

THE MODIFIED ENSKOG EQUATION

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Synopsis

Arguments are presented for a modified form of the nonlinear Enskog equation, which describes the time dependence of the single-particle distribution function in a dense gas of hard spheres. Unlike the usual Enskog equation it is not restricted to small spatial non-uniformities, and may thus be used to derive Burnett and higher-order hydrodynamic equations. In a single-component system both equations are equivalent at the level of the Navier–Stokes equations. The main importance of the modified Enskog equation becomes manifest when it is extended to mixtures of hard spheres. It is shown that the existing versions of Enskog’s theory for mixtures lead to results which are in conflict with irreversible thermodynamics (more specifically, the Onsager symmetry relations do not hold), whereas the present modified Enskog theory gives results in complete agreement with irreversible thermodynamics.

It is further shown that the linearized form of the modified Enskog equation yields an equation which has been derived by several authors for the description of space- and time-dependent fluctuations in a hard-sphere fluid.

1. *Introduction.* In an attempt to generalize the Boltzmann equation to higher densities, Enskog^{1,2}) has proposed a kinetic equation for the single-particle distribution function (D.F.) in a dense gas of hard spheres by modifying the “stosszahlansatz” in two ways:

- (i) he took into account that the centres of two colliding spheres are a distance σ apart, equal to the hard-sphere diameter;
- (ii) he increased the collision frequency by a factor χ , which is equal to the local-equilibrium pair D.F. for two spheres in contact and takes into account the correlations between the positions of two colliding spheres. These two modifications lead to the Enskog equation for the single-particle D.F., $F(\mathbf{v}, \mathbf{r}; t)$, in the

form

$$\begin{aligned} & \frac{\partial}{\partial t} F(\mathbf{v}_1, \mathbf{r}_1) + \mathbf{v}_1 \cdot \nabla F(\mathbf{v}_1, \mathbf{r}_1) \\ &= \int d\mathbf{v}_2 \sigma^2 \int' d\hat{\sigma} (\mathbf{v}_{21} \cdot \hat{\sigma}) \{ \chi(\sigma | n(\mathbf{r}_1 + \frac{1}{2}\sigma\hat{\sigma})) F(\mathbf{v}_1, \mathbf{r}_1) F(\mathbf{v}_2, \mathbf{r}_1 + \sigma\hat{\sigma}) \\ & \quad - \chi[\sigma | n(\mathbf{r}_1 - \frac{1}{2}\sigma\hat{\sigma})] F(\mathbf{v}_1, \mathbf{r}_1) F(\mathbf{v}_2, \mathbf{r}_1 - \sigma\hat{\sigma}) \}. \end{aligned} \quad (1.1)$$

Here \mathbf{r}_i ($i = 1, 2$) is the position of i th particle, \mathbf{v}_i ($i = 1, 2$) the velocity of the i th particle before the 1-2 collision, and \mathbf{v}_i^* ($i = 1, 2$) the corresponding velocity after the 1-2 collision. The prime on the integration sign indicates that the integration over the solid angle $d\hat{\sigma}$ is restricted to $\mathbf{v}_{21} \cdot \hat{\sigma} > 0$, where $\mathbf{v}_{21} = \mathbf{v}_2 - \mathbf{v}_1$; a caret on a vector, e.g., $\hat{\sigma}$, indicates a unit vector. The function $\chi(\sigma | n(\mathbf{R}))$ is the equilibrium value of the pair D.F. for $r_{21} = |\mathbf{r}_2 - \mathbf{r}_1| = \sigma$, evaluated as a function of the local density $n(\mathbf{R})$ at position $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$.

We observe that the function χ in (1.1) is not exactly the local equilibrium pair D.F., (describing the nonuniform equilibrium state) for two hard spheres at \mathbf{r}_1 and \mathbf{r}_2 . In a nonuniform state the local-equilibrium D.F. may be expected to involve gradients of the local density, higher powers of these gradients, as well as space derivatives of higher order than the first. In fact, the explicit form of the pair D.F. in a local-equilibrium state is well known³). For hard spheres it can be expressed as a nonlocal functional of the local density, which may be expanded around some fixed points; thus yielding explicitly all space derivatives mentioned above.

In this paper we propose to replace the function χ in (1.1) by the exact local-equilibrium pair D.F., $\bar{\chi}(\mathbf{r}_1, \mathbf{r}_2)$, which takes fully into account the spatial non-uniformities in the local equilibrium state. This replacement is completely in accordance with Enskog's arguments for modifying the "stosszahlansatz". In section 2 we give the explicit form for the local-equilibrium pair D.F. in a single and multicomponent system, together with the modified form of the Enskog equation for the corresponding cases. The implications of the modified form are investigated in the remaining sections. In section 2 we shall show that the function χ in the usual form (1.1) of the Enskog equation for a single-component system takes properly into account $\mathcal{O}(\nabla)$ terms in the spatial non-uniformities, *i.e.*, terms linear in the gradients of the local densities. Therefore, the usual and modified forms of the Enskog equation both lead to the same Navier-Stokes equations and to the same expression for the corresponding transport coefficients. However, the Enskog equation in the usual form does not account properly for $\mathcal{O}(\nabla^2)$ terms and higher, and may not be used to derive (linear and nonlinear) Burnett and higher-order hydrodynamic equations, and corresponding transport coefficients, as is well known in the literature⁴). The modified form, on the other hand, can in principle be used for this purpose.

The main importance of our modification concerns the extension of Enskog's

theory to mixtures of hard spheres. In the extensions, given in the literature^{5,6,7}), the collision term contains a function χ_{ij} , which is the equilibrium value of the pair D.F. of two particles in contact, belonging respectively to species i and j , and which is evaluated as a function of the local partial densities at some point \mathbf{R} . In the literature different choices have been made for this point \mathbf{R} , e.g., the midpoint of the line connecting the centres of two colliding spheres⁵), or the point of contact of the two colliding spheres^{6,7}). Each choice leads to a different solution of the kinetic equation. This implies that the linear relations between thermodynamic fluxes and driving forces differ for each choice of \mathbf{R} , and so do the Navier–Stokes equations.

In our extension of the Enskog theory to mixtures the collision term contains the exact local-equilibrium D.F., $\bar{\chi}(\mathbf{r}_i, \mathbf{r}_j)$ for two particles in contact at position \mathbf{r}_i and \mathbf{r}_j , belonging to species i and j , respectively. First, we shall see that none of the existing extensions of Enskog's theory to mixtures takes correctly into account the spatial non-uniformities in the local-equilibrium D.F. to linear order in the gradients of the partial densities. Consequently, our solution of the kinetic equation to linear order in the gradients differs from any of the above solutions, and so do our linear relations between the thermodynamic fluxes and driving forces, as well as the Navier–Stokes equations. Next, we show that the linear relations between fluxes and forces in the old theories are in conflict with irreversible thermodynamics (i.e., they do not satisfy the Onsager symmetry relations) whereas the linear relations derived from our modified Enskog equation are in complete agreement with irreversible thermodynamics.

Finally we discuss in section 3 the linearized form of the modified Enskog equation, and we show that this linearized equation is identical to an equation^{8,9}), describing space- and time-dependent fluctuations in thermal equilibrium. A short account of these results has already been published¹⁰).

2. Modified Enskog equation. In this section the modified form of the Enskog equation for single and multicomponent systems is given, together with explicit expressions for the local-equilibrium D.F. in both cases. We further discuss the assumptions and limitations, under which the modified form can be derived from the Liouville equation, as well as a brief discussion of the relevance of Enskog's theory for theoretical and experimental studies of transport coefficients.

