemical potential. Therefore coexistence of many phases with the same chemical potential and different densities is allowed in general. For the comparison Resibois proved only that the density is constant under periodic boundary conditions and in absence of external potential. It was proved that Eq. (4.30) leads to a stationary solution of Enskog equation.⁽²⁶⁾ Here we proved that this is the only solution.

5. LOCAL *H*-THEOREM

We shall formulate the local *H*-theorem that local entropy production is non-decreasing.^(27, 28) Our purpose is to prove the following local entropy balance equation for functions depending on one position variable \mathbf{r}

$$\frac{\partial s(\mathbf{r}, t)}{\partial t} + \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{J}(\mathbf{r}, t) = \sigma(\mathbf{r}, t) \geq 0 \tag{5.1}$$

where functions s , \mathbf{J} , and σ depend on the state of the system, probability distribution.

Firstly, we introduce some auxiliary notation. For any quantity X dependent on the probability distribution determined by $\gamma_1, \gamma_2, \dots$ we define the quantity $X(\alpha)$ for α from 0 to ∞ as

$$X(\alpha) = X[\gamma_1(\alpha), \gamma_2, \gamma_3, \dots], \quad \gamma_1(\alpha) = \gamma_1 + \alpha. \tag{5.2}$$

Actually we shall use this formula for $\psi(\alpha)$, $F_1(\alpha)$, and $Q_{1m}(\alpha)$ where Q is defined by Eq. (4.19). Then $X(\infty) = 0$ and $X(0) = X$. Due to $F_1 = -\delta\psi/\delta\gamma_1$ (see Eq. (A.6)) we have

$$\psi = -\int_0^\infty d\alpha \frac{d\psi(\alpha)}{d\alpha} = \int_0^\infty d\alpha \int d\mathbf{1} F(\mathbf{1}; \alpha). \tag{5.3}$$

The definition of s is

$$s(\mathbf{r}) = \sum_{m>0} \int d'\mathbf{m} F_m \gamma_m + \int_0^\infty d\alpha \int d'\mathbf{1} F(\mathbf{1}; \alpha) \tag{5.4}$$

where

$$\mathbf{d}'\mathbf{m} = \frac{1}{m} \mathbf{d}\mathbf{m} \sum_{i \in \mathbf{m}} \delta(\mathbf{r}_i - \mathbf{r}). \quad (5.5)$$

One can check that

$$\int \mathbf{d}\mathbf{r} s(\mathbf{r}) = S. \quad (5.6)$$

In the case $l=1$ an alternative definition of entropy density is used in refs. 8, 14, and 28

$$\tilde{s}(\mathbf{r}) = h^{-3} \int \mathbf{d}^3 \mathbf{p} F(\mathbf{r}, \mathbf{p}) \left(1 - \ln F(\mathbf{r}, \mathbf{p}) + \int_0^1 c(\mathbf{r} | \alpha n_1) \, \mathrm{d}\alpha \right) \quad (5.7)$$

where n is given by Eq. (4.28) and $c_1 = \ln F_1 + \gamma_1$ is a direct one point correlation function. However αn_1 is not well defined if the phase transition occurs and n_1 cannot get arbitrary value due to the density gap. On the contrary our definition (5.4) allows phase transitions since α corresponds to the chemical potential which is continuous.

We will analyze the time evolution of s

$$\begin{aligned} \frac{\partial s}{\partial t} &= \sum_{m>0} \int \mathbf{d}'\mathbf{m} \gamma_m \partial_t F_m + \sum_{m>0} \int \mathbf{d}'\mathbf{m} F_m \partial_t \gamma_m \\ &+ \sum_{m>0} \int_0^\infty \mathrm{d}\alpha \int \mathbf{d}'\mathbf{1} \mathbf{d}\mathbf{m} \frac{\delta F(1; \alpha)}{\delta \gamma_m} \partial_t \gamma_m. \end{aligned} \quad (5.8)$$

Taking into account that $\delta F_1 / \delta \gamma_m = -Q_{1m} = -Q_{m1}$ and

$$F(\mathbf{m}) = - \int_0^\infty \mathrm{d}\alpha \int \mathbf{d}'\mathbf{1} \frac{\delta F(\mathbf{m}; \alpha)}{\delta \gamma(\mathbf{1})} \quad (5.9)$$

we obtain

$$\frac{\partial s}{\partial t} = \sum_{m>0} \int \mathbf{d}'\mathbf{m} \gamma_m \partial_t F_m - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{J}_A. \quad (5.10)$$

The current \mathbf{J}_A is obtained from the useful identity

$$\int \mathbf{d}\mathbf{r}' [X(\mathbf{r}, \mathbf{r}') - X(\mathbf{r}', \mathbf{r})] = - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{J}_X \quad (5.11)$$

where

$$\mathbf{J}_X = \int_0^1 d\lambda \int d^3\mathbf{r}' \mathbf{r}' X(\mathbf{r} + \lambda\mathbf{r}', \mathbf{r} - (1-\lambda)\mathbf{r}'). \quad (5.12)$$

In our case

$$A(\mathbf{r}_a, \mathbf{r}_b) = -\int_0^\infty d\alpha \int d\mathbf{l} d\mathbf{m} \sum_{i \in \mathbf{m}} \frac{\delta(\mathbf{r}_a - \mathbf{r}_i) \delta(\mathbf{r}_b - \mathbf{r}_i)}{m} Q_{1m}(\alpha) \partial_i \gamma_m. \quad (5.13)$$

We emphasize that $\partial_i \gamma_m$ is expressed by $\partial_i F_k$, $k \leq l$ from Eq. (3.11) by the relation

$$\partial_i \gamma_m = \sum_{k=1}^l \int d\mathbf{k} \frac{\delta \gamma_m}{\delta F_k} \partial_i F_k. \quad (5.14)$$

The next term follows from BBGKY hierarchy for $\partial_i F_m$

$$\sum_{m>0} \int d^3\mathbf{m} \gamma_m \sum_{i \in \mathbf{m}} \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial F_m}{\partial \mathbf{p}_i} = \int d^3\mathbf{r}' [B(\mathbf{r}, \mathbf{r}') - B(\mathbf{r}', \mathbf{r})], \quad (5.15)$$

$$B(\mathbf{r}_a, \mathbf{r}_b) = \sum_{m>0} \int d\mathbf{m} \sum_{i \neq j} \frac{\delta(\mathbf{r}_b - \mathbf{r}_i) \delta(\mathbf{r}_a - \mathbf{r}_j)}{m} \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial F_m}{\partial \mathbf{p}_i} \gamma_m \quad (5.16)$$

(see Appendix D). The free streaming term is (see Appendix D)

$$-\sum_{m>0} \int d^3\mathbf{m} \gamma_m \sum_{i \in \mathbf{m}} \mathbf{v}_i \cdot \frac{\partial F_m}{\partial \mathbf{r}_i} = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{J}_s - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{J}_C + \sigma_C \quad (5.17)$$

where the current \mathbf{J}_s is defined as

$$\mathbf{J}_s = \sum_{m>0} \int d\mathbf{m} \sum_{i \in \mathbf{m}} \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{v}_i \gamma_m F_m + \int d^3\mathbf{1} \mathbf{v}_1 F_1, \quad (5.18)$$

and \mathbf{J}_C is defined by

$$C(\mathbf{r}_a, \mathbf{r}_b) = \sum_{m>0} \int d\mathbf{m} \sum_{i \neq j} \frac{\delta(\mathbf{r}_a - \mathbf{r}_i) \delta(\mathbf{r}_b - \mathbf{r}_j)}{m} \mathbf{v}_i \cdot \frac{\partial F_m}{\partial \mathbf{r}_i} \gamma_m + \int d^2 \delta(\mathbf{r}_a - \mathbf{r}_1) \delta(\mathbf{r}_b - \mathbf{r}_2) \mathbf{v}_1 \cdot \hat{\mathbf{r}}_{12} \delta(r_{12} - d^+) F_2. \quad (5.19)$$

