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ON SOME ASYMPTOTIC RELATIONS IN THE BOLTZMANN-ENSKOG MODEL *

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ABSTRACT

The coefficients in the $t^{-3/2}$ asymptotics of the time autocorrelation functions are successively determined in the framework of the non-linear Boltzmann-Enskog model. The left and right eigenfunction systems are constructed for the Boltzmann-Enskog operator.

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In the computer experiments [1] on hard-sphere systems, by studying the density dependence of the diffusion coefficient after a long time t, Alder and Wainwright discovered a surprisingly slow decay of the velocity autocorrelation function, the positive tail $\sim ct^{-3/2}$ (for the three-dimensional systems). Autocorrelation function behaviour was studied on the basis of the molecular-dynamic theory and by means of the numerical solution of the hydrodynamic Navier-Stokes equations. Later this result was theoretically obtained at low densities both for the hydrodynamic model [2] taking into account the local equilibrium assumption and transport coefficient expressions [3] and from the point of view of kinetic theory [4-6]. It was possible to show that not only the velocity autocorrelation function but also other time correlation functions important for studying transport phenomena have $\sim ct^{-3/2}$ behaviour. Hauge [7] derived non-exponential decay of the time correlation functions starting from the non-linear Boltzmann model, which describes systems in the low-density limit.

However, it is essential to point out the following. Although computer experiments discovered the slow decay over the wide density region of the hard-sphere systems up to the fluid region, maximum deviations from the ordinary decay (which is usually supposed to be exponential) were found at the volumes of the system V compared with the close-packed volume $V_0 (V/V_0 \sim 3)$, that is for the comparatively dense systems. In this connection it is undoubtedly interesting to consider the asymptotic behaviour of the time correlation functions on the basis of the non-linear Boltzmann-Enskog equation, which possesses, as was first proved by Bogolubov [8], exact microscopic solutions corresponding to the exact description of the hard-sphere system dynamics and therefore may serve as a base for obtaining higher approximations in the density. In the papers [7,9] the connection between different derivations of the tails of time correlation functions was established for the different models at low densities and the asymptotic coefficient C was calculated [3,4,9]. Let us note that Dorfman and Cohen [4] reached the best agreement with Alder and Wainwright's experimental data by using Enskog expressions of the transport coefficients with the higher density terms to calculate the autocorrelation functions, though usually these terms are believed to exceed the accuracy of the model. Calculating the asymptotical coefficient, however, they assumed that Boltzmann transport coefficients may be replaced by the values from Enskog transport coefficient (up to terms $\sim n^2$). But the degree of validity of this assumption is not clear. Also it is not known what order of density should be neglected.

Calculations of higher order density corrections and their theoretical grounds are extremely important since the $\sim ct^{-3/2}$ tail was found in computer experiments for dense systems (possessing the volume 3-5 times exceeding the close-packed volume) and since the investigation of the long-time behaviour of autocorrelation functions is very difficult at low densities.[1] In the present paper the asymptotic expressions for the kinetic parts of the time correlation functions are obtained successively from the non-linear Boltzmann-Enskog model, which takes into account the effects of particle sizes. As it should be expected, this model gives the correct asymptotic behaviour without additional assumptions on the density. It is interesting to note that, in the first approximation on the non-linearity, the kinetic parts of time correlation functions are independent from potential terms which are presented in a linearized version of the model. However, in the second order these potential terms are important and give higher density corrections for the transport coefficients in the expressions for the tails. The justice of the mode-mode formula with the Enskog transport coefficients up to first order in density is grounded on the solution of the non-linear Boltzmann-Enskog equation. The account of the following order is complicated by the fact that the right and left eigenfunction systems constructed turn out to be non-orthogonal, but in principle it is possible.