The local equilibrium pair D.F. in a non-uniform state for a gas of identical hard spheres is a functional of the local density $n(\mathbf{r}; t) = \int d\mathbf{v} F(\mathbf{v}; \mathbf{r}; t)$ and can be expressed in the form of a density expansion as

$$g(\mathbf{r}_1\mathbf{r}_2) = W(\mathbf{r}_{12}) \bar{\chi}(\mathbf{r}_1\mathbf{r}_2), \quad (2.1a)$$

$$\begin{aligned} \bar{\chi}(\mathbf{r}_1\mathbf{r}_2) = & 1 + \int d\mathbf{r}_3 n(\mathbf{r}_3) V(\mathbf{r}_1\mathbf{r}_2 | \mathbf{r}_3) \\ & + \frac{1}{2} \int d\mathbf{r}_3 d\mathbf{r}_4 n(\mathbf{r}_3) n(\mathbf{r}_4) V(\mathbf{r}_1\mathbf{r}_2 | \mathbf{r}_3\mathbf{r}_4) + \dots, \end{aligned} \quad (2.1b)$$

where $V(\mathbf{r}_1\mathbf{r}_2 | \mathbf{r}_3 \dots \mathbf{r}_l)$ represents the sum of all Mayer graphs of l labelled points (vertices), which become bi-connected¹¹), when the (12) bond is added. The (ij) bond represents the Mayer function $f(r_{ij})$, which reads for the case of hard spheres

$$f(r) = W(r) - 1 = -\theta(\sigma - r), \quad (2.2)$$

where $\theta(x)$ is the unit step function

$$\theta(x) = \begin{cases} 1 & x > 0, \\ 0 & x \leq 0. \end{cases}$$

The pair D.F. (2.1) depends on the local densities only in a small neighbourhood of the positions \mathbf{r}_1 and \mathbf{r}_2 .

For a single-component system the modified Enskog equation becomes now

$$\frac{\partial}{\partial t} F(x_1) + \mathbf{v}_1 \cdot \nabla F(x_1) = \int dx_2 T(12) \bar{\chi}(\mathbf{r}_1\mathbf{r}_2) F(x_1) F(x_2). \quad (2.3)$$

Here $x = (\mathbf{v}, \mathbf{r})$ and for compactness of notation we have introduced the binary collision operator $T(12)$ as

$$T(12) = \sigma^2 \int' d\hat{\sigma} (\mathbf{v}_{21} \cdot \hat{\sigma}) [\delta(\mathbf{r}_{21} - \sigma\hat{\sigma}) R_{\hat{\sigma}} - \delta(\mathbf{r}_{21} + \sigma\hat{\sigma})], \quad (2.4)$$

where the prime on the integration sign indicates again that $\mathbf{v}_{21} \cdot \hat{\sigma} > 0$; the operator $R_{\hat{\sigma}}$ acts on \mathbf{v}_i ($i = 1, 2$) as $R_{\hat{\sigma}}\mathbf{v}_i = \mathbf{v}_i^*$, and the Dirac δ function in (2.4) ensures that $r_{12} = \sigma$, so that $T(12)g(\mathbf{r}_1\mathbf{r}_2) = T(12)\bar{\chi}(\mathbf{r}_1\mathbf{r}_2)$.

The extension to mixtures is straightforward. Consider an s -component mixture of hard spheres with diameter σ_i , where $i = (1, 2, \dots, s)$ labels the different species in the mixture. We denote the single-particle D.F. of species i by $F_i(x_i) = F_i$, where $x_i = (\mathbf{v}_i, \mathbf{r}_i)$. We make the convention that the subscript i labels simultaneously the particle, as well as the species to which it belongs. The extension of (2.3) to a multicomponent mixture then reads

$$\frac{\partial}{\partial t} F_i(x_i) + \mathbf{v}_i \cdot \nabla F_i(x_i) = \sum_j \int dx_j T_{ij} \bar{\chi}_{ij}(\mathbf{r}_i\mathbf{r}_j) F_i(x_i) F_j(x_j). \quad (2.5)$$

The sum runs over all s components in the mixture, and T_{ij} is defined, analogously to (2.4), as

$$T_{ij} = \sigma_{ij}^2 \int' d\hat{\sigma} (\mathbf{v}_{ji} \cdot \hat{\sigma}) [\delta(\mathbf{r}_{ji} - \sigma_{ji}\hat{\sigma}) R_{\hat{\sigma}} - \delta(\mathbf{r}_{ji} + \sigma_{ij}\hat{\sigma})],$$

where $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ and $R_{\hat{\sigma}}$ acts only on \mathbf{v}_i and \mathbf{v}_j as

$$\begin{aligned} R_{\hat{\sigma}}\mathbf{v}_i &\equiv \mathbf{v}_i^* = \mathbf{v}_i - (2\mu_{ij}/m_i)(\mathbf{v}_{ij} \cdot \hat{\sigma})\hat{\sigma}, \\ R_{\hat{\sigma}}\mathbf{v}_j &\equiv \mathbf{v}_j^* = \mathbf{v}_j + (2\mu_{ij}/m_j)(\mathbf{v}_{ij} \cdot \hat{\sigma})\hat{\sigma}. \end{aligned} \quad (2.6)$$

Here m_i ($i = 1, 2, \dots, s$) is the mass of a particle of the i th species, and $\mu_{ij}^{-1} = m_i^{-1} + m_j^{-1}$ is the reduced mass. The local-equilibrium pair D.F. is given, in complete analogy with (2.1), as

$$g_{ij}(\mathbf{r}_i \mathbf{r}_j) = W_{ij}(\mathbf{r}_{ij}) \bar{\chi}_{ij}(\mathbf{r}_i \mathbf{r}_j), \quad (2.7a)$$

$$\begin{aligned} \bar{\chi}_{ij}(\mathbf{r}_i \mathbf{r}_j) = & 1 + \sum_i \int d\mathbf{r}_i n_i(\mathbf{r}_i) V(\mathbf{r}_i \mathbf{r}_j | \mathbf{r}_i) \\ & + \frac{1}{2!} \sum_{i, i'} \int d\mathbf{r}_i d\mathbf{r}_{i'} n_i(\mathbf{r}_i) n_{i'}(\mathbf{r}_{i'}) V(\mathbf{r}_i \mathbf{r}_j | \mathbf{r}_i \mathbf{r}_{i'}) + \dots, \end{aligned} \quad (2.7b)$$

where

$$W_{ij}(r) = 1 + f_{ij}(r) = 1 - \theta(\sigma_{ij} - r) \quad (2.8)$$

and $n_l(\mathbf{r}_l; t) = \int d\mathbf{v}_l F_l(x_l; t)$ ($l = 1, 2, \dots, s$) are the local partial densities of the mixture. The sum runs over all s components in the mixture.

In addition to the intuitive arguments given for the validity of the nonlinear modified Enskog equation (2.3) and (2.5), we have also derived it from the Liouville equation by means of a diagrammatic method, in which the collision operator takes into account to all orders in the density the instantaneous collisions between the particles. Further, we have restricted ourselves to an initial N -particle D.F., $D(x_1 x_2 \dots x_N; t = 0)$ of the form $(N!)^{-1} W(\mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_N) \prod_{i=1}^N D(x_i; 0)$, where $W(\mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_N)$ equals one when all relative distances $r_{ij} \geq \sigma$, and vanishes elsewhere [compare (2.8)].

Under these conditions our modified Enskog equation becomes exact for times much shorter than the mean free time between collisions. It, therefore, describes on this time scale the single-particle D.F. for arbitrary spatial variations. The assumption of instantaneous collisions, *i.e.*, the neglect of all successive binary collisions, is justified for very short times where the probability for correlated collisions becomes vanishingly small compared to the probability of uncorrelated collisions. The derivation of the modified Enskog equation from the Liouville equation will be presented in a forthcoming paper.