The potential term of entropy production is

$$\sigma_C = \int d^2 \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} \delta(r_{12} - d^+) F_2. \quad (5.20)$$

For the collision operator we have (compare Eq. (4.7))

$$\begin{aligned} & \sum_{m>0} \int d^m \mathbf{m} d\mathbf{l} F_{m+1} \sum_{i \in \mathbf{m}} T_+(i\mathbf{l}) \gamma_m \\ &= \sum_{m>1} \int d^m \mathbf{m} F_m \sum_{i \neq j} T_+(ij) \gamma(\mathbf{m}-j) - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{J}_D \end{aligned} \quad (5.21)$$

where

$$D(\mathbf{r}_a, \mathbf{r}_b) = \sum_{m>0} \int d\mathbf{m} d\mathbf{l} F_{m+1} \sum_{ij \in \mathbf{m}} \frac{\delta(\mathbf{r}_b - \mathbf{r}_i) \delta(\mathbf{r}_a - \mathbf{r}_j)}{m(m+1)} T_+(i\mathbf{l}) \gamma_m. \quad (5.22)$$

Finally adding up collision terms we arrive at

$$\sum_{m>0} \int d^m \mathbf{m} F_m \sum_{i>j} T_+(ij) [\gamma_m + \gamma(\mathbf{m}-i) + \gamma(\mathbf{m}-j)] = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{J}_E + \sigma_E \quad (5.23)$$

where

$$\begin{aligned} E(\mathbf{r}_a, \mathbf{r}_b) &= \sum_{m>1} \int d\mathbf{m} F_m \sum_{\substack{ijk \in \mathbf{m} \\ i>j}} \delta(\mathbf{r}_a - \mathbf{r}_k) \frac{\delta(\mathbf{r}_b - \mathbf{r}_i) + \delta(\mathbf{r}_b - \mathbf{r}_j)}{2m} \\ &\quad \times T_+(ij) [\gamma_m + \gamma(\mathbf{m}-i) + \gamma(\mathbf{m}-j)] \end{aligned} \quad (5.24)$$

$$\begin{aligned} \sigma_E &= \frac{1}{2} \sum_{m>1} \int d\mathbf{m} F_m \sum_{i>j} [\delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_j)] \\ &\quad \times T_+(ij) [\gamma_m + \gamma(\mathbf{m}-i) + \gamma(\mathbf{m}-j)]. \end{aligned} \quad (5.25)$$

The quantities \mathbf{J} and σ appearing in Eq. (5.1) are found as

$$\mathbf{J} = \mathbf{J}_s + \mathbf{J}_A + \mathbf{J}_B + \mathbf{J}_C + \mathbf{J}_D + \mathbf{J}_E, \quad \sigma = \sigma_C + \sigma_E. \quad (5.26)$$

Note that only \mathbf{J}_s is a real macroscopic current since the rest is due to the microscopic non-local correlations. By expressing σ_C and σ_E by $\tilde{\rho}$ (see Appendix D), we get

$$\sigma = -\frac{1}{2} \sum_{n=2}^{\infty} \int d\mathbf{n} W_n \sum_{i>j} [\delta(\mathbf{r}-\mathbf{r}_i) + \delta(\mathbf{r}-\mathbf{r}_j)] \quad (5.27)$$

$$\times [\tilde{\rho}_n T_+(ij) \ln \tilde{\rho}_n - T_+(ij) \tilde{\rho}_n] \geq 0. \quad (5.28)$$

We have applied inequality (4.9) to $x = \tilde{\rho}(\mathbf{n})$ and $y = \tilde{\rho}(\mathbf{n}')$, similarly as in Eq. (4.10).

6. REVISED ENSKOG EQUATION

In the previous sections we have developed a method of closing BBGKY hierarchy for hard spheres. Here we show that in one special limiting case ($l = 1$) our formalism leads to the revised Enskog equation (REE) used by Resibois.⁽¹²⁾

Cutting at $l = 1$ means that $\gamma_k = 0$ for $k > 1$ and the only evolution equation is

$$\left\{ \frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} - \frac{\partial \phi(\mathbf{r}_1)}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} \right\} F(1) = \int d2 \bar{T}_-(12) F(12). \quad (6.1)$$

The above equation gives the evolution of F_1 but contains F_2 . However since $\gamma_k = 0$ for $k > 1$ it is possible to express F_m for $m > 1$ as a functional of F_1 . We shall find the form of this functional by writing F_m , given by Eq. (2.4), in terms of γ_1

$$F(\mathbf{m}) = \mathcal{E}^{-1} \prod_{j \in \mathbf{m}} w(j) \sum_{n=0}^{\infty} \int d\mathbf{n} W_{n+m} \prod_{i \in \mathbf{n}} w(i) \quad (6.2)$$

where $w(i) = \exp\{-\gamma(i)\}$ and

$$\mathcal{E} = \exp \psi = \sum_{n=0}^{\infty} \int d\mathbf{n} W_n \prod_{i \in \mathbf{n}} w(i). \quad (6.3)$$

Since there are no velocity correlations it is convenient to introduce the fugacity $z(\mathbf{r})$ defined as

$$z(\mathbf{r}) = h^{-3} \int d^3 \mathbf{p} w(\mathbf{r}, \mathbf{p}) \quad (6.4)$$

and k -particle density $n(\mathbf{r}_1, \dots, \mathbf{r}_k)$ given by

$$n(\mathbf{r}_1, \dots, \mathbf{r}_k) = h^{-3k} \int d^3 \mathbf{p}_1 \cdots d^3 \mathbf{p}_k F_k \quad (6.5)$$

so that $n(\mathbf{r})$ coincides with Eq. (4.28). From Eq. (6.2) we obtain the functional relation between n_k and $z(\mathbf{r})$

$$n(\mathbf{r}_1, \dots, \mathbf{r}_k) = \mathcal{E}^{-1} \prod_{j \in \mathbf{k}} z(\mathbf{r}_j) \sum_{m=0}^{\infty} \frac{1}{m!} \int d^3 \mathbf{r}_{k+1} \cdots d^3 \mathbf{r}_{k+m} W_{k+m} \prod_{i \in \mathbf{m}} z(\mathbf{r}_i) \quad (6.6)$$

and

$$\mathcal{E} = \sum_{m=0}^{\infty} \frac{1}{m!} \int d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_m W_m \prod_{i \in \mathbf{m}} z(\mathbf{r}_i). \quad (6.7)$$

The functional relation between $n_1(\mathbf{r}) \equiv n(\mathbf{r})$ and $z(\mathbf{r})$ can be inverted. Then k -particle density n_k is a functional of $n(\mathbf{r})$. Taking into account that velocities are uncorrelated we obtain

$$F(\mathbf{k}) = g(\mathbf{r}_1, \dots, \mathbf{r}_k) \prod_{i \in \mathbf{k}} F(\mathbf{r}_i, \mathbf{v}_i) \quad (6.8)$$

where

$$g(\mathbf{r}_1, \dots, \mathbf{r}_k) = \frac{n(\mathbf{r}_1, \dots, \mathbf{r}_k)}{n(\mathbf{r}_1) \cdots n(\mathbf{r}_k)} \quad (6.9)$$

is the same functional of $n(\mathbf{r})$ as in a nonuniform hard sphere fluid in equilibrium.^(29,30) Hence, taking $F(12) = g(12) F(1) F(2)$ in Eq. (6.1) we obtain revised Enskog equation. By taking $l = 1$ in our global and local H -theorem we obtain the well known proofs of Resibois,⁽¹²⁾ Mareschal *et al.*,⁽²⁷⁾ and Piasecki.⁽²⁸⁾ However, as we already noted, our proof allows general boundary geometry and external potential, which is novel.