We shall study a long-time behaviour of the correlation functions being interested only in their kinetic parts. This is not as severe a restriction as it may seem for the reasons enumerated in paper [3]. The expression for the kinetic parts of the autocorrelation functions in the form [10]

$$C_\varepsilon^\kappa(t) = \lim_{\substack{V\to\infty \\ \frac{V}{N}=const}} V^{-1}\left\langle \sum_\kappa j_\varepsilon(v_\kappa(0)) \sum_\ell j_\varepsilon(v_\ell(t))\right\rangle$$

will be the starting point for the investigation of the dynamical systems of N identical hard spheres moving in a macroscopic volume V. Here $V_k(t)$ is the velocity of k^{th} particle in the time t, $\langle\cdots\rangle$ denotes an average over a grand canonical equilibrium ensemble $\varepsilon = (\eta,\lambda)$;

$$j_\eta(v) = m v_x v_y\ , \quad j_\lambda(v) = \frac{1}{2}(mv^2 - 5\beta^{-1})v_x\ , \quad \beta = \frac{1}{k_B T}\ ,$$

T is the temperature, m is the mass of the sphere. After integration over time of the functions $C_\eta^\kappa(t)$, $C_\lambda^\kappa(t)$ we obtain the kinetic contribution to the shear viscosity and heat conductivity, respectively. It is easy to show that $C_\varepsilon^k(t)$ are expressed from the one-particle distribution function in the following manner:

$$C_\varepsilon^\kappa(t) = n^2\int dv_0\, \varphi(v_0) j_\varepsilon(v_0)\int dr\, dv\, \varphi(v) j_\varepsilon(v)\, \xi(t,r,v)\ ,$$

where $\xi(t,r,v)$ is the relative deviation of the distribution function $F(t,r,v)$ from the equilibrium value $\varphi(v)$,

$$F(t,r,v) = \varphi(v)(1+\xi(t,r,v))\ ,$$

$$\varphi(v) = \left(\frac{\beta m}{2\pi}\right)^{3/2} exp\left(-\frac{1}{2}\beta m v^2\right).$$

The function $\xi(t,r,v)$ is satisfied by the initial condition [9]

$$\xi(0,r,v) = [n\varphi(v_0)]^{-1}\, W(r-r_0)\,\delta(v-v_0) + f(r)\ , \quad (1)$$

corresponding to δ-form deviation from the equilibrium velocity distribution of a single particle. The deviation from equilibrium in the coordinate space is described by the function $W(r-r_0)$, which is normalized by

$$\int dr\, W(r-r_0) = 1\ , \qquad (2)$$

$f(\tau)$ depends only on the coordinates and does not change the asymptotical form of the function $C_\varepsilon^\kappa(t)$, as will be shown later.

Following the paper of Bogolubov[8], let us suppose that a non-linear Boltzmann-Enskog equation possessing exact microscopic solutions may serve as a source for obtaining higher approximations in the density and correctly describes the hard-sphere system behaviour for times much longer than the time of collision. In this case the function $\xi(t,\tau,v)$ obeys the equation

$$\frac{\partial \xi(t,\tau,v)}{\partial t} + v\frac{\partial \xi(t,\tau,v)}{\partial \tau} - n\hat{\Lambda}(v)\xi(t,\tau,v) = \tag{3}$$

$$= a^2 n \int\limits_{(v'-v)\sigma \geq 0} [(v'-v)\sigma]\,\hat{T}\,[\xi(t,\tau,v)\xi(t,\tau,v')]\,\varphi(v')\,dv'd\sigma,$$

where as usual σ is the unit vector, a is the diameter of the sphere, operators $\hat{\Lambda}(v)$ and $\hat{T}$ act on the functions $\xi(t,\tau,v)$, $\xi(t,\tau,v')$ in the following way:

$$\hat{\Lambda}(v)\xi(t,\tau,v) = a^2 \int\limits_{(v'-v)\sigma \geq 0} [(v'-v)\sigma]\,[\xi(t,\tau,v^*) + \tag{4}$$

$$+ \xi(t,\tau+a\sigma,v^{*\prime}) - \xi(t,\tau,v) - \xi(t,\tau-a\sigma,v')]\,\varphi(v')\,dv'd\sigma,$$

($\hat{\Lambda}(v)$ is the linearized collision operator),

$$v^* = v + \sigma((v'-v)\sigma), \qquad v^{*\prime} = v' - \sigma((v'-v)\sigma),$$

$$\hat{T}\,[\xi(t,\tau,v)\xi(t,\tau,v')] = \tag{5}$$

$$= \xi(t,\tau,v^*)\xi(t,\tau+a\sigma,v^{*\prime}) - \xi(t,\tau,v)\xi(t,\tau-a\sigma,v').$$