In the next section we shall use the modified form (2.3) and (2.5) to derive hydrodynamic equations and transport coefficients. This means that we go *outside* the time regime for which it has been derived. In fact, it is well known that the Enskog equation is not exact in this time regime, just because it does not take into account correlations between collisions. However, there exists theoretical and experimental evidence that Enskog's theory gives fairly good results for the density dependence of transport coefficients. The initial slope of hard-sphere transport coefficients (plotted *versus* density) as predicted by the Enskog theory and the exact theory agree to within a few percent^{12,13}). Molecular-dynamics calculations¹⁴) of hard-sphere transport coefficients show that heat conductivity, and shear and bulk

viscosity are predicted by Enskog's theory correctly within a few percent up to densities of about half the close-packing density. For the coefficient of self-diffusion the differences between computer experiments and Enskog's theory are larger. Measurements of transport coefficients in noble gases are also in fairly good agreement with the results of Enskog's theory^{14,15}). In recent measurements¹⁶) of the self-diffusion of krypton, however, the density dependence is found to exhibit a structure which cannot be explained by Enskog's theory. Recently, also modifications of Enskog's theory have been proposed which account for the attractive part of the intermolecular potential¹⁷).

3. *Comparison with other theories.* In this section we want to make a comparison between the usual nonlinear Enskog equation and the modified form (2.3). This will be done first for a single-component system, where we shall find that the usual Enskog equation is consistent with (2.3) up to terms of $\mathcal{O}(\nabla^2)$. Secondly, we compare the modified Enskog equation (2.5) for mixtures with existing extensions of Enskog's theory to mixtures. These existing extensions lead to results, which are in conflict with irreversible thermodynamics.

In order to investigate the first point we expand the densities in (2.1) around some fixed point \mathbf{R} , to be chosen later on, yielding

$$\bar{\chi}(\mathbf{r}_1\mathbf{r}_2) = \chi(r_{12} | n(\mathbf{R})) + \int d\mathbf{r}_3 H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3 | n(\mathbf{R})) (\mathbf{r}_3 - \mathbf{R}) \cdot \nabla_{\mathbf{R}} n(\mathbf{R}) + \mathcal{O}(\nabla^2), \quad (3.1)$$

where

$$H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3 | n(\mathbf{R})) = [\delta\bar{\chi}(\mathbf{r}_1\mathbf{r}_2)/\delta n(\mathbf{r}_3)]_{n(\dots)=n(\mathbf{R})} \quad (3.2a)$$

$$\begin{aligned} &= V(\mathbf{r}_1\mathbf{r}_2 | \mathbf{r}_3) + n(\mathbf{R}) \int d\mathbf{r}_4 V(\mathbf{r}_1\mathbf{r}_2 | \mathbf{r}_3\mathbf{r}_4) \\ &+ (1/2!) n^2(\mathbf{R}) \int d\mathbf{r}_4 d\mathbf{r}_5 V(\mathbf{r}_1\mathbf{r}_2 | \mathbf{r}_3\mathbf{r}_4\mathbf{r}_5). \end{aligned} \quad (3.2b)$$

In (3.2a) we introduced the functional derivative of $\bar{\chi}(\mathbf{r}_1\mathbf{r}_2)$ with respect to $n(\mathbf{r}_3)$. After taking the derivative all local densities $n(\mathbf{r}_i)$ are replaced by $n(\mathbf{R})$. Since $H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)$ depends only on relative distances, and is symmetric under interchange of labels 1 and 2, we can show the following equality

$$\begin{aligned} \int d\mathbf{r}_3 H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3) \mathbf{r}_{31} &= \hat{\mathbf{r}}_{21} \int d\mathbf{r}_3 H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3) \mathbf{r}_{31} \cdot \hat{\mathbf{r}}_{21} \\ &= \frac{1}{2} \hat{\mathbf{r}}_{21} \int d\mathbf{r}_3 H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3) (\mathbf{r}_{31} \cdot \hat{\mathbf{r}}_{21} + \mathbf{r}_{32} \cdot \hat{\mathbf{r}}_{12}) \\ &= \frac{1}{2} \mathbf{r}_{21} \int d\mathbf{r}_3 H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3). \end{aligned} \quad (3.3)$$

In the second equality we have used that the coefficient of $\hat{\mathbf{r}}_{21}$ is symmetric under interchange of labels 1 and 2.

We deduce from (3.3) that $(\mathbf{r}_3 - \mathbf{R})$ in the second term on the right-hand side of (3.1) may be replaced by $\frac{1}{2}\mathbf{r}_{21} + \mathbf{r}_1 - \mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) - \mathbf{R}$. Therefore, by choosing $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ the $\mathcal{O}(\nabla)$ term in (3.1) vanishes. Similarly, one can verify that the $\mathcal{O}(\nabla^2)$ terms in (3.1) do not vanish in $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, so that¹⁸⁾

$$\bar{\chi}(\mathbf{r}_1\mathbf{r}_2) = \chi(r_{12} | n(\frac{1}{2}\mathbf{r}_1 + \frac{1}{2}\mathbf{r}_2)) + \mathcal{O}(\nabla^2). \tag{3.4}$$

Insertion of (3.4) in (2.3) gives the usual Enskog equation (1.1), which is therefore consistent with our equation (2.3) up to $\mathcal{O}(\nabla)$ terms inclusive.

Next we turn our attention to mixtures of hard spheres. The Enskog equation for mixtures, used in the literature, is of the general form

$$\frac{\partial}{\partial t} F_i(x_i) + \mathbf{v}_i \cdot \nabla F_i(x_i) = \sum_j \int dx_j T_{ij} \chi_{ij}(\sigma_{ij} | n(\mathbf{R}_{ij})) F_i(x_i) F_j(x_j), \tag{3.5}$$

where the local partial densities are taken at the point $\mathbf{R}_{ij} = (1 - \alpha_{ij})\mathbf{r}_i + \alpha_{ij}\mathbf{r}_j$, which lies on the line connecting the centres of the two colliding spheres. Different values are used for α_{ij} by different authors. In Chapman and Cowling's book the theory of Thorne⁵⁾ is given, where $\alpha_{ij} = \frac{1}{2}$. The same choice for α_{ij} has been made in many other places⁵⁾. Garcia-Colin and coworkers⁶⁾, on the other hand, have chosen for $\alpha_{ij} = \sigma_i/2\sigma_{ij}$, so that \mathbf{R}_{ij} is the point of contact of the two colliding spheres. In a recent paper by Barajas *et al.*⁷⁾ the choices for α_{ij} with $0 < \alpha_{ij} < 1$ are discussed, and the corresponding results for the fluxes of mass, energy and momentum, obtained from the Enskog equation, are compared with the theory of irreversible thermodynamics. Barajas *et al.* also observe that the driving forces for the mass fluxes, obtained from the Enskog equation (3.5) are not in agreement with irreversible thermodynamics to general order in the partial densities. Here we show that the modified Enskog equation (2.5) for mixtures is in complete agreement with irreversible thermodynamics, and that the old versions (3.5) are not.