7. LINEAR KINETIC THEORY

Let us consider a state of the system close to equilibrium determined by γ^{eq} and F^{eq} , described by T and μ

$$k_B T \gamma^{\text{eq}}(\mathbf{r}, \mathbf{v}) = M v^2 / 2 + \phi(\mathbf{r}) - \mu$$

$$\gamma_n^{\text{eq}} = 0 \quad \text{for } n > 1.$$

We shall denote the deviation from equilibrium by $\delta\gamma$ and δF

$$\gamma_n = \gamma_n^{\text{eq}} + \delta\gamma_n,$$

$$F_n = F_n^{\text{eq}} + \delta F_n.$$

We consider only such states that $\delta\gamma$ and δF are initially localized in space. Moreover, the average number of particles (2.21) and energy (2.20) is the same as in equilibrium, hence

$$\int d\mathbf{l} \gamma_1^{\text{eq}} \delta F_1 = 0. \tag{7.1}$$

The total momentum is equal to 0. Due to the conservation laws these properties are preserved during the evolution.

By linearization of relations (4.1) we get $\delta\gamma_k = 0$ for $k > l$ so that δF_m is a linear functional of $\delta\gamma_k$, $0 < k \leq l$. This functional is given explicitly by the integral operator with the kernel Q defined by Eq. (4.19) and calculated for the equilibrium distribution.

$$\delta F_m = - \sum_{i=1}^l \int d\mathbf{i} Q_{mi}^{\text{eq}} \delta\gamma_i \tag{7.2}$$

and the explicit form of Q^{eq} is given by Eq. (A.8) with distribution functions F replaced by equilibrium functions F^{eq} . The BBGKY hierarchy (3.11) for δF is the same as for F since F^{eq} is its stationary solution, i.e.,

$$\begin{aligned} & \{\partial_t + \bar{L}_-(\mathbf{m})\} \delta F(\mathbf{m}) \\ &= \sum_{i \in \mathbf{m}} \int d(m+1) \bar{T}_-(i, m+1) \delta F(\mathbf{m}+1), \quad t > 0, \quad m = 1, 2, \dots \end{aligned} \tag{7.3}$$

Since we need δF_{l+1} we must invert the functional relation (7.2). The general methods to determine the inverse functional, i.e., to find an operator $[Q^{\text{eq}}]^{-1}$ are discussed in ref. 13 and the references therein.

The H -theorem proved by Bławdziewicz *et al.*⁽¹³⁾ is obtained by linearization of our general theorem. Taking into account the definition of entropy (2.19) and the operator Q (4.19) we obtain an expression for the deviation from equilibrium of the function $\delta S = S - S^{\text{eq}}$

$$\delta S = -\delta\mathcal{H} + o(\delta\gamma^2) \tag{7.4}$$

where

$$\delta \mathcal{H} = \frac{1}{2} \sum_{i,m=1}^l \int \mathbf{d}\mathbf{i} \mathbf{d}\mathbf{m} \delta \gamma_m Q_{mk}^{\text{eq}} \delta \gamma_i. \quad (7.5)$$

From our H -theorem we get

$$\frac{d\delta \mathcal{H}}{dt} = -\frac{d\delta S}{dt} \leq 0 \quad (7.6)$$

and $\delta \gamma$ as well as $\delta \mathcal{H}$ and must tend to 0.

8. THE CASE $l=2$

Here we present a set of new kinetic equations satisfying H -theorem from Section 3. Applying our theorem in the case $l=2$, we get a closed dynamics including two-particle correlations, especially velocity correlations. The system may start from any state described by F_1 and F_2 or γ_1 and γ_2 . During the time evolution only γ_1 and γ_2 are nonzero. The isolated system eventually will attain its equilibrium according to the initial energy and mean number of spheres, invariants of motion. Then γ_2 will tend to zero and γ_1 to its equilibrium value.

We can write two first equations of (3.11)

$$\{\partial_t + L_0(1)\} F(1) = \int \mathbf{d}2 \bar{T}_-(12) F(12) \quad (8.1)$$

$$\{\partial_t + L_0(12)\} F(12) = \bar{T}_-(12) F(12) + \int \mathbf{d}3 (\bar{T}_-(13) + \bar{T}_-(23)) F(123)$$

where the free propagation is defined by Eq. (4.21).

To close the hierarchy we should express F_3 or F_1 and F_2 . We define correlation functions G_m by

$$F(\mathbf{m}) = G(\mathbf{m}) \prod_{i \in \mathbf{m}} F(i). \quad (8.2)$$

It is possible to express G_3 in terms of F_1 and $H_2 = G_2 - 1$ in the graphical way proposed by Morita and Hiroike.⁽¹⁹⁾ One can construct graphs where white points correspond to 1, black points correspond to $\int \mathbf{d}\mathbf{m} F(\mathbf{m})$ and lines correspond to H_2 . Let us consider graphs consisting of three white points, an arbitrary number of black points and lines (lines do not connect white points). To each such graph we assign a symmetry number—the

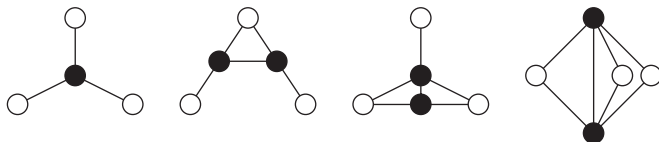


Fig. 1. All types of graphs in ω_3 with one or two black points. The second and the third graph corresponds to three graphs with different numerations of white points. The last graph has the symmetry number 2.

number of permutations of black points unchanging the graph. The integral corresponding to the graph is divided by its symmetry number. Furthermore we say that a graph is double connected if removing any two points cannot leave some black points disconnected off white points. We write G_3 in the form

$$G(123) = G(12) G(13) G(23) \exp \omega(123). \quad (8.3)$$

Then ω_3 is a sum of all double connected graphs. Some of them are presented in Fig. 1. One can for example take the convolution approximation

$$\omega(123) \simeq \int d4 F(4) H(14) H(24) H(34). \quad (8.4)$$

It is clear that taking equilibrium radial distribution function given by Eq. (6.9) for G_2 , namely

$$F(12) = g(12) F(1) F(2) \quad (8.5)$$

where $l \equiv \mathbf{r}_l$, since g depends only on positions l and 2 , we get

$$F(\mathbf{m}) = g(\mathbf{m}) \prod_{i \in \mathbf{m}} F(i). \quad (8.6)$$

We can refer the evolution equations to the Enskog equation by writing F_2 in the form

$$F(12) = g(12) F(1) F(2) + \tilde{H}(12). \quad (8.7)$$

The functional $F(123 | F_1, \tilde{H}_2)$ can be represented graphically or by a Taylor series. It is possible to express ω_3 from Eq. (8.3) by a sum of double connected graphs with thick lines $h_2 = g_2 - 1$ and dashed lines corresponding to $\tilde{h}(12) = \tilde{H}(12) / F(1) F(2)$ as shown in Fig. 2. The equilibrium correlations occur if no dashed line touches black circle so that we can omit the integration of F_1 over velocity putting n_1 instead.