The terms $\pm a\sigma$ in the arguments of function ξ in Eq. (3) correspond to the account of the particle sizes and arise as a singular limit in the total expressions of this type of kinetic equations considered by Bogolubov[11]. The perturbation $\xi(t,\tau,v)$ is believed to be small. It is necessary to note that in spite of the function $\xi(0,\tau,v)$ being proportional to $\delta(v-v_0)$, an application of the perturbation theory in the vicinity of the point $t=0$ is valid because the non-linear part of the Boltzmann-Enskog equation is equal to zero when $t=0$. The deviation $\xi(t,\tau,v)$ becomes small for long times when the system approaches the equilibrium state. On taking into account the paper[9] we write the solution of Eq.(3) as the series

$$\xi = \xi^{(1)} + \xi^{(2)} + \dots,$$

assuming that $\xi^{(1)} \gg \xi^{(2)}$. Then $\xi^{(1)}$ satisfies the linearized Boltzmann-Enskog equation

$$\frac{\partial \xi^{(1)}}{\partial t} + v\frac{\partial \xi^{(1)}}{\partial \tau} - n\hat{\Lambda}(v)\xi^{(1)}(t,\tau,v) = 0. \tag{6}$$

There is a linear non-uniform equation for the $\xi^{(2)}$:

$$\frac{\partial \xi^{(2)}}{\partial t} + v\,\frac{\partial \xi^{(2)}}{\partial r} - n\,\hat{\Lambda}(v)\,\xi^{(2)}(t,r,v) = \tag{7}$$

$$= a^2 n \int\limits_{(v'-v)\sigma \geq 0} [(v'-v)\sigma]\,\hat{T}\left[\xi^{(1)}(t,r,v)\,\xi^{(1)}(t,r,v')\right]\varphi(v')\,dv'd\sigma.$$

It is convenient to introduce the operator $\hat{S}$,

$$\hat{S} = v\frac{\partial}{\partial r} - n\hat{\Lambda}(v) \,. \tag{8}$$

Then Eqs.(6) and (7) may be rewritten as

$$\frac{\partial \xi^{(1)}}{\partial t} + \hat{S}\,\xi^{(1)} = 0 \,, \quad \frac{\partial \xi^{(2)}}{\partial t} + \hat{S}\,\xi^{(2)} = \Omega(t,r,v), \tag{9}$$

where we denote $\Omega(t,r,v) =$

$$= a^2 n \int\limits_{(v'-v)\sigma \geq 0} [(v'-v)\sigma]\,\varphi(v')\,\hat{T}\left[\xi^{(1)}(t,r,v)\,\xi^{(1)}(t,r,v')\right]dv'd\sigma.$$

The initial conditions for the functions $\xi^{(1)}$ **and** $\xi^{(2)}$ **are taken in the form**

$$\xi^{(1)}(0,r,v) = \xi(0,r,v)\,; \quad \xi^{(2)}(0,r,v) = 0\,. \tag{10}$$

On solving Eq.(9) with initial conditions (10), one can find

$$\xi^{(1)} = e^{-\hat{S}t}\,\xi(0,r,v)\,; \tag{11}$$

$$\xi^{(2)} = \int_0^t e^{\hat{S}(t'-t)}\,\Omega(t',r,v)\,dt'.$$

Using the expressions (11) obtained for $\xi(t,r,v)$, **we** have for the **kinetic parts of the autocorrelation functions**

$$C_\varepsilon^{K}(t) = C_\varepsilon^{(1)K}(t) + C_\varepsilon^{(2)K}(t),$$

where

$$C_\varepsilon^{(1)K}(t) = n^2\int dv_0\,\varphi(v_0)\,j_\varepsilon(v_0)\int dr\,dv\,j_\varepsilon(v)\,\varphi(v)\times$$

$$\times\, e^{-\hat{S}t}\,\xi(0,r,v)\,;$$

$$C_\varepsilon^{(2)K}(t) = n^2\int dv_0\,\varphi(v_0)\,j_\varepsilon(v_0)\int dr\,dv\,j_\varepsilon(v)\,\varphi(v)\times$$

$$\times\Big[a^2 n\int_0^t e^{-\hat{S}(t-t')}\int\limits_{(v'-v)\sigma > 0}[(v'-v)\sigma]\,\varphi(v')\,\times$$

$$\times\,\hat{T}\left(\left(e^{-\hat{S}t}\,\xi(0,r,v)\right)\left(e^{-\hat{S}t'}\,\xi(0,r,v')\right)dv'd\sigma\right].$$