Let us compare the kinetic equations (3.5) and (2.5). In order to do so we expand the local pair D.F. (2.7) around \mathbf{R} , yielding

$$\begin{aligned} \bar{\chi}_{ij}(\mathbf{r}_i\mathbf{r}_j) &= \chi_{ij}(r_{ij} | n(\mathbf{R})) \\ &+ \sum_l \int d\mathbf{r}_l H_{ijl}(\mathbf{r}_i\mathbf{r}_j\mathbf{r}_l | n(\mathbf{R})) (\mathbf{r}_l - \mathbf{R}) \cdot \nabla_{\mathbf{R}} n_l(\mathbf{R}) + \mathcal{O}(\nabla^2), \end{aligned} \tag{3.6}$$

where

$$H_{ijl}(\mathbf{r}_i\mathbf{r}_j\mathbf{r}_l | n(\mathbf{R})) = [\delta \bar{\chi}_{ij}(\mathbf{r}_i\mathbf{r}_j) / \delta n_l(\mathbf{r}_l)]_{n=n(\mathbf{R})} \tag{3.7a}$$

$$\begin{aligned} &= V_{ijl}(\mathbf{r}_i\mathbf{r}_j | \mathbf{r}_l) + \sum_k n_k(\mathbf{R}) \int d\mathbf{r}_k V_{ijkl}(\mathbf{r}_i\mathbf{r}_j | \mathbf{r}_l\mathbf{r}_k) \\ &+ (1/2!) \sum_{k,k'} n_k(\mathbf{R}) n_{k'}(\mathbf{R}) \int d\mathbf{r}_k d\mathbf{r}_{k'} V_{ijklk'}(\mathbf{r}_i\mathbf{r}_j | \mathbf{r}_l\mathbf{r}_k\mathbf{r}_{k'}) + \dots \end{aligned} \tag{3.7b}$$

However, if species $i \neq j$, the function $H_{ijl}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_l)$ is no longer symmetric under interchange of particle and species labels i and j . Therefore, equalities of the type (3.3) no longer hold, and it is impossible to choose a point \mathbf{R} such that the second term on the right-hand side of (3.6) vanishes. Consequently, the Enskog equation (3.5) for mixtures, as used in the literature, differs from our modified equation (2.5) already in $\mathcal{O}(\nabla)$ terms. Therefore, the normal solutions $F_i(x_i)$ of both kinetic equations differ in $\mathcal{O}(\nabla)$ terms, and so do the relations between the thermodynamic fluxes and conjugate driving forces, as well as the Navier–Stokes equations.

In order to show the differences more explicitly we determine, by means of the Chapman–Enskog method¹⁹), the normal solutions of the kinetic equations (3.5) and (2.5) in the form of an expansion in powers of a uniformity parameter, which is proportional to the gradients in the system. The time variation of the normal solutions, which depend on time only through the local partial densities, the local mass velocity and the local temperature, can be calculated by means of the hydrodynamic equations.

The first step is to expand all local quantities in (3.5) and (2.5) around the point \mathbf{r}_i , yielding

$$F_j(\mathbf{v}_j, \mathbf{r}_j) = F_j(\mathbf{v}_j) + \mathbf{r}_{ji} \cdot \nabla F_j(\mathbf{v}_j) + \mathcal{O}(\nabla^2) \quad (3.8)$$

and

$$\chi_{ij}(\sigma_{ij} | n(\mathbf{R}_{ij})) = \chi_{ij}(\sigma_{ij} | n(\mathbf{r}_i)) + \alpha_{ij} \mathbf{r}_{ij} \cdot \nabla \chi_{ij}(\sigma_{ij} | n(\mathbf{r}_i)) + \mathcal{O}(\nabla^2), \quad (3.9')$$

$$\bar{\chi}_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \chi_{ij}(\sigma_{ij} | n(\mathbf{r}_i)) + \sum_l \int d\mathbf{r}_l H_{ijl}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_l | n(\mathbf{r}_i)) \mathbf{r}_{il} \cdot \nabla n_l(\mathbf{r}_i) + \mathcal{O}(\nabla^2), \quad (3.9'')$$

where $F_j(\mathbf{v}_j)$ and all partial densities are taken at the point \mathbf{r}_i . Eq. (3.9'') is obtained from (3.6) upon replacing \mathbf{R} by \mathbf{r}_i . Similarly, we write the single-particle D.F.'s in (3.5) and (2.5) as

$$F_i(\mathbf{v}_i) = F_i^{(0)}(\mathbf{v}_i) + F_i^{(1)}(\mathbf{v}_i) + \mathcal{O}(\nabla^2), \quad (3.10)$$

where $F_i^{(\alpha)}(\mathbf{v}_i)$ ($\alpha = 0, 1$) are the $\mathcal{O}(\nabla^\alpha)$ terms in the expansion of $F_i(\mathbf{v}_i)$ in powers of the gradients. By inserting (3.8)–(3.10) into (3.5) and (2.5), and collecting $\mathcal{O}(\nabla^0)$ terms one finds an integral equation for $F_i^{(0)}$, the solution of which is the local equilibrium D.F., defined by

$$F_i^{(0)}(\mathbf{v}_i) = n_i(\mathbf{r}_i; t) \left(\frac{m_i}{2\pi k_B T(\mathbf{r}_i; t)} \right)^{3/2} \exp \left(\frac{-m_i [\mathbf{v}_i - \mathbf{u}(\mathbf{r}_i; t)]^2}{2k_B T(\mathbf{r}_i; t)} \right). \quad (3.11)$$

Here $n_i(\mathbf{r}_i; t)$, $T(\mathbf{r}_i; t)$ and $\mathbf{u}(\mathbf{r}_i; t)$ are respectively the local partial densities ($l = 1, 2, \dots, s$), the local temperature (k_B is Boltzmann's constant), and the local mass velocity.

In the next order we obtain the following inhomogeneous linear integral equation for $F_i^{(1)}$,

$$\begin{aligned} & \sum_j \chi_{ij} \int dx_j T_{ij} (F_i^{(0)} F_j^{(1)} + F_i^{(1)} F_j^{(0)}) \\ &= \frac{\partial}{\partial t} F_i^{(0)} + v_i \cdot \nabla F_i^{(0)} - \sum_j \chi_{ij} \int dx_j T_{ij} F_i^{(0)} r_{ji} \cdot \nabla F_j^{(0)} - A_i, \end{aligned} \quad (3.12)$$

where $\chi_{ij} \equiv \chi_{ij}(\sigma_{ij} | n)$ and where $(\partial F_i^{(0)} / \partial t)$ is determined from the Euler equations, using (3.11). The inhomogeneous term A_i , originating from the $\theta(\nabla)$ term in (3.9) differs for (3.5) and (2.5), and has respectively the form

$$A_i' = \sum_j \int dx_j T_{ij} F_i^{(0)} F_j^{(0)} \alpha_{ij} r_{ji} \cdot \nabla \chi_{ij} = F_i^{(0)} \sum_j n_j \tilde{f}_{ij}(0) \alpha_{ij} V_i \cdot \nabla \chi_{ij} \quad (3.13')$$

and

$$\begin{aligned} A_i'' &= \sum_j \int dx_j T_{ij} F_i^{(0)} F_j^{(0)} \sum_l \int dr_l H_{ilj} (r_l r_j r_l | n) r_{li} \cdot \nabla n_l \\ &= F_i^{(0)} \sum_j [\tilde{C}_{ij}(0) - \chi_{ij} \tilde{f}_{ij}(0)] V_i \cdot \nabla n_j, \end{aligned} \quad (3.13'')$$

where $V_i = v_i - u$ and

$$\tilde{f}_{ij}(0) = \int dr_{ij} f_{ij}(r_{ij}) = - (4\pi/3) \sigma_{ij}^3; \quad \tilde{C}_{ij}(0) = \int dr_{ij} C_{ij}(r_{ij}), \quad (3.14)$$

are the long-wavelength limits of the Fourier transforms of the Mayer function $f_{ij}(r_{ij})$ and the direct correlation function $C_{ij}(r_{ij})$, which is defined by the Ornstein-Zernike relation

$$G_{ij}(r_{ij}) = C_{ij}(r_{ij}) + \sum_l n_l \int dr_l C_{il}(r_{il}) G_{lj}(r_{lj}). \quad (3.15)$$

Here, $G_{ij}(r_{ij}) = W_{ij}(r_{ij}) \chi_{ij}(r_{ij} | n) - 1$ is the equilibrium value of the pair correlation function, in which all partial densities are taken at position r_i . The final expressions for A_i in (3.13) are derived in an appendix.