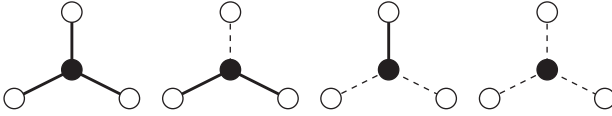


Fig. 2. Graphs contributing to ω_3 with one black circle.

Another way is to write F_3 in the form

$$F(123) = g(123) \prod_{i=1}^3 F(i) + \sum_{m=1}^{\infty} \int \frac{d\mathbf{2}_1 \cdots d\mathbf{2}_m}{m!} \left(\frac{\delta F(123)}{\delta F(\mathbf{2}_1) \cdots \delta F(\mathbf{2}_m)} \right)_{F_1}^E \prod_{i=1}^m \tilde{H}(\mathbf{2}_i) \quad (8.8)$$

where E denotes that the derivative is taken for the Enskog distribution functions (8.6). The first functional derivative can be evaluated

$$\left(\frac{\delta F(123)}{\delta F(45)} \right)_{F_1} = Q_{32}^{\beta}(123 | 45) \quad (8.9)$$

where the definition of Q^{β} is found in ref. 18 but here F_1 is a nonequilibrium distribution. Therefore only equilibrium correlation functions g_m , $m=2, 3, 4, 5$ are necessary in this approximation. This is a nonlinear version of Enskog-like renormalization performed in refs. 17 and 18. We cannot, however, prove an H -theorem for this particular approximation since it is inconsistent with the maximum entropy principle. We suppose that only a full expansion (8.8) or a linearization of F_1 give H -theorem.

The overlap function $W(12)$ and the excluded volume effects of other particles are then included in g_2 . The function \tilde{H}_2 is a correction that depends also on velocities. Its evolution is obtained from the couple of Eqs. (8.1) and some auxiliary identities.

The time evolution of g_2 is given indirectly by evolution of n_1 .

$$\frac{\partial g(12, t)}{\partial t} = \int d^3 \mathbf{r}_3 \frac{\delta g(12)}{\delta n(3)} \frac{\partial n(3, t)}{\partial t} \quad (8.10)$$

where

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{u}(\mathbf{r}) n(\mathbf{r}) \quad (8.11)$$

and local velocity \mathbf{u} is defined by

$$n(\mathbf{r}) \mathbf{u}(\mathbf{r}) = h^{-3} \int d^3 \mathbf{p} \mathbf{v} F(\mathbf{r}, \mathbf{v}). \quad (8.12)$$

The functional derivative is evaluated as follows

$$\frac{\delta g(12)}{\delta n(3)} = h(123) - h(12)(c(13) + c(23)) - \int d4 n(4) c(34) h(124) \quad (8.13)$$

where $d4 \equiv d^3 \mathbf{r}_4$, c_2 is a direct two point correlation function⁽³¹⁾ defined by Ornstein-Zernike equation

$$h(12) = c(12) + \int d3 n(3) h(13) c(32), \quad (8.14)$$

and h_3 is defined by

$$g(123) = 1 + h(12) + h(23) + h(31) + h(123). \quad (8.15)$$

We get the final equation in the form

$$\{\partial_t + \bar{L}_-(12)\} \tilde{H}(12) = A_A(12) + A_B(12) + A_C(12) \quad (8.16)$$

where

$$A_A(12) = \bar{T}_-(12) g(12) F(1) F(2) \quad (8.17)$$

$$A_B(12) = \int d3 \bar{T}_-(13)(F(123) - g(12) F(2) F(13)) + 1 \leftrightarrow 2 \quad (8.18)$$

$$A_C(12) = F(1) F(2) \left(\int d3 \frac{\delta g(12)}{\delta n(3)} \frac{\partial}{\partial \mathbf{r}_3} \cdot n(3) \mathbf{u}_{1+2}(3) + \mathbf{v}_{21} \cdot \frac{\partial g(12)}{\partial \mathbf{r}_{12}} \right) \quad (8.19)$$

where

$$\mathbf{u}_{1+2}(3) = \mathbf{u}(3) - \frac{\mathbf{v}_1 + \mathbf{v}_2}{2} \quad (8.20)$$

and

$$\frac{\partial}{\partial \mathbf{r}_{12}} = \frac{1}{2} \left(\frac{\partial}{\partial \mathbf{r}_1} - \frac{\partial}{\partial \mathbf{r}_2} \right) \quad (8.21)$$

due to the identity

$$\sum_{i=1}^2 \frac{\partial g(12)}{\partial \mathbf{r}_i} + \int d3 \frac{\partial n(3)}{\partial \mathbf{r}_3} \frac{\delta g(12)}{\delta n(3)} = 0. \quad (8.22)$$

One may interpret A_A , A_B , and A_C as terms corresponding to the internal collision, collision with another particle and mean field interaction, respectively.

9. DISCUSSION

The H -theorem (4.11) is a generalization of ideas of Boltzmann and Resibois. The isolated hard sphere fluid attains equilibrium determined by integrals of motion: number of spheres, momentum and energy.

Our theorems contain all previous results and allows to include in the picture of dynamics more complicated events and correlations. Moreover, the theorem holds under general boundary geometry and an external potential. We emphasize that we got the condition that in equilibrium the chemical potential μ is independent of the position but not necessarily the density n . Therefore coexistence of phases with different densities is possible. Expressing γ by F is hard but in principle possible.^(19–21) The correspondence between γ and F is not unique at high densities, because corresponding integrals are not convergent. One may think about an analytic continuation but coexistence of phases must be allowed. The kinetic equations given in section 6 or linearized theory presented in ref. 8 can be used especially for the analysis of time correlation functions.

An H theorem holds for every level of truncation l . It is unknown, however, whether entropy production grows or shrinks with increasing l . A very interesting question is whether the entropy production tends to a nonzero value if $l \rightarrow \infty$ or vanishes. Another interesting problem is how to construct kinetic equations containing ring and repeated ring terms^(23, 24) without breaking H theorem. This is the purpose of authors' current research.

APPENDIX A

The fact that Eq. (2.22) gives maximum possible entropy at given U and N follows from more general maximum entropy formalism. The purpose of maximum entropy formalism (MEF)^(8, 9) is to find such a probability distribution ρ with given $F_1 \cdots F_l$ constrained that entropy is maximal. This implies that all averages of cluster functions from Eq. (2.10) with $a_k = 0$ for $k > l$ are also constrained including energy (2.20) and number of particles (2.21). We use the standard variational technique by introducing a functional

$$I = S - \sum_{m=1}^l \int \mathbf{d}\mathbf{m} F_m \lambda_m \quad (\text{A.1})$$

where functions $\lambda(\mathbf{m})$, $0 < m \leq l$ are Lagrange multipliers related to the constraints. The variational principle requires that for arbitrary variations of the probability distribution given by a set of $\delta\gamma_i$, $i > 0$ we must obtain

$$\delta I = 0. \tag{A.2}$$

We have from Eq. (A.1) with (2.19) that

$$\begin{aligned} \delta I = & \sum_{m=1}^l \int \mathbf{d}\mathbf{m} (\delta F_m) (\gamma_m - \lambda_m) + \sum_{m=l+1}^{\infty} \int \mathbf{d}\mathbf{m} (\delta F_m) \gamma_m \\ & + \delta\psi + \sum_{m=1}^{\infty} \int \mathbf{d}\mathbf{m} (\delta\gamma_m) F_m. \end{aligned} \tag{A.3}$$

Taking into account the normalization condition (2.3), we get

$$0 = \sum_{n=0}^{\infty} \int \mathbf{d}\mathbf{n} \delta\rho_n = \sum_{n=0}^{\infty} \int \mathbf{d}\mathbf{n} \rho_n \delta \ln \tilde{\rho}_n. \tag{A.4}$$

From Eqs. (2.14) and (2.11), we obtain

$$\delta\psi = - \sum_{m=1}^{\infty} \int \mathbf{d}\mathbf{m} F_m \delta\gamma_m \tag{A.5}$$

or

$$\frac{\delta\psi}{\delta\gamma_m} = -F_m. \tag{A.6}$$

Hence, the last two terms in Eq. (A.3) vanish.