The contribution from the linearised approximation of the Boltzmann-Enskog equation to the kinetic parts of the autocorrelation functions is

$$C_\varepsilon^{(1)K}(t) = n\int dr\,dv\,j_\varepsilon(v)\,\varphi(v)\,e^{-\hat{S}t}\left(W(r-r_0)\,j_\varepsilon(v)\right).$$

Then applying the determination (8) and condition(2) we finally obtain:

$$C_\varepsilon^{(1)K}(t) = n\left(j_\varepsilon(v)\,,\ e^{n\hat{\Lambda}_0(v)t}\,j_\varepsilon(v)\right),$$

where the scalar product is defined with the weight $\varphi(v)$, $\hat{\Lambda}_0$ is the linearized Boltzmann operator. It is of great importance that potential terms containing $\pm a\sigma$ in expressions (4) and (5), which distinguish the Boltzmann-Enskog equation from the Boltzmann, do not influence the kinetic parts $C_\varepsilon^{(1)K}(t)$ of the autocorrelation functions obtained from a linearized version of the Boltzmann-Enskog equation. The functions $C_\varepsilon^{(1)K}(t)$ are exponentially decreasing in time since the eigenvalues of $\hat{\Lambda}_0$ corresponding to the eigenfunctions by which the currents $j_\varepsilon(v)$ are decomposed, are known to be negative.[11] Consequently to study the asymptotic behaviour of the kinetic parts of the autocorrelation functions at long times and to calculate the density corrections to $C_\varepsilon^{(2)K}(t)$ in the non-linear case, the idea of Bogolubov [8] was taken into account, i.e. that it is natural to use the non-linear Boltzmann-Enskog equation for the hard-sphere systems for obtaining the higher density approximations since it has the exact microscopic solutions. Let us observe the influence of the potential terms $\pm a\sigma$ in the equations contained on the asymptotical tails and their coefficients. For these purposes we introduce the operators $\hat{\Lambda}_K(v)$, $\hat{T}_K$, and define their action on functions of v, v' as follows:

$$\hat{\Lambda}_K(v)\Psi(v) = a^2 \int\limits_{(v'-v)\sigma\geq 0} [(v'-v)\sigma]\,\varphi(v') \times$$

$$\times\,[\Psi(v^*) + e^{iak\sigma}\Psi(v^{*\prime}) - \Psi(v) - e^{-iak\sigma}\Psi(v')]\,dv'd\sigma ,$$

$\hat{\Lambda}_K(v)$ is the linearized Boltzmann-Enskog operator,

$$\hat{T}_K\, Z(v,v') = a^2 \int\limits_{(v'-v)\sigma\geq 0} [(v'-v)\sigma] \times$$

$$\times \left(Z(v^*, v^{*\prime})\, e^{-iak\sigma} - Z(v,v')\, e^{iak\sigma} \right) d\sigma .$$

The functions $C_\varepsilon^{(2)K}(t)$, which take into account the contribution of potential terms in the non-linear equation to the density dependence of kinetic parts of autocorrelation functions can be expressed as

$$C_\varepsilon^{(2)K}(t) = \frac{n}{(2\pi)^3} \int dk \int dv\, j_\varepsilon(v)\varphi(v) \int_0^t e^{(t-t')n\hat{\Lambda}_0(v)} \times \tag{12}$$

$$\times \int dv'\varphi(v')\, \hat{T}_K \Big\{ \exp\left[-t'\left(ik(v-v') - n\hat{\Lambda}_K(v) - n\hat{\Lambda}_{-K}(v')\right)\right] \times$$

$$\times \left(\frac{j_\varepsilon(v)}{\varphi(v)} |W_K|^2 \delta(v-v') + n f_K W_K^* j_\varepsilon(v') + n f_K^* W_K j_\varepsilon(v) \right) \Big\} .$$