The inhomogeneous terms in (3.12) consist of terms proportional to the gradient of the local temperature, the local mass velocity and the local partial densities. The integral equations (3.12) resulting from (3.5) and (2.5) differ only in the term A_i , which is a linear combination of gradients of partial densities. Therefore, the solutions $F_i^{(1)}$ of the kinetic equations are only different in the terms containing gradients of partial densities. To appreciate the full difference between the usual Enskog equation (3.5) and the modified form (2.5), we collect all inhomogeneous terms containing gradients of partial densities, resulting from $(V_i \cdot \nabla F_i^{(0)})$ and the third and fourth terms on the right-hand side of (3.12). The evaluation of the contribution from the third term is similar to (3.13'), for which we refer to the ap-

pendix, and yields $F_i^{(0)} \sum_j \chi_{ij} \tilde{f}_{ij}(0) \mathbf{V}_i \cdot \nabla n_j$. The sum, B_i , of all inhomogeneous terms proportional to the gradients of the partial densities now becomes

$$B'_i = -F_i^{(0)} \mathbf{V}_i \cdot \left(\nabla \log n_i - \sum_j \tilde{f}_{ij}(0) (\chi_{ij} \nabla n_j + n_j \alpha_{ij} \nabla \chi_{ij}) \right), \quad (3.16')$$

$$B''_i = -F_i^{(0)} \mathbf{V}_i \cdot \sum_j [\delta_{ij} - n_j \tilde{\mathcal{C}}_{ij}(0)] \nabla \log n_j = -F_i^{(0)} (\mathbf{V}_i / k_B T) \cdot (\nabla \mu_i)_T, \quad (3.16'')$$

where $\mu_i(r_i; t)$ is the local chemical potential per particle of species i at the point r_i . The symbol $(\nabla \mu_i)_T$ indicates that μ_i is considered as a function of the local partial densities n_j and the local temperature T , where T is kept constant in taking the gradient. To prove the second equality in (3.16'') we need to show

$$\delta_{ij} - n_j \tilde{\mathcal{C}}_{ij}(0) = \frac{n_j}{k_B T} \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T, n_i \neq j}. \quad (3.17)$$

In taking the derivative we keep the temperature and all partial densities n_i , except n_j , constant. Eq. (3.17) follows from the observation that $\delta_{ij} - n_j \tilde{\mathcal{C}}_{ij}(0)$ is the matrix inverse of $\delta_{ij} + n_j \tilde{\mathcal{G}}_{ij}(0)$, where $\tilde{\mathcal{G}}_{ij}(0) = \int d\mathbf{r}_{ij} G_{ij}(r_{ij})$. This follows directly by taking the Fourier transform of the Ornstein-Zernike relation (3.15). From the formulae for the fluctuations in a grand canonical ensemble one has

$$\begin{aligned} \delta_{ij} + n_j \tilde{\mathcal{G}}_{ij}(0) &= \langle N_i \rangle^{-1} \langle (N_i - \langle N_i \rangle) (N_j - \langle N_j \rangle) \rangle \\ &= (k_B T / n_i) (\partial n_i / \partial \mu_j)_{T, \mu_i \neq j}, \end{aligned} \quad (3.18)$$

where $\langle \dots \rangle$ indicates an average over a grand canonical ensemble. By applying the chain rule of differentiation one easily verifies that the thermodynamic derivatives in (3.17) and (3.18) are each other's matrix inverse, which proves (3.17).

Up till now we have left out of consideration the terms proportional to the local densities originating from $\partial F_i^{(0)} / \partial t + \mathbf{u} \cdot \nabla F_i^{(0)}$ in (3.12). Adding these contributions to (3.16') yields for the full inhomogeneous terms proportional to ∇n_i in the old versions

$$(1/k_B T) F_i^{(0)} m_i \mathbf{V}_i \cdot \sum_j (\delta_{ij} - \varrho_j / \varrho) X'_j, \quad (3.19)$$

where X'_i is defined as

$$X'_i = -(k_B T / m_i n_i) \left(\nabla n_i - \sum_j n_j \tilde{f}_{ij}(0) (\chi_{ij} \nabla n_j + n_j \alpha_{ij} \nabla \chi_{ij}) \right). \quad (3.20)$$

Analogously one finds in the modified version an expression equal to (3.19) after replacing X'_j by X_j , defined as

$$X_i = -\frac{1}{m_i} (\nabla \mu_i)_T = -\frac{k_B T}{m_i} \sum_j \left(\frac{\delta_{ij}}{n_j} - \tilde{\mathcal{C}}_{ij}(0) \right) \nabla n_j. \quad (3.21)$$

Let us compare X'_i and X_i . We notice first that

$$\sum_i \varrho_i X'_i = \sum_i \varrho_i X_i = -(\nabla p)_T, \tag{3.22}$$

which follows directly from the Gibbs–Duhem relation and the expression for the hard-sphere pressure $p = k_B T [n - \sum_{ij} \alpha_{ij} n_i n_j \tilde{f}_{ij}(0) \chi_{ij}]$ with the choices of α_{ij} discussed below (3.5) with $\alpha_{ij} + \alpha_{ji} = 1$. We further observe that X'_i and X_i are the *same* to lowest and first order in the density [since $\chi_{ij} = 1$ and $\tilde{C}_{ij}(0) = \tilde{f}_{ij}(0)$ to lowest order in the density], but *differ* in higher-order terms. Only in the exceptional case that the diameters σ_i ($i = 1, 2, \dots, s$) of all species are equal (the masses m_i may still be different), X'_i and X_i are the same to all orders in the density.

Summarizing the above results, we have found that the inhomogeneous terms in the integral equation (3.12), proportional to the ∇n_i 's are given in the old versions by (3.19) and in the modified version by (3.19) after replacing X'_i by X_i , whereas all inhomogeneous terms proportional to ∇T and ∇u are identical in both cases. Hence, the solution $F_i^{(1)}$ of (3.12) in the old versions has the form

$$F_i^{(1)} = E_{i0}(V_i) \cdot X_0 + \sum_j E_{ij}(V_i) \cdot X'_j + E_{iu}(V_i) : X_u, \tag{3.23}$$

where $X_0 = -\nabla T/T$ and $X_u = -\nabla u$, and the E_i 's are certain functions of the velocity V_i . In the modified version the solution $F_i^{(1)}$ is of the same form, but X'_j is replaced by X_j , while X_0 , X_u and all functions $E_i(V_i)$ are the same as in the old versions.

From expressions (3.23) one can directly calculate the fluxes of mass, momentum and energy, which are found to be proportional to the gradients X_0 , X_j (or X'_j) and X_u . The coefficients of proportionality, which are linear transport coefficients, are identical in the old and modified versions.