We express the variation δF by arbitrary variations $\delta\gamma$ using definitions (2.4) and (2.14)

$$\delta F_j = - \sum_{i=1}^{\infty} \int \mathbf{d}\mathbf{i} Q_{ji} \delta\gamma_i \tag{A.7}$$

where the kernel Q_{ji} is defined by Eq. (4.19) Explicit calculation of the kernel gives

$$Q(\mathbf{i} | \mathbf{j}) = F(\mathbf{i} + \mathbf{j}) - F(\mathbf{i}) F(\mathbf{j}) + \sum_{\substack{\mathbf{m} \subseteq \mathbf{i} \\ \mathbf{m}' \subseteq \mathbf{j}}} \frac{\delta(\mathbf{m} - \mathbf{m}')}{m!} F(\mathbf{i} + \mathbf{j} - \mathbf{m}) \tag{A.8}$$

where the sum is taken over all sequences of m elements from the sets \mathbf{i} and \mathbf{j} . The operator Q defines bilinear form for functions $a = \{a(\mathbf{n}), n > 0\}$ and $b = \{b(\mathbf{n}), n > 0\}$

$$\sum_{i,j} \int d\mathbf{i} d\mathbf{j} a_i Q_{ij} b_j = \sum_{k,l,m} \int d\mathbf{k} d\mathbf{l} d\mathbf{m} [F_{k+l+m} - \delta_{m,0} F_k F_l] a_{k+m} b_{l+m}. \quad (\text{A.9})$$

This form is symmetric, positive definite and invertible for non-overlapping configurations since

$$\sum_{i,j} \int d\mathbf{i} d\mathbf{j} a_i Q_{ij} a_j = \langle (\mathcal{A} - \langle \mathcal{A} \rangle)^2 \rangle > 0, \quad (\text{A.10})$$

$$\mathcal{A}(\mathbf{n}) = \sum_{\mathbf{m} \subseteq \mathbf{n}} a(\mathbf{m}). \quad (\text{A.11})$$

Therefore δF_m for $m > 0$ can take an arbitrary value and lastly

$$\gamma_m = \begin{cases} \lambda_m & \text{for } m \leq l, \\ 0 & \text{otherwise.} \end{cases} \quad (\text{A.12})$$

To find maximum entropy at given average energy and number of particles one must take $\lambda_k = 0$ for $k > 1$ and

$$\lambda_1 = A(\phi(\mathbf{r}_1) + p_1^2/2M) + B \quad (\text{A.13})$$

where A and B are arbitrary constants (Lagrange multipliers). Since maximum entropy is obtained for $\gamma_1 = -\lambda_1$, we identify $k_B T A = -1$ and $k_B T B = \mu$ in Eq. (2.22).

APPENDIX B

To derive Eq. (4.4) we start with integration by parts

$$-\sum_{m=1}^l \int d\mathbf{m} \gamma_m \sum_{i \in \mathbf{m}} \mathbf{v}_i \cdot \frac{\partial F_m}{\partial \mathbf{r}_i} = \sum_{m=1}^l \int d\mathbf{m} F_m \sum_{i \in \mathbf{m}} \mathbf{v}_i \cdot \frac{\partial \gamma_m}{\partial \mathbf{r}_i} - \int d\mathbf{m} \frac{\partial}{\partial \mathbf{r}_i} \cdot (\mathbf{v}_i F_m \gamma_m). \quad (\text{B.1})$$

From Eqs. (2.1) and (2.11) for \mathcal{A} given by (2.10) with

$$a_m = \sum_{i \in \mathbf{m}} \mathbf{v}_i \cdot \frac{\partial \gamma_m}{\partial \mathbf{r}_i} \quad (\text{B.2})$$

and from Eq. (2.14) we have

$$\begin{aligned}
 & \sum_{m=1}^l \int d\mathbf{m} F_m \sum_{i \in \mathbf{m}} \mathbf{v}_i \cdot \frac{\partial \gamma_m}{\partial \mathbf{r}_i} \\
 &= - \sum_{n=1}^{\infty} \int d\mathbf{n} W_n \tilde{\rho}_n \sum_{i \in \mathbf{n}} \mathbf{v}_i \cdot \frac{\partial \ln \tilde{\rho}_n}{\partial \mathbf{r}_i} = - \sum_{n=1}^{\infty} \int d\mathbf{n} W_n \sum_{i \in \mathbf{n}} \mathbf{v}_i \cdot \frac{\partial \tilde{\rho}_n}{\partial \mathbf{r}_i} \\
 &= \sum_{n=2}^{\infty} \int d\mathbf{n} \sum_{i \in \mathbf{n}} \mathbf{v}_i \cdot \frac{\partial W_n}{\partial \mathbf{r}_i} \tilde{\rho}_n - \sum_{n=1}^{\infty} \int d\mathbf{n} \sum_{i \in \mathbf{n}} \frac{\partial}{\partial \mathbf{r}_i} \cdot (\mathbf{v}_i \rho_n) \\
 &= \sum_{n=2}^{\infty} \int d\mathbf{n} \sum_{i \neq j} \mathbf{v}_i \cdot \frac{\partial W(ij)}{\partial \mathbf{r}_i} \tilde{\rho}_n \prod_{(pq) \neq (ij)} W(pq) - \int d\mathbf{l} \frac{\partial}{\partial \mathbf{r}_1} \cdot (\mathbf{v}_1 F_1). \quad (\text{B.3})
 \end{aligned}$$

Next

$$\begin{aligned}
 \sum_{n=2}^{\infty} \int d\mathbf{n} \sum_{i \neq j} \mathbf{v}_i \cdot \frac{\partial W(ij)}{\partial \mathbf{r}_i} \tilde{\rho}_n \prod_{(pq) \neq (ij)} W(pq) &= \sum_{n=2}^{\infty} \int d\mathbf{n} \sum_{i \neq j} \delta(r_{ij} - d^+) \mathbf{v}_i \cdot \hat{\mathbf{r}}_{ij} \rho_n \\
 &= \int d\mathbf{2} \delta(r_{12} - d^+) \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12} F_2 \quad (\text{B.4})
 \end{aligned}$$

where we have used the relation

$$\frac{\partial W(ij)}{\partial \mathbf{r}_i} = \delta(r_{ij} - d) \hat{\mathbf{r}}_{ij} \quad (\text{B.5})$$

and replaced d by d^+ to write ρ_n instead $\tilde{\rho}_n$.

The boundary terms

$$\int d\mathbf{l} \frac{\partial}{\partial \mathbf{r}_1} \cdot (\mathbf{v}_1 F_1) \quad \text{and} \quad \sum_{m>0} \int d\mathbf{m} \sum_{i \in \mathbf{m}} \frac{\partial}{\partial \mathbf{r}_i} \cdot (\mathbf{v}_i \gamma_m F_m) \quad (\text{B.6})$$

in Eqs. (B.1) and (B.3), respectively are equal to zero for an isolated system. For such a system, when \mathbf{r}_i is at the boundary then F_m and γ_m must be even functions of $v_{i\perp}$ (the component of \mathbf{v}_i perpendicular to the boundary).