In these formulas W_K , f_K are the Fourier components of the functions $W(r-r_0)$ and $f(r)$ from (1), respectively. For the sake of convenience, the Laplace transformation was applied to (12) for studying the time asymptotic behaviour of $C_\varepsilon^{(2)K}(t)$. We found

$$C_\varepsilon^{(2)K}(t) = \int e^{+pt}\, C_\varepsilon^{(2)K}(p)\, dp ,$$

where

$$C_\varepsilon^{(2)}(p) = n \left(\frac{j_\varepsilon(v)}{p - n\hat{\Lambda}_0(v)} , \int dv'\varphi(v') \int \frac{dk}{(2\pi)^3} \times \right.$$

$$\times \hat{T}_{\kappa} \left\{ \left[p + i\kappa(v-v') - n\hat{\Lambda}_{\kappa}(v) - n\hat{\Lambda}_{-\kappa}(v') \right]^{-1} A_{\kappa}(v,v') \right\} \Big), \tag{13}$$

here the notation [9] is introduced:

$$A_{\kappa}(v,v') = \frac{j_{\varepsilon}(v)}{\varphi(v)} |W_{\kappa}|^2 \delta(v-v') + n f_{\kappa} W_{\kappa}^{*} j_{\varepsilon}(v') + n f_{\kappa}^{*} W_{\kappa} j_{\varepsilon}(v). \tag{14}$$

It is easy to see that the extreme right singularity of $C_{\varepsilon}^{(2)\kappa}(p)$ in the complex p- plane is in $p=0$. For our purposes it is enough to study the behaviour of $C_{\varepsilon}^{(2)\kappa}(p)$ in the vicinity of this point. In this domain one can take $p=0$ on the left-hand side of the scalar product (13), because the currents $j_{\varepsilon}(v)$ are orthogonal to the eigenfunctions of the Boltzmann operator $\hat{\Lambda}_0(v)$, which corresponds to the zero eigenvalue. Let us also decompose the quantity $A_{\kappa}(v,v')$ on the eigenfunctions of $\hat{S}_{\kappa}(v)$,

$$\hat{S}_{\kappa}(v) = i\kappa v - n\hat{\Lambda}_{\kappa}(v).$$

The expression (13) may then be presented as

$$C_{\varepsilon}^{(2)\kappa}(p) \approx n \Big(\frac{j_{\varepsilon}(v)}{-n\hat{\Lambda}_0(v)}, \int dv' \varphi(v') \int \frac{d\kappa}{(2\pi)^3} \times \tag{15}$$

$$\times \sum_{\ell,m} \hat{T}_{\kappa} \tilde{\psi}_{\kappa}^{(\ell)}(v) \tilde{\psi}_{-\kappa}^{(m)}(v') A_{\kappa}^{(\ell,m)} \left(p + z_{\kappa}^{(\ell)} + z_{-\kappa}^{(m)} \right)^{-1} \Big),$$

where $z_{\kappa}^{(\ell)}$, $\tilde{\psi}_{\kappa}^{(\ell)}$ are the eigenvalues and eigenfunctions

of the operator $\hat{S}_{\kappa}(v)$; $A_{\kappa}^{(\ell,m)}$ are the coefficients in the decomposition of $A_{\kappa}(v,v')$ on $\{\tilde{\psi}_{\kappa}^{(\ell)}(v)\}$, $\{\tilde{\psi}_{-\kappa}^{(m)}(v')\}$. The eigenfunctions $\tilde{\psi}_{\kappa}^{(\ell)}(v)$ are, in general, not orthogonal. To find the asymptotic expressions for kinetic parts of autocorrelation functions, $C_{\varepsilon}^{(2)\kappa}(t)$, it is convenient to make the inverse Laplace transformation in (15):

$$C_{\varepsilon}^{(2)\kappa}(t) \approx n \Big(\frac{j_{\varepsilon}(v)}{-n\hat{\Lambda}_0(v)}, \int dv' \varphi(v') \int \frac{d\kappa}{(2\pi)^3} \times$$

$$\times \sum_{\ell,m} e^{-t\left(z_{\kappa}^{(\ell)} + z_{-\kappa}^{(m)}\right)} \hat{T}_{\kappa} \tilde{\psi}_{\kappa}^{(\ell)}(v) \tilde{\psi}_{-\kappa}^{(m)}(v') A_{\kappa}^{(\ell,m)} \Big). \tag{16}$$

Here the sum goes over those eigenvalues of $\hat{S}_{\kappa}(v)$ that tend to zero when $|\kappa| \to 0$.