In the last part of this section we want to compare the above results with irreversible thermodynamics. It will turn out that the modified Enskog theory is consistent with the results of irreversible thermodynamics, and that the old versions are not. Irreversible thermodynamics²⁰⁾ tells us that the matrix of transport coefficients $L_{\alpha\beta}$, defined through $J_\alpha = \sum_\beta L_{\alpha\beta} X_\beta$, is symmetric (Onsager reciprocity relations) and non-negative definite (positive entropy production), provided the fluxes J_α and the driving forces X_β are chosen in conjugate pairs, which can be found from the irreversible entropy production $\sigma = (1/T) \sum_\alpha J_\alpha X_\alpha$. Furthermore, any linear transformation of the X_α 's among themselves, and of the J_α 's among themselves, which leaves σ invariant, yields equivalent conjugate sets of fluxes and driving forces, with a new matrix of transport coefficients which is also symmetric and non-negative definite. A possible choice of J_α 's and X_α 's is given in the literature²¹⁾

$$\sigma T = -J_q \cdot \nabla T/\hat{T} - \sum_i J_i (T/m_i) \cdot \nabla (\mu_i/T) + \dots, \tag{3.24}$$

where \mathbf{J}_q and \mathbf{J}_i are respectively the energy flux and the mass flux of species i . We have omitted the contributions from the momentum flux. For our purpose $\mathbf{X}_0, \mathbf{X}_i (i = 1, \dots, s)$ is a convenient set of driving forces, which are related to the driving forces in (3.24) through the linear transformation

$$T \nabla \left(\frac{\mu_i}{T} \right) = (\nabla \mu_i)_T + T \left(\frac{\partial (\mu_i/T)}{\partial T} \right)_{n_j} \nabla T = (\nabla \mu_i)_T - \frac{3}{2} k_B \nabla T, \quad (3.25)$$

where we have used the Maxwell relation

$$\left(\frac{\partial (\mu_i/T)}{\partial (1/T)} \right)_{n_j} = \left(\frac{\partial e}{\partial n_i} \right)_{T, n_j \neq i} = \frac{3}{2} k_B T,$$

with $e = \frac{3}{2} n k_B T$ for the hard-sphere gas. Insertion of (3.25) in (3.24) yields then for the conjugate fluxes

$$\sigma T = \mathbf{J}_0 \cdot \mathbf{X}_0 + \sum_i \mathbf{J}_i \cdot \mathbf{X}_i \quad (3.26)$$

with

$$\mathbf{J}_0 = \mathbf{J}_q - \sum_i (3k_B T/2m_i) \mathbf{J}_i. \quad (3.27)$$

In the modified Enskog theory the linear transport coefficients can now be calculated from (3.23) with \mathbf{X}'_i replaced by \mathbf{X}_i with the result

$$\mathbf{J}_0 = L_{00} \mathbf{X}_0 + \sum_i L_{0i} \mathbf{X}_i, \quad \mathbf{J}_i = L_{i0} \mathbf{X}_0 + \sum_j L_{ij} \mathbf{X}_j. \quad (3.28)$$

We have calculated $L_{\alpha\beta} (\alpha, \beta = 0, 1, \dots, s)$ in (3.28), and shown that it is non-negative definite and satisfies the following relations

$$L_{\alpha\beta} = L_{\beta\alpha}; \quad \sum_{\alpha \neq 0} L_{\alpha\beta} = \sum_{\beta \neq 0} L_{\alpha\beta} = 0. \quad (3.29)$$

The details of these calculations together with explicit expressions for $L_{\alpha\beta}$ will be published separately²²). We may conclude that the modified Enskog theory is in complete agreement with irreversible thermodynamics.

Next, we consider the old versions of Enskog's theory, which yield for \mathbf{J}_0 and \mathbf{J}_i , using (3.23)

$$\mathbf{J}_0 = L_{00} \mathbf{X}_0 + \sum_i L_{0i} \mathbf{X}'_i, \quad \mathbf{J}_i = L_{i0} \mathbf{X}_0 + \sum_j L_{ij} \mathbf{X}'_j, \quad (3.30)$$

where the transport matrix $L_{\alpha\beta}$ is identical to the one in (3.28), as follows from (3.23). This by no means implies that the old versions of Enskog's theory agree with

irreversible thermodynamics, because the fluxes (J_0, J_i) and forces (X_0, X'_i) are not conjugate in the sense of (3.26). In order to verify whether the transport coefficients in (3.30) satisfy the requirements of irreversible thermodynamics, we express (3.30) in terms of the conjugate fluxes (J_0, J_i) and forces (X_0, X_i). To that end we eliminate X'_i in favour of X_i by means of the relation

$$m_i X'_i = \sum_j N_{ij} m_j X_j, \tag{3.31}$$

which follows from (3.20) and (3.21), and where $\{N_{ij}\}$ is an $s \times s$ matrix which does *not depend* on the masses m_i ($i = 1, 2, \dots, s$), and *differs* from the unit matrix. This difference shows up in terms of second order in the density, since X'_i and X_i differ at the same order. Furthermore, $\{N_{ij}\}$ satisfies the relation

$$\sum_i n_i N_{ij} = n_j, \tag{3.32}$$

which follows from (3.31) after multiplication by n_i and summation over i , by virtue of (3.22) and the linear independence of the X'_i 's. The explicit form of $\{N_{ij}\}$ is irrelevant for the discussion.

The linear relations (3.30) in terms of conjugate fluxes and forces read now

$$J_2 = L_{00} X_0 + \sum_i L'_{0i} X_i, \quad J_i = L_{i0} X_0 + \sum_j L'_{ij} X_j, \tag{3.33}$$

where L' follows from (3.30) and (3.31):

$$L'_{\alpha i} = \sum_j L_{\alpha j} N_{ji} (m_i/m_j) \quad (\alpha = 0, 1, 2, \dots, s). \tag{3.34}$$

For the Onsager symmetry relations to be valid in (3.33) it is necessary that

$$L_{i0} = L'_{0i}; \quad L'_{ij} = L'_{ji}. \tag{3.35}$$

Consider for simplicity a binary mixture ($i, j = 1, 2$), where we have from (3.29) $L_{01} = -L_{02} = -L_{20} = L_{10}$ and $L_{11} = -L_{12} = -L_{21} = L_{22}$. Using now (3.34) the relations $L_{10} = L'_{01}$ and $L_{20} = L'_{02}$ imply

$$1 = N_{11} - N_{21} (m_1/m_2), \quad 1 = N_{22} - N_{12} (m_2/m_1). \tag{3.36}$$

Since $\{N_{ij}\}$ satisfies (3.32) we have in addition

$$n_1 N_{11} + n_2 N_{21} = n_1, \quad n_1 N_{12} + n_2 N_{22} = n_2. \tag{3.37}$$

As $\{N_{ij}\}$ does not depend on the masses (which can be chosen arbitrarily) eqs. (3.36) and (3.37) require that $N_{ij} = \delta_{ij}$, which is in contradiction with the properties of

N_{ij} , mentioned below (3.31). Hence the Onsager symmetry relations (3.35) cannot be satisfied in the old versions of Enskog's theory for the binary mixture. The above argument can be extended directly to multicomponent mixtures, from which we deduce that the old versions of Enskog's theory for mixtures are in general in conflict with irreversible thermodynamics.

4. *Space- and time-dependent fluctuations in hard-sphere fluids.* An interesting implication of the modified Enskog equation is its connection with fluctuations in a hard-sphere fluid. By means of many-body methods Mazenko, Wei and Yip⁸) have recently derived an equation describing space- and time-dependent fluctuations for short times in a hard-sphere gas. A completely different approach developed by Konijnendijk and Van Leeuwen⁹), also describing the short-time behaviour of fluctuations in a hard-sphere fluid, has lead to an equation very similar to the one of Mazenko *et al.*

In this section we shall show that linearization of the modified Enskog equation (2.3) around thermal equilibrium yields exactly the equation derived by Konijnendijk and Van Leeuwen.

We shall present the derivation for a mixture of hard spheres. This is done, because it does not introduce any extra complications and we shall need these equations later on for a derivation of the linear Navier–Stokes equations and the corresponding transport coefficients in a mixture.