The right hand side of (4.7) can be written in terms of ρ if we simply use Eq. (2.4)

$$\begin{aligned}
 & \sum_{m=2}^{l+1} \int d\mathbf{m} F_m \sum_{i>j} T_+(ij) \{ \gamma(\mathbf{m}) + \gamma(\mathbf{m}-i) + \gamma(\mathbf{m}-j) \} \\
 &= \sum_{n=0}^{\infty} \sum_{m=2}^{l+1} \int d\mathbf{m} d\mathbf{n} \rho_{n+m} \sum_{\substack{i>j \\ ij \in \mathbf{m}}} T_+(ij) \{ \gamma(\mathbf{m}) + \gamma(\mathbf{m}-i) + \gamma(\mathbf{m}-j) \}. \quad (\text{B.7})
 \end{aligned}$$

By the symmetry of ρ_n we can distribute the combinatorial factor $\binom{n}{m}$ into all subsets \mathbf{m} of \mathbf{n} . We get

$$\sum_{n=2}^{\infty} \int d\mathbf{n} \rho_n \sum_{m=2}^{l+1} \sum_{\mathbf{m} \subseteq \mathbf{n}} \sum_{\substack{i>j \\ ij \in \mathbf{m}}} T_+(ij) \{ \gamma(\mathbf{m}) + \gamma(\mathbf{m}-i) + \gamma(\mathbf{m}-j) \}. \quad (\text{B.8})$$

Finally we take into account that $T_+(ij)$ does not affect $\gamma_m(\mathbf{m})$ if $\mathbf{m} \cap \{ij\} = \emptyset$. Lastly, we obtain

$$\sum_{n=2}^{\infty} \int d\mathbf{n} \rho_n \sum_{i>j} T_+(ij) \sum_{\mathbf{m} \subseteq \mathbf{n}} \gamma(\mathbf{m}) \quad (\text{B.9})$$

and use the definitions (2.14) and (3.18).

APPENDIX C

We shall evaluate the right hand side of Eq. (4.20), using Eqs. (2.4), (4.19), and (3.16)

$$\begin{aligned} \sum_{m>0} \int d\mathbf{m} Q_{km} L_{0,m} \gamma_m &= - \sum_{m>0} \int d\mathbf{m} \frac{\delta F_k}{\delta \gamma_m} L_{0,m} \gamma_m \\ &= - \sum_{m>0} \sum_{n=0}^{\infty} \int d\mathbf{n} d\mathbf{m} W_{k+n} \frac{\delta \tilde{\rho}_{k+n}}{\delta \gamma_m} L_{0,m} \gamma_m \\ &= - \sum_{n=0}^{\infty} \int d\mathbf{n} W_{k+n} L_{0,k+n} \tilde{\rho}_{k+n} \\ &= - \sum_{n=0}^{\infty} \int d\mathbf{n} W_{k+n} L_{k+n} \tilde{\rho}_{k+n} \\ &= - \sum_{n=0}^{\infty} \int d\mathbf{n} \bar{L}_{k+n} \rho_{k+n} \end{aligned} \quad (\text{C.1})$$

where we have taken into account that $T_-(ij) \rho_n = 0$ due to Eq. (4.17) The last expression coincides with Eq. (3.11).

To prove Eq. (4.27) we need only Eqs. (3.2) and (4.26). Let us apply tensor operator

$$\frac{\partial^2}{\partial \mathbf{v}_1 \partial \mathbf{v}_2} \quad (\text{C.2})$$

to both sides of Eq. (4.26), i.e.,

$$\gamma(\mathbf{r}_1, \mathbf{v}_1) + \gamma(\mathbf{r}_2, \mathbf{v}_2) = \gamma(\mathbf{r}_1, \mathbf{v}'_1) + \gamma(\mathbf{r}_2, \mathbf{v}'_2), \quad |\mathbf{r}_1 - \mathbf{r}_2| = d \quad (\text{C.3})$$

where \mathbf{v}'_1 and \mathbf{v}'_2 are related to \mathbf{v}_1 and \mathbf{v}_2 by the elastic collision law (3.2). We get

$$\begin{aligned} \hat{\mathbf{R}} \left(\hat{\mathbf{R}} \cdot \frac{\partial^2 \gamma(\mathbf{r}_1, \mathbf{v}'_1)}{\partial \mathbf{v}'_1 \partial \mathbf{v}'_1} \right) - \hat{\mathbf{R}} \hat{\mathbf{R}} \left(\hat{\mathbf{R}} \hat{\mathbf{R}} : \frac{\partial^2 \gamma(\mathbf{r}_1, \mathbf{v}'_1)}{\partial \mathbf{v}'_1 \partial \mathbf{v}'_1} \right) \\ + \hat{\mathbf{R}} \left(\hat{\mathbf{R}} \cdot \frac{\partial^2 \gamma(\mathbf{r}_2, \mathbf{v}'_2)}{\partial \mathbf{v}'_2 \partial \mathbf{v}'_2} \right) - \hat{\mathbf{R}} \hat{\mathbf{R}} \left(\hat{\mathbf{R}} \hat{\mathbf{R}} : \frac{\partial^2 \gamma(\mathbf{r}_2, \mathbf{v}'_2)}{\partial \mathbf{v}'_2 \partial \mathbf{v}'_2} \right) = 0 \end{aligned} \quad (\text{C.4})$$

where $\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1$ and $\hat{\mathbf{R}} = \mathbf{R}/d$. Taking \mathbf{v}'_1 and \mathbf{v}'_2 as independent variables we obtain

$$\hat{\mathbf{R}} \cdot \frac{\partial^2 \gamma(\mathbf{r}, \mathbf{v})}{\partial \mathbf{v} \partial \mathbf{v}} - \hat{\mathbf{R}} \left(\hat{\mathbf{R}} \hat{\mathbf{R}} : \frac{\partial^2 \gamma(\mathbf{r}, \mathbf{v})}{\partial \mathbf{v} \partial \mathbf{v}} \right) = \mathbf{g}(\mathbf{r}, \hat{\mathbf{R}}) \quad (\text{C.5})$$

for every \mathbf{v} , \mathbf{r} , and $\hat{\mathbf{R}}$, where \mathbf{g} is an arbitrary vector function. Let us choose such a reference system xyz that $\hat{\mathbf{R}} = (1, 0, 0)$. Then taking y component of the above equation we have

$$\frac{\partial^2 \gamma(\mathbf{r}, \mathbf{v})}{\partial v_x \partial v_y} = g_y(\mathbf{r}). \quad (\text{C.6})$$

Hence

$$\gamma(\mathbf{r}, \mathbf{v}) = g_y v_y v_x + f_a(\mathbf{r}, v_x, v_z) + f_b(\mathbf{r}, v_y, v_z) \quad (\text{C.7})$$

where f_a and f_b are arbitrary functions. Repeating this reasoning for z we arrive at

$$\gamma(\mathbf{r}, \mathbf{v}) = f_c(\mathbf{r}, v_x) + f_d(\mathbf{r}, v_y, v_z) \quad (\text{C.8})$$

and $g_y = g_z = 0$. This is true in every possible reference system. If we turn coordinates v_z and v_x by an angle ϕ around the axis v_y in the way

$$v_z^* = v_z \cos \phi - v_x \sin \phi, \quad v_x^* = v_x \cos \phi + v_z \sin \phi \quad (\text{C.9})$$

then

$$f_c(\mathbf{r}, v_x) + f_d(\mathbf{r}, v_y, v_z) = f_c^*(\mathbf{r}, v_x^*) + f_d^*(\mathbf{r}, v_y, v_z^*). \quad (\text{C.10})$$