The equation (16) represents the appropriate specialization of the mode-mode formula [12], which here has been derived directly from the non-linear Boltzmann-Enskog equation. Thus the asymptotics of the time behaviour of the kinetic parts of autocorrelation functions $C_{\varepsilon}^{(2)\kappa}(t)$ is certainly determined completely by the dispersive dependence of the sum $(z_{\kappa}^{(\ell)} + z_{-\kappa}^{(m)})$ composed of eigenvalues of the operator $\hat{S}_{\kappa}(v)$. Hence it is interesting to calculate these eigenvalues. In the case of the small wave numbers κ, the Boltzmann-Enskog operator $\hat{\Lambda}_{\kappa}(v)$ is given by the expansion

$$\hat{\Lambda}_{\kappa}(v) = \sum_{\ell=0}^{\infty} (ia|\kappa|)^{\ell} \frac{\hat{\Lambda}_{\ell}(v)}{\ell!}, \tag{17}$$

where $\hat{\Lambda}_0(v)$ is the linearized Boltzmann operator,

$$\hat{\Lambda}_1(v)\Psi(v) = a^2 \int\limits_{(v'-v)\sigma \geq 0} [(v'-v)\sigma](e\sigma)\varphi(v') \times$$
$$\times \left[\Psi(v^{*\prime}) + \Psi(v')\right] dv' d\sigma \, ;$$
$$\hat{\Lambda}_2(v)\Psi(v) = a^2 \int\limits_{(v'-v)\sigma \geq 0} [(v'-v)\sigma](e\sigma)^2\varphi(v') \times$$
$$\times \left[\Psi(v^{*\prime}) - \Psi(v')\right] dv' d\sigma \, ;$$

. . . .

It is important to note that $z_K^{(\ell)}, z_{-K}^{(m)}$ contain the higher order density corrections distinguishing them from eigenvalues of the operator $(i\kappa v - n\hat{\Lambda}_0(v))$.
The functions $\tilde{\psi}_K^{(\ell)}(v), \tilde{\psi}_{-K}^{(m)}(v')$ are also a power series in the density

$$\lim_{|K|\to 0} \tilde{\psi}_K^{(\ell)}(v) \simeq \psi_e^{(\ell)}(v) + n\sum_m C^{(1)}_{\ell,m}\psi_e^{(m)} + n^2\sum_m C^{(2)}_{\ell,m}\psi_e^{(m)} \dots$$

where $\psi_e^{(\ell)}$ are the well known eigenfunctions of the operator $(i\kappa v - n\hat{\Lambda}_0(v))$ [13], corresponding to zero eigenvalue of the Boltzmann operator:

$$\psi_e^{(1,2)} = \frac{1}{\sqrt{30}}\beta m v^2 \pm \left(\frac{1}{2}\beta m\right)^{1/2} ev \, ;$$

$$\psi_e^{(3)} = \frac{1}{\sqrt{10}}\left(\beta m v^2 - 5\right),$$

$$\psi_e^{(4)} = (\beta m)^{1/2} e_{1\perp} v \, , \quad \psi_e^{(5)} = (\beta m)^{1/2} e_{2\perp} v \, ,$$

here $e = \frac{\kappa}{|\kappa|}$, the unit vectors $e_{1\perp}$, $e_{2\perp}$ together with the vector e form the orthogonal basis.

In the acoustic approximation it is necessary to account in the first order of the perturbation theory only that term which is proportional to $|\kappa|$. The third term in (17), which is of the order of κ^2 should be used in calculations of the sound damping corrections. We consider the operator $(i\kappa v - ia|\kappa|n\hat{\Lambda}_1(v))$ at $\kappa \to 0$ as a small addition to the operator $-n\hat{\Lambda}_0(v)$. On writing the eigenvalues and eigenfunctions in the form

$$z_K = b_0 + b_1|\kappa| + b_2|\kappa|^2 + \dots,$$

$$\tilde{\psi}_K(v) = \sum_{i=1}^{5} C_{0i}\psi_e^{(i)} + |\kappa|\sum_{i=1}^{5} C_{1i}\psi_e^{(i)} + |\kappa|\sum_m{}' C_{1m}\psi^{(m)} + \dots,$$

where $b_0 = 0$ denotes the zero eigenvalue, $\psi^{(m)}$ are the eigenfunctions corresponding to the non-zero eigenvalues of the Boltzmann operator, we get for the coefficients b_1 in the framework of the standard perturbation theory the following expressions [14]:

$$b_1^{(1,2)} = \pm\frac{i}{(\beta m)^{1/2}}\left(\alpha^2 - \delta^2 - 2\gamma^2\right)^{1/2}, \qquad (18)$$

$$b_1^{(3)} = b_1^{(4)} = b_1^{(5)} = 0 \, ,$$

where

$$\alpha = \sqrt{\frac{5}{3}} + \frac{10\pi n a^3}{3\sqrt{15}} \, ; \quad \delta = \frac{2\pi n a^3}{\sqrt{15}} \, ; \quad \gamma = -\frac{2\pi n a^3}{3\sqrt{5}} \, ,$$

and construct the right eigenfunction system of the $\hat{S}_\kappa(v)$ operator in the first order:

$$\tilde{\psi}_e^{(1,2)} = (\alpha^2-\alpha\delta)^{-1/2}\left[\tfrac{1}{2}\left(\alpha-\delta\pm\sqrt{\alpha^2-\delta^2-2\gamma^2}\right)\psi_e^{(1)} + \tfrac{1}{2}\left(\alpha-\delta\mp\sqrt{\alpha^2-\delta^2-2\gamma^2}\right)\psi_e^{(2)} - \gamma\psi_e^{(3)}\right], \qquad (19)$$

$$\tilde{\psi}_e^{(3)} = \left(2\gamma^2+(\alpha+\delta)^2\right)^{-1/2}\left[-\gamma\left(\psi_e^{(1)}+\psi_e^{(2)}\right) + (\alpha+\delta)\psi_e^{(3)}\right]; \quad \tilde{\psi}_e^{(4,5)} = \psi_e^{(4,5)} .$$

Then (18) and (19) reduce to

$$b_1^{(1,2)} = \pm\frac{i}{(\beta m)^{1/2}}\sqrt{\frac{5}{3}}\left(1+\frac{2\pi}{3}na^3\right),$$

$$\tilde{\psi}_e^{(1,2)} = \psi_e^{(1,2)} - \frac{\pi na^3}{5}\psi_e^{(2,1)} + \frac{2\pi na^3}{5\sqrt{3}}\psi_e^{(3)},$$

$$\tilde{\psi}_e^{(3)} = \frac{2\pi}{5\sqrt{3}}\left(\psi_e^{(1)}+\psi_e^{(2)}\right) + \psi_e^{(3)}$$

with the accuracy $\sim na^3$ in the dimensionless density.

As should be expected, the functions $\tilde{\psi}_e^{(1,2,3)}$ are not orthogonal. It is necessary to point out that the eigenfunctions (19) are exact for the $\hat{S}_\kappa(v)$ operator in the limit $|\kappa|\to 0$ because the higher order corrections from the expansion (17) vanish in this limit. In the second order of the perturbation theory with the operator $|\kappa|\left(iev - ian\hat{\Lambda}_1(v)\right)$ we obtain:

$$b_2^{(1,2)} = \frac{1}{n}\left[-u - \frac{q\gamma^2}{\alpha^2-\delta^2-2\gamma^2} + \frac{\gamma r(2\delta+\gamma\sqrt{3})}{\alpha^2-\delta^2-2\gamma^2}\right],$$

$$b_2^{(3)} = -\frac{1}{n}\left[\frac{(\alpha-\delta)\left(-2r\gamma+r\sqrt{3}(\alpha+\delta)\right)}{\alpha^2-\delta^2-2\gamma^2} + \frac{2\gamma\left(-\gamma(u+q)+(\alpha+\delta)r\right)}{\alpha^2-\delta^2-2\gamma^2}\right]; \quad b_2^{(4,5)} = -\frac{s}{n}; \qquad (21)$$

here

$$u = -\frac{\Gamma_s^{(E)}}{2}; \quad q = -n\left[\frac{1}{3}D_T^{(E)} - \frac{2}{3}D_\eta^{(E)}\right],$$

$$r = -\frac{n}{\sqrt{3}}D_T^{(E)}, \quad s = -nD_\eta^{(E)},$$

$D_T^{(E)}$, $D_\eta^{(E)}$ are the thermodiffusion and shear viscosity coefficients in the Boltzmann-Enskog model with accuracy up to order na^3- terms:

$$D_T^{(E)} = D_T\left(1+\frac{4\pi}{5}na^3\right), \quad D_\eta^{(E)} = D_\eta\left(1+\frac{8\pi}{15}na^3\right).$$

The operator $\hat{\Lambda}_2(v)$ has been eliminated in this approximation. If one keeps only zero and first-order terms in the expressions (21) then one gets for the $b_2^{(i)}$ ($i = 1,2,\ldots 5$) the usual Enskog values

$$b_2^{(1,2)} = \frac{\Gamma_s^{(E)}}{2}, \quad b_2^{(3)} = D_T^{(E)}, \quad b_2^{(4,5)} = D_\eta^{(E)},$$

as expected.