In order to linearize the modified Enskog equation we restrict ourselves to small deviations from overall thermal equilibrium, and write the single-particle D.F., F_i ,

$$\text{as } F_i = \varphi_i (1 + \delta h_i), \quad (4.1)$$

where φ_i is the Maxwell–Boltzmann D.F.,

$$\varphi_i = \varphi_i(v_i) = n_i (\beta m_i / 2\pi)^{3/2} \exp(-\frac{1}{2}\beta m_i v_i^2). \quad (4.2)$$

Here $\beta = (k_B T)^{-1}$ and T is the equilibrium temperature; the n_i 's are the partial densities in equilibrium; and $\delta h_i = \delta h_i(v_i, \mathbf{r}_i; t)$ describes the relative deviation of F_i from its equilibrium value. In order to linearize $\bar{\chi}_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ we use the relation

$$\bar{\chi}_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \chi_{ij}(r_{ij} | n) + \delta \chi_{ij}(\mathbf{r}_i, \mathbf{r}_j | n), \quad (4.3)$$

where $\chi_{ij}(r_{ij} | n)$ is obtained from (2.1) by replacing all $n_i(\mathbf{r}_i)$ by their equilibrium values n_i and

$$\delta \chi_{ij}(\mathbf{r}_i, \mathbf{r}_j | n) = \sum_l \int d\mathbf{r}_l H_{ijl}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_l | n) \delta n_l(\mathbf{r}_l). \quad (4.4)$$

The functional derivative $H_{ijl}(\dots | n)$, defined in (3.2a), is taken at thermal equilibrium, and

$$\delta n_l(\mathbf{r}_l) = \int d\mathbf{v}_l \varphi_l \delta h_l, \quad (4.5)$$

is the deviation of the local partial density from its equilibrium value. Inserting the above equations in (2.5) and retaining only terms linear in the deviations from equilibrium, one obtains

$$\frac{\partial}{\partial t} \delta h = -L \delta h, \quad (4.6)$$

where

$$L = K + D + A, \quad (4.7)$$

with

$$(K \delta h)_i = v_i \cdot \nabla \delta h_i, \quad (4.7a)$$

$$(D \delta h)_i = -\sum_j \int dx_j \varphi_j T_{ij} \delta \chi_{ij}, \quad (4.7b)$$

$$(A \delta h)_i = -\sum_j \chi_{ij} \int dx_j \varphi_j T_{ij} (\delta h_i + \delta h_j), \quad (4.7c)$$

where $\chi_{ij} = \chi_{ij}(\sigma_{ij} | n)$. In deriving (4.6) we have used the relations

$$T_{ij} \varphi_i \varphi_j \dots = \varphi_i \varphi_j T_{ij} \dots; \quad \int dx_j T_{ij} \varphi_i \varphi_j = 0.$$

For the operator D , with $\delta \chi_{ij}$ given by (4.4), we deduce by means of (A.3) and (A.5) of the appendix

$$(D \delta h)_i = -v_i \cdot \sum_l \int dr_l \frac{\partial}{\partial r_{il}} [C_{il}(r_{il}) - \chi_{il} f_{il}(r_{il})] \delta n_l(r_l), \quad (4.8)$$

where $C_{ij}(r_{ij})$ is the equilibrium value of the direct correlation function, defined in (3.15).

Introducing the Fourier transform of some function $g(\mathbf{r})$ as

$$\tilde{g}(\mathbf{k}) = \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} g(\mathbf{r}) \quad (4.9)$$

and taking the Fourier transform of (4.6) we obtain the linearized Enskog equation for the Fourier transform $\tilde{h}_i = \tilde{h}_i(v_i, \mathbf{k}; t)$ of $\delta h_i(x_i; t)$ in the form

$$\frac{\partial}{\partial t} \tilde{h} = -\tilde{L} \tilde{h}, \quad (4.10)$$

where

$$\tilde{L} = \tilde{L}(\mathbf{k}) = \tilde{K}(\mathbf{k}) + \tilde{D}(\mathbf{k}) + \tilde{A}(\mathbf{k}), \quad (4.11)$$

with

$$(\tilde{K}\tilde{h})_i = i\mathbf{k} \cdot \mathbf{v}_i \tilde{h}_i, \quad (4.11a)$$

$$(\tilde{D}\tilde{h})_i = -i\mathbf{k} \cdot \mathbf{v}_i \sum_j [\tilde{C}_{ij}(k) - \chi_{ij} \tilde{f}_{ij}(k)] \int d\mathbf{v}_j \varphi_j \tilde{h}_j, \quad (4.11b)$$

$$(\tilde{A}\tilde{h})_i = -\sum_j \chi_{ij} \int d\mathbf{v}_j \varphi_j \sigma_{ij}^2 \int' d\hat{\sigma} (\mathbf{v}_{ji} \cdot \hat{\sigma}) (\tilde{h}_i^* - \tilde{h}_i + e^{+i\mathbf{k} \cdot \hat{\sigma} \sigma_{ij}} \tilde{h}_j^* - e^{-i\mathbf{k} \cdot \hat{\sigma} \sigma_{ij}} \tilde{h}_j). \quad (4.11c)$$

We have used the abbreviations $\tilde{\psi}_i^* = \tilde{\psi}_i(\mathbf{v}_i^*)$, etc.; the Fourier transform of the Mayer function can be calculated explicitly as

$$\tilde{f}_{ij}(k) = -(4\pi\sigma_{ij}^2/k) j_1(k\sigma_{ij}); \quad \tilde{f}_{ij}(0) = -(4\pi/3) \sigma_{ij}^3, \quad (4.12)$$

where $j_1(x) = -x^{-1} \cos x + x^{-2} \sin x$ is a spherical Bessel function.

Eqs. (4.10) and (4.11) for the single-component case give precisely the equation derived by Konijnendijk and Van Leeuwen for the short-time behaviour of space- and time-dependent fluctuations. We also note that linearization of the usual Enskog equation (1.1) yields in the long-wavelength limit ($\mathbf{k} \rightarrow 0$) the same result as the long-wavelength limit of (4.10) and (4.11). The linearized form of the Enskog equation for mixtures (3.5), as used in the literature, does not coincide with the long-wavelength limit of (4.10) and (4.11).

5. Conclusion. We have introduced a modified form of the nonlinear Enskog equation. The difference with the usual Enskog equation consists in the factor χ , which corrects the collision frequency in a dense hard-sphere system by taking into account the statistical correlations between colliding particles. We have taken this factor to be strictly equal to the local-equilibrium pair D.F., containing all spatial non-uniformities, whereas in the usual Enskog theory χ is chosen to be the pair D.F. in total equilibrium, evaluated as a function of the density at the midpoint between the centres of the colliding spheres. In a single-component system both equations are equivalent at the level of the Navier–Stokes equations, but the modified Enskog equation can also be used to derive higher-order hydrodynamic equations, in contrast with the usual Enskog equation. In multicomponent systems of hard spheres the existing extensions and the modified form of Enskog's theory yield results which are different at the Navier–Stokes level. The existing versions (3.5) of Enskog's theory contain a factor χ_{ij} , which does not take into account in a correct way the spatial non-uniformities in the local-equilibrium pair D.F. to linear order in the gradients. Therefore, the Navier–Stokes equations and corresponding transport coefficients, obtained from these equations for mixtures, are in general not correct within the framework of assumptions in which Enskog's theory is supposed to be applicable, and do not agree with the results of irreversible thermodynamics. The differences between the usual form (3.5) and the

modified form (2.5) show themselves only at second order in the partial densities, and only in the heat flux and diffusion fluxes, all of which depend on the gradients of the partial densities.

If we make a comparison of the usual and the modified form of the Enskog equation the following points can be mentioned in favour of the latter:

(i) The modified Enskog equation can be derived from the Liouville equation under certain restrictions on the initial ensemble and under the assumption that all correlations between velocities in different collisions may be neglected. This assumption, usually called the assumption of molecular chaos, is one of the basic assumptions in the usual Enskog theory as well. Furthermore the modified Enskog equation becomes exact for very short times, when neglecting velocity correlations is indeed justified.