Applying $\partial^2/\partial v_x \partial v_z$ to this equation, we get

$$\sin \phi \cos \phi \left(\frac{\partial^2 f_c^*}{\partial v_x^{*2}} - \frac{\partial^2 f_d^*}{\partial v_z^{*2}} \right) = 0. \quad (\text{C.11})$$

Renaming the variables we arrive at

$$f_c = a(\mathbf{r}) v_x^2 + b_x(\mathbf{r}) v_x + c_1(\mathbf{r}), \quad f_d = a(\mathbf{r}) v_z^2 + h(\mathbf{r}, v_y) v_z + c_2(\mathbf{r}, v_y) \quad (\text{C.12})$$

where a , b_x , h , c_1 , and c_2 are arbitrary functions. Finally, taking into account invariance under rotations around axes v_x and v_z , we obtain

$$\gamma(\mathbf{r}, \mathbf{v}) = a(\mathbf{r}) v^2 + \mathbf{b}(\mathbf{r}) \cdot \mathbf{v} + f(\mathbf{r}) \quad (\text{C.13})$$

where a , \mathbf{b} , and f are arbitrary functions of \mathbf{r} .

We use again Eq. (4.26) and get

$$(\mathbf{v}_{12} \cdot \hat{\mathbf{R}})[a(\mathbf{r}_1) - a(\mathbf{r}_2)](\mathbf{v}_1 + \mathbf{v}_2) \cdot \hat{\mathbf{R}} + [\mathbf{b}(\mathbf{r}_1) - \mathbf{b}(\mathbf{r}_2)] \cdot \hat{\mathbf{R}}(\hat{\mathbf{R}} \cdot \mathbf{v}_{12}) = 0 \quad (\text{C.14})$$

for every \mathbf{v}_1 , \mathbf{v}_2 , \mathbf{r}_1 , and $\hat{\mathbf{R}}$. Hence $a(\mathbf{r}_1) = a(\mathbf{r}_2) = a$ and

$$\mathbf{b}(\mathbf{r}) \cdot \hat{\mathbf{R}} = \mathbf{b}(\mathbf{r} + d\hat{\mathbf{R}}) \cdot \hat{\mathbf{R}}. \quad (\text{C.15})$$

We apply now operator

$$\left(\hat{\mathbf{R}} \times \frac{\partial}{\partial \hat{\mathbf{R}}} \right)^2 = -2\hat{\mathbf{R}} \cdot \frac{\partial}{\partial \hat{\mathbf{R}}} + \left(\frac{\partial}{\partial \hat{\mathbf{R}}} \right)^2 - \hat{\mathbf{R}}\hat{\mathbf{R}} : \frac{\partial^2}{\partial \hat{\mathbf{R}} \partial \hat{\mathbf{R}}} \quad (\text{C.16})$$

to Eq. (C.15). We obtain

$$0 = 2 \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{b} - 4\hat{\mathbf{R}}\hat{\mathbf{R}} : \frac{\partial \mathbf{b}}{\partial \mathbf{r}} + \left(\frac{\partial}{\partial \mathbf{r}} \right)^2 \mathbf{b} \cdot \mathbf{R} - \left(\hat{\mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{r}} \right)^2 \mathbf{b} \cdot \mathbf{R} \quad (\text{C.17})$$

at $\mathbf{r} + \mathbf{R}$. By the change $\hat{\mathbf{R}} \rightarrow -\hat{\mathbf{R}}$ we get

$$0 = \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{b} - 2\hat{\mathbf{R}}\hat{\mathbf{R}} : \frac{\partial \mathbf{b}}{\partial \mathbf{r}}. \quad (\text{C.18})$$

Due to the arbitrariness of the direction $\hat{\mathbf{R}}$ the symmetric part of $\partial\mathbf{b}/\partial\mathbf{r}$ is zero, namely

$$\frac{\partial b_x}{\partial x} = \frac{\partial b_y}{\partial y} = \frac{\partial b_z}{\partial z} = 0, \quad (\text{C.19})$$

$$\frac{\partial b_x}{\partial y} + \frac{\partial b_y}{\partial x} = \frac{\partial b_y}{\partial z} + \frac{\partial b_z}{\partial y} = \frac{\partial b_z}{\partial x} + \frac{\partial b_x}{\partial z} = 0. \quad (\text{C.20})$$

It follows that $b_x = b_x(y, z)$, $b_y = b_y(x, z)$, and $b_z = b_z(x, y)$ From Eq. (C.20) we get

$$\frac{\partial b_y}{\partial x} = -\frac{\partial b_x}{\partial y} = c_z(z) \quad (\text{C.21})$$

where c_z is an arbitrary function. Hence

$$b_x = -c_z(z) y + f_a(z), \quad b_y = c_z(z) x + f_b(z) \quad (\text{C.22})$$

where f_a and f_b are arbitrary functions and using

$$\frac{\partial b_z}{\partial y} = -\frac{\partial b_y}{\partial z} = c_x(x), \quad \frac{\partial b_x}{\partial z} = -\frac{\partial b_z}{\partial x} = c_y(y) \quad (\text{C.23})$$

where c_x and c_y are arbitrary functions we finally arrive at

$$\mathbf{b}(\mathbf{r}) = \mathbf{b}_0 + \mathbf{c} \times \mathbf{r} \quad (\text{C.24})$$

where \mathbf{b}_0 , \mathbf{c} are constants. Lastly,

$$\gamma(\mathbf{r}, \mathbf{v}) = av^2 + \mathbf{b} \cdot \mathbf{v} + \mathbf{c} \times \mathbf{r} + f(\mathbf{r}) \quad (\text{C.25})$$

where a , \mathbf{b} , and \mathbf{c} are constants and f is an arbitrary function of \mathbf{r} .

APPENDIX D

To find the function B we use Eqs. (2.1), (2.11) for \mathcal{A} given by (2.10) with

$$a_m = \sum_{i \in \mathbf{m}} \delta(\mathbf{r} - \mathbf{r}_i) \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial \gamma_m}{\partial \mathbf{p}_i} \quad (\text{D.1})$$

and Eq. (2.14) in the identity

$$\begin{aligned}
0 &= -\sum_{n=1}^{\infty} \int \mathbf{d}\mathbf{n} \sum_{i \in \mathbf{n}} \delta(\mathbf{r}-\mathbf{r}_i) \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial \rho_n}{\partial \mathbf{p}_i} \\
&= \sum_{n=1}^{\infty} \int \mathbf{d}\mathbf{n} \sum_{i \in \mathbf{n}} \delta(\mathbf{r}-\mathbf{r}_i) \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \sum_{\mathbf{m} \subseteq \mathbf{n}} \frac{\partial \gamma(\mathbf{m})}{\partial \mathbf{p}_i} \rho_n \\
&= \sum_{m>0} \int \mathbf{d}\mathbf{m} \sum_{i \in \mathbf{m}} \delta(\mathbf{r}-\mathbf{r}_i) \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial \gamma_m}{\partial \mathbf{p}_i} F_m \\
&= -\sum_{m>0} \int \mathbf{d}\mathbf{m} \sum_{i \in \mathbf{m}} \delta(\mathbf{r}-\mathbf{r}_i) \frac{\partial \phi(\mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \frac{\partial F_m}{\partial \mathbf{p}_i} \gamma_m. \tag{D.2}
\end{aligned}$$