It should be noted that the calculation of the higher order in na^3 requires also the consideration of the following term in the decomposition (17), $\hat{\Lambda}_2(v)$, even in the first order of the perturbation theory. Thus we have determined the dispersion dependence for the eigenvalues $z_\kappa^{(\ell)}$, $z_{-\kappa}^{(m)}$ of the $\hat{S}_\kappa(v)$ operator and have constructed its right and left eigenfunctions (note that the left eigenfunctions may be obtained from the right ones by the index and argument replacement $1 \rightleftarrows 2$ and $\alpha \to -\alpha$ in (18)). The next problem is to analyse formula (16), which exhibits the asymptotic behaviour of the kinetic parts of the autocorrelation functions for long times. It is obvious both the second and third terms in expression (14) for $A_\kappa(v,v')$ are orthogonal to the functions $\tilde{\psi}_e^{(\ell)}$ and do not contribute to the quantities $A_\kappa^{(\ell,m)}$ if $|\kappa|$ goes to zero. The fact that $z_\kappa^{(\ell)} + z_{-\kappa}^{(m)} \sim (b_2^{(\ell)} + b_2^{(m)})\kappa^2$ has enabled us finally to obtain the leading asymptotical terms in the mode-mode formula (16) on substituting the variable and doing the integration on $|\kappa|$ in the following form

$$C_\varepsilon^{(2)\kappa}(t) \simeq t^{-3/2} \sum_{\ell,m=1}^{5} \int \frac{d\Omega_\kappa}{(2\pi)^3}\, 4\left[\pi\left(b_2^{(\ell)} + b_2^{(m)}\right)\right]^{-3/2} \times$$

$$\times \sum_{\substack{\ell',m' \\ \ell'',m''}} C_{\ell\ell'}\, C_{mm''} \left(C^{-1}\right)_{\ell''\ell} \left(C^{-1}\right)_{m''m} \tilde{A}^{*(\varepsilon)(e)}_{\ell''m'}, \tag{22}$$

here $\tilde{A}^{(\varepsilon)(e)}_{\ell'm'} = \left(j_\varepsilon(v),\ \psi_e^{(\ell')}(v)\,\psi_{-e}^{(m')}(v)\right)$.

The matrix $C_{\ell\ell'}$ connects the functions $\tilde{\psi}_e^{(\ell)}$, $\psi_e^{(\ell')}$:

$$\tilde{\psi}_e^{(\ell)} = \sum_{\ell'} C_{\ell\ell'}\, \psi_e^{(\ell')}$$

and naturally depends on the density. In zeroth order on the parameter na^3 this matrix is equal to $\delta_{\ell\ell'}$ and the expression (22) coincides with the ordinary mode-mode formula. Note that in first order on na^3 the matrix $C_{\ell\ell'}$ is symmetric, as it is easy to see from (20) and, therefore, the effects of non-orthogonality of the $\hat{S}_\kappa(v)$ eigenfunctions do not contribute to the mode-mode formula in this approximation also. However, if the second-order terms are taken into account then the same reciprocal compensation does not take place and these effects are expected to lead to the modification of the mode-mode formula according to (22). Thus one can say that the assumption previously made about the application of the Enskog transport coefficients in the mode-mode formula is guaranteed up to na^3 order in density. In the framework of the Enskog model it is necessary by calculating the higher order in density to account for the non-orthogonal effects of the eigenfunctions of the corresponding linearized operator. The results obtained turn into those derived in the paper [9] for the non-linear Boltzmann equation in the low-density limit. We should like to emphasise especially that the existence of an exact solution in the non-linear Boltzmann-Enskog model justifies the attempts to calculate the higher order correction terms in density. In the framework of the kinetic theory based on some way of BBGKI-hierarchy truncation, the successive inclusion of these terms appears to lead to the equivalent of the mode-mode formula modification (22).

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