(ii) In none of the existing generalizations of Enskog's theory to mixtures, can we find any clear physical argument why one chooses to evaluate the pair D.F. χ_{ij} at a particular point (such as midpoint, point of contact, centre of gravity, of two colliding spheres). In the modified form (2.5), however, no such ambiguity exists, if one wants to extend the single-component theory to the multicomponent case.

(iii) The modified form of Enskog's theory for mixtures leads in a very direct way to the linear relations of irreversible thermodynamics between conjugate sets of fluxes and driving forces where the matrix of transport coefficients is symmetric and positive definite. In the old versions of Enskog's theory for mixtures the Onsager relations are not valid.

(iv) From the modified Enskog equation for single and multicomponent systems higher-order hydrodynamic equations can be derived, which are consistent within the framework provided by the molecular-chaos assumption. The usual Enskog equation is only consistent at the level of the Navier-Stokes equations, as already pointed out by Enskog⁴).

(v) The method of Konijnendijk and Van Leeuwen yields an equation for the linear fluctuations in a hard-sphere fluid, which is identical to the linearized form (4.10) for the single-component case of our modified Enskog equation (2.3). The long-wavelength limit of (4.10) in the single-component case is identical to the linearized form of the usual Enskog equation (1.1) for the single-component case. From the structure of Konijnendijk and Van Leeuwen's theory it is clear that their theory for multicomponent systems would also yield (4.10). However, the long-wavelength limit of (4.10) does not coincide with the linearized form of the usual form (3.5) of the Enskog theory for mixtures. This fact indicates again that the (linearized) Navier-Stokes equations for mixtures derived from (the linearized form of) the usual Enskog equation (3.5) are not correct in general.

APPENDIX A

Proof of (3.13). The integrands in (3.13') and (3.13'') are both of the form

$$T_{ij}F_i^{(0)}F_j^{(0)}K(\mathbf{r}_i\mathbf{r}_j) = F_i^{(0)}F_j^{(0)}\mathbf{v}_{ji} \cdot \sigma_{ij}^2 \int d\hat{\boldsymbol{\sigma}} \delta(r_{ji} - \sigma_{ij}\hat{\boldsymbol{\sigma}}) K(\mathbf{r}_i\mathbf{r}_j), \quad (\text{A.1})$$

as can be deduced directly from (2.5). By writing

$$\delta(\mathbf{r}_{ji} - \sigma_{ij}\hat{\boldsymbol{\sigma}}) = r_{ij}^{-2} \delta(r_{ij} - \sigma_{ij}) \delta(\hat{\mathbf{r}}_{ji} - \hat{\boldsymbol{\sigma}}) \quad (\text{A.2})$$

and using (2.8) we obtain for (A.1)

$$\begin{aligned} T_{ij}F_i^{(0)}F_j^{(0)}K(\mathbf{r}_i\mathbf{r}_j) &= F_i^{(0)}F_j^{(0)}\mathbf{v}_{ji} \cdot \hat{\mathbf{r}}_{ji} \delta(r_{ij} - \sigma_{ij}) K(\mathbf{r}_i\mathbf{r}_j) \\ &= F_i^{(0)}F_j^{(0)}\mathbf{v}_{ji} \cdot (\partial f_{ij}(r_{ij})/\partial \mathbf{r}_{ji}) K(\mathbf{r}_i\mathbf{r}_j); \end{aligned} \quad (\text{A.3})$$

with the help of (A.3) and after partial integration with respect to \mathbf{r}_{ji} the second equality in (3.13') follows. By virtue of (A.3) eq. (3.13'') can be written as

$$A_i'' = -F_i^{(0)}\mathbf{v}_i \cdot \sum_l \int d\mathbf{r}_l \left(\sum_j n_j \int d\mathbf{r}_j \frac{\partial f_{lj}}{\partial \mathbf{r}_{jl}} H_{lj}(\mathbf{r}_l\mathbf{r}_j\mathbf{r}_i | n) \right) \mathbf{r}_{li} \cdot \nabla n_l. \quad (\text{A.4})$$

Consider now the following identity, to be derived below,

$$\sum_j n_j \int d\mathbf{r}_j \frac{\partial f_{lj}}{\partial \mathbf{r}_{jl}} H_{lj}(\mathbf{r}_l\mathbf{r}_j\mathbf{r}_i | n) = \frac{\partial}{\partial \mathbf{r}_{li}} [C_{li}(r_{li}) - \chi_{li}f_{li}(r_{li})]. \quad (\text{A.5})$$

Inserting (A.5) in (A.4) and performing a partial integration with respect to \mathbf{r}_{li} yields the second equality in (3.13'').

In order to prove (A.5) we consider for simplicity a single-component system, and write (A.5) in the form

$$\frac{\partial C(r_{12})}{\partial \mathbf{r}_{21}} = \chi(\sigma) \frac{\partial f(r_{12})}{\partial \mathbf{r}_{21}} + n \int d\mathbf{r}_3 \frac{\partial f(r_{13})}{\partial \mathbf{r}_{31}} H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3). \quad (\text{A.6})$$

Notice that $H(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)$ is not symmetric in \mathbf{r}_2 and \mathbf{r}_3 .

The direct correlation function can be represented by Mayer graphs¹¹⁾ as

$$C(r_{12}) = f(r_{12}) + \sum_{l=3}^{\infty} \frac{n^{l-2}}{(l-2)!} \int d\mathbf{r}_3 \cdots d\mathbf{r}_l B(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3 \cdots \mathbf{r}_l), \quad (\text{A.7})$$

where $B(\mathbf{r}_1\mathbf{r}_2 \cdots \mathbf{r}_l)$ is the sum of all biconnected Mayer graphs of the particles 1, 2, ..., l^3 . After grouping together all terms in which $(\partial/\partial \mathbf{r}_{21})$ acts on the same

Mayer function, one obtains

$$\begin{aligned} \frac{\partial C(r_{12})}{\partial r_{21}} &= \frac{\partial f(r_{12})}{\partial r_{21}} + \sum_{i=3}^{\infty} \frac{n^{i-2}}{(i-2)!} \int dr_3 \cdots dr_i \\ &\times \left(\frac{\partial f(r_{12})}{\partial r_{21}} V(r_1 r_2 | r_3 \cdots r_i) + \frac{\partial f(r_{13})}{\partial r_{31}} V(r_1 r_3 | r_2 r_4 \cdots r_i) \right. \\ &\left. + \cdots + \frac{\partial f(r_{1i})}{\partial r_{i1}} V(r_1 r_i | r_2 r_3 \cdots r_{i-1}) \right), \end{aligned} \quad (\text{A.8})$$

where $V(r_1 r_2 | r_3 \cdots r_i)$ is the sum of all Mayer graphs of the particles 1, 2, ..., i which become bi-connected by adding $f(r_{12})$. By virtue of (2.1b) the first two terms on the right-hand side can be combined into $(\partial f(r_{12})/\partial r_{21}) \chi(r_{12})$, where $\chi(r_{12})$ may be replaced by $\chi(\sigma)$ since $(\partial f(r_{12})/\partial r_{21})$ is only non-vanishing for $r_{12} = \sigma$. The remaining $(i-2)$ terms, which are all equal, can be united into $n \int dr_3 \times (\partial f(r_{13})/\partial r_{31}) H(r_1 r_3 r_2)$, with the aid of (3.2b). This proves (A.6) for the single-component case. The proof of (A.5) for multicomponent systems involves only some additional labels of species, and is completely analogous to the transition from (2.1b) to (2.7b).

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