To find function C , J_s , and σ_C we use the identity

$$\begin{aligned}
0 &= \sum_{n=1}^{\infty} \int \mathbf{d}\mathbf{n} \sum_{i \in \mathbf{n}} \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{v}_i \delta(\mathbf{r}-\mathbf{r}_i) \rho_n \\
&= -\frac{\partial}{\partial \mathbf{r}} \cdot \sum_{n=1}^{\infty} \int \mathbf{d}\mathbf{n} \sum_{i \in \mathbf{n}} \mathbf{v}_i \delta(\mathbf{r}-\mathbf{r}_i) \rho_n \\
&\quad + \sum_{n=1}^{\infty} \int \mathbf{d}\mathbf{n} \sum_{i \in \mathbf{n}} \delta(\mathbf{r}-\mathbf{r}_i) \mathbf{v}_i \cdot \left(\tilde{\rho}_n \frac{\partial W_n}{\partial \mathbf{r}_i} + W_n \frac{\partial \tilde{\rho}_n}{\partial \mathbf{r}_i} \right) \\
&= -\frac{\partial}{\partial \mathbf{r}} \cdot \int \mathbf{d}'\mathbf{1} \mathbf{v}_1 F_1 + \int \mathbf{d}\mathbf{2} \sum_{i \neq j} \delta(\mathbf{r}-\mathbf{r}_i) \mathbf{v}_i \cdot \frac{\partial W(ij)}{\partial \mathbf{r}_i} F_2 \\
&\quad - \sum_{m>0} \int \mathbf{d}\mathbf{m} F_m \sum_{i \in \mathbf{m}} \delta(\mathbf{r}-\mathbf{r}_i) \mathbf{v}_i \cdot \frac{\partial \gamma_m}{\partial \mathbf{r}_i} \tag{D.3}
\end{aligned}$$

and

$$\begin{aligned}
& - \sum_{m>0} \int \mathbf{d}\mathbf{m} F_m \sum_{i \in \mathbf{m}} \delta(\mathbf{r}-\mathbf{r}_i) \mathbf{v}_i \cdot \frac{\partial \gamma_m}{\partial \mathbf{r}_i} \\
&= -\frac{\partial}{\partial \mathbf{r}} \cdot \sum_{m>0} \int \mathbf{d}\mathbf{m} F_m \gamma_m \sum_{i \in \mathbf{m}} \mathbf{v}_i \delta(\mathbf{r}-\mathbf{r}_i) + \sum_{m>0} \int \mathbf{d}\mathbf{m} \gamma_m \sum_{i \in \mathbf{m}} \delta(\mathbf{r}-\mathbf{r}_i) \mathbf{v}_i \cdot \frac{\partial F_m}{\partial \mathbf{r}_i}. \tag{D.4}
\end{aligned}$$

ACKNOWLEDGMENTS

The authors are very grateful to Professor J. Piasecki for a fruitful discussion and helpful remarks.

REFERENCES

1. J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Dover, New York, 1960).
2. A. I. Khinchin, *Mathematical Foundations of Information Theory* (Dover, New York, 1957).
3. J. L. Lebowitz, Boltzmann's entropy and time's arrow, *Phys. Today* **46**:36–38 (1993).
4. J. L. Lebowitz, Microscopic reversibility and macroscopic behavior: Physical explanations and mathematical derivations, in *25 Years of Non-Equilibrium Statistical Mechanics*, Proceedings, Sitges Conference, Barcelona, Spain, 1994, in *Lecture Notes in Physics*, J. J. Brey, J. Marro, J. M. Rubí, and M. San Miguel, eds. (Springer, 1995).
5. L. Boltzmann, *Lectures on Gas Theory* (Dover, New York, 1995).
6. J. Karkheck and G. Stell, Maximization of entropy, kinetic equations and irreversible thermodynamics, *Phys. Rev. A* **25**:3302–3334 (1982).
7. J. Karkheck, H. van Beijeren, I. de Schepper, and G. Stell, Kinetic theory and H theorem for a dense square well fluid, *Phys. Rev. A* **32**:2517–2520 (1965).
8. J. Bławdziewicz and G. Stell, Local H -theorem for a Kinetic Variational Theory, *J. Stat. Phys.* **56**:821–840 (1989).
9. L. Romero-Salazar, M. Mayorga, and R. M. Velasco, Maximum entropy formalism for a dense gas, *Physica A* **237**:150–168 (1997).
10. H. van Beijeren, Kinetic theory of dense gases and liquids, *Fundamental Problems in Statistical Mechanics*, Vol. VII, H. van Beijeren, ed. (North-Holland, Amsterdam, 1990).
11. C. Cercignani, V. I. Gerasimenko, and D. Ya. Petrina, *Many-Particle Dynamics and Kinetic Equations* (Kluwer, Dordrecht, 1997).
12. P. Resibois, H -theorem for the (modified) Enskog equation, *J. Stat. Phys.* **19**:593–609 (1978).
13. J. Bławdziewicz, B. Cichocki, and H. van Beijeren, H -theorem for a linear kinetic theory, *J. Stat. Phys.* **66**:607–633 (1992).
14. R. Evans, The nature of the liquid-vapour interface and other topics in the statistical mechanics of nonuniform classical fluids, *Adv. Phys.* **28**:143–200 (1979).
15. A. Planes and E. Vives, Entropic formulation of statistical mechanics, *J. Stat. Phys.* **106**:827–850 (2002).
16. D. Ruelle, *Statistical Physics. Rigorous Results* (Benjamin, New York Amsterdam, 1969).
17. J. Bławdziewicz and B. Cichocki, Linear kinetic theory of hard sphere fluid, *Physica A* **127**:38–71 (1984).
18. B. Cichocki, Enskog renormalization in linear kinetic theory, *Physica A* **142**:245–272 (1987).
19. T. Morita and K. Hiroike, A new approach to the theory of classical fluids, *Prog. Theor. Phys.* **25**:537–578 (1961).
20. R. J. Baxter, Three-particle hyper-netted chain approximation, *Ann. Phys. (N.Y.)* **46**:509–545 (1968).
21. A. Bednorz, Graphical representation of the excess entropy, *Physica A* **298**:400–418 (2001).
22. M. H. Ernst, J. R. Dorfman, W. R. Hoegy, and J. M. J. van Leeuwen, *Physica* **45**:127 (1969).
23. H. van Beijeren, Ph.D. thesis, University Nijmegen (1974).
24. H. van Beijeren and M. H. Ernst, *J. Stat. Phys.* **12**:125 (1979).
25. J. Piasecki, Kinetic theory of dense gases, *Fundamental Problems in Statistical Mechanics*, Vol. IV, E. G. D. Cohen and W. Fiszdon, eds. (Ossolineum, Wrocław, 1978).
26. H. van Beijeren, Equilibrium distribution of hard-sphere systems and revised Enskog theory, *Phys. Rev. Lett.* **51**:1503–5 (1983).

27. M. Mareschal, J. Bławdziewicz, and J. Piasecki, Local entropy production from the revised Enskog equation, *Phys. Rev. Lett.* **52**:1169–1172 (1984).
28. J. Piasecki, Local H -theorem for the revised Enskog equation, *J. Stat. Phys.* **48**:1203–1211 (1987).
29. G. E. Uhlenbeck and G. W. Ford, in *Studies in Statistical Mechanics I*, G. E. Uhlenbeck and J. de Boer, eds. (North-Holland, Amsterdam, 1962).
30. G. Stell, Cluster expansions for classical systems in equilibrium, in *The Equilibrium Theory of Classical Fluids*, H. Frish and J. Lebowitz, eds. (Benjamin, New York, 1964).
31. J. Percus, Theory of fluids, in *The Equilibrium Theory of Classical Fluids*, H. Frish and J. Lebowitz, eds. (Benjamin, New York, 1964).