Green’s functions and hydrodynamics for isotopic binary diffusion

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Abstract. We study classical binary fluid mixtures in which densities vary on very short time (ps) and length (nm) scales, such that hydrodynamics does not apply. In a pure fluid with a localized heat pulse the breakdown of hydrodynamics was overcome using Green’s functions which connect the initial densities to those at later times. Numerically it appeared that for long times the results from the Green’s functions would approach hydrodynamics. In this paper we extend the Green’s functions theory to binary mixtures. For the case of isothermal isobaric mutual diffusion in isotopic binary mixtures and ideal binary mixtures, which is easier to handle than heat conduction yet still non-trivial, we show analytically that in the Green’s function approach one recovers hydrodynamic behaviour at long time scales provided the system reaches local equilibrium at long times. This is a first step toward giving the Green’s function theory a firmer basis because it can for this case be considered as an extension of hydrodynamics.

Dated 10 August 2005

PACS numbers: 47.10.+g, 05.20.Jj, 66.10.Cb, 05.60.Cd

KEYWORDS: Transport properties (theory), dynamical processes (theory), dynamical heterogeneities (theory), binary mixtures, isotopes, Green’s functions, hydrodynamics
1. Introduction

With the increase in miniaturization nanoscale technology is developing rapidly. However, at such small scales the physics of thermodynamic properties and transport processes will deviate from that at larger scales. Certainly one sees finite size effects and appreciable fluctuations on measurable quantities. It is likely that new physics exists at the nanoscale.

Of course, on large time and length scales transport processes in fluids are well described by hydrodynamics which contain the transport coefficients such as the diffusion constants, viscosity and thermal conductivity [1]. Kinetic theory can provide low density approximations to these coefficients [2] while linear response theory yields the Green-Kubo relations which express the transport coefficients in terms of integrals of time-correlation functions of the appropriate current fluctuations in equilibrium [3, 4]. Thus once one has determined the transport coefficients by studying the equilibrium time-correlation functions, one can attack a wide range of non-equilibrium transport problems described by hydrodynamics not too far from equilibrium. In contrast, the description of the non-equilibrium behaviour at shorter times and smaller length scales remains mostly unsolved despite its importance, in principle, to the understanding of nanostructures. Even low density kinetic theories cannot describe time scales below the average duration of a collision. Attempts to generalize hydrodynamics stranded at first because a straightforward further expansion in the gradients, i.e. beyond the...
linear laws, leads to higher order Burnett coefficients which are infinite [5]. Recently a theory was proposed by Prof. J.M. Kincaid using Green’s functions to describe processes at small length and time scales which avoids these divergences [6–9]. Like hydrodynamics the Green’s function approach can also treat the hydrodynamic fields (density, momentum and energy) but unlike in hydrodynamics currents need not be linear in the gradients. Another contrast with hydrodynamics is that the Green’s function approach is not restricted to long times. Thus the Green’s function approach should be able to attack a wider range of problems than standard hydrodynamics. Indeed the Green’s function approach has been numerically applied with success to self-diffusion [6] and heat transport [7–9] on nanometre and picosecond scales. In these applications, the Green’s functions are resummed into an infinite series that needs to be truncated. It was shown using computer simulations that if just a few terms from the infinite sum are taken into account, accurate results were obtained for all time scales for those systems [6–9]. Also, for long times the numerical results were seen to approach the numerical hydrodynamic results [9].

In this paper we formulate the Green’s function approach for mixtures, focusing on mutual diffusion in isotopic and ideal binary mixtures. Apart from adapting the Green’s function approach for mass transport in mixtures, this paper is mainly dedicated to the question whether the truncated expressions for the Green’s functions describe the right very short time behaviour and whether they do indeed reduce to hydrodynamics at long time scales and for small gradients; if the latter is true then the Green’s function approach can rightfully be called an extension of hydrodynamics. For self-diffusion in a single component fluid the truncation was already shown analytically to give the right hydrodynamic-like behaviour for long times [6]. Mutual diffusion in an isotopic or ideal mixture is the simplest case to consider next (simplest both in thermodynamic and in hydrodynamic aspects) Ideally one would like to show analytically that the Green’s functions reproduce not just mutual diffusion but the full hydrodynamic equations in all cases where gradients are small and times are long, but this would be an enormous undertaking. Therefore, as a first step, we restrict ourselves in this paper to the already nontrivial case of diffusion in isotopic and ideal mixtures.

2. Classical isotopic and ideal binary mixtures

2.1. Definitions

We consider a classical mixture of two components where the particles interact through short-range pair potentials. The total system consists of $N$ particles of which $N_1$ particles are of component 1 and $N_2 = N - N_1$ particles are of component 2. The system is enclosed in a volume $V$. We denote the (three-dimensional) position of particle $i$ of component $\lambda$ as $r_{\lambda i}$ and its velocity as $v_{\lambda i}$, where the index $\lambda$ equals 1 or 2, and $i$ is an index which runs from 1 to $N_{\lambda}$. The mass of particles of component $\lambda$ will be denoted as $m_\lambda$. We restrict ourselves to two related classes of mixtures: isotopic mixtures, for
which the pair potentials are the same independent of the components to which the interacting particles belong, and ideal mixtures, whose pair potentials can be neglected as far as thermodynamic properties are concerned.

The system is prepared in a non-equilibrium state described by some given, non-equilibrium initial ensemble in phase space $\mathcal{P}_{ne}(\Gamma)$, where $\Gamma = \{r_{\lambda i}, \mathbf{v}_{\lambda i}\}$. In the initial non-equilibrium ensemble — and consequently also at later times — the particles of each component are indistinguishable. After the initial preparation in the non-equilibrium state, the system stays isolated, i.e. the system does not interact with the outside.

The macroscopic (i.e. averaged) local density of component $\lambda$ is defined as [10]

$$n_\lambda(r, t) \equiv \int d\Gamma \mathcal{P}_{ne}(\Gamma) \sum_{i=1}^{N_\lambda} \delta(r - r_{\lambda i}(t)) = N_\lambda \langle \delta(r - r_{\lambda 1}(t)) \rangle_{ne}$$  \hspace{1cm} (1)

where the subscript “ne” on the average indicates its non-equilibrium nature. In this equation we used the indistinguishability of the particles of the same component to express the densities $n_\lambda(r, t)$ in terms of the properties of a representative particle of each component i.e. in terms of $r_{\lambda 1}(t)$.

Due to the non-equilibrium nature of $\mathcal{P}_{ne}$, the local densities $n_\lambda(r, t)$ will in general not be uniform at $t = 0$. In this paper we are mainly interested in the time evolution of these densities. This is in principle determined by the microscopic time evolution governed by the Hamiltonian

$$H(\Gamma) = \sum_{\lambda=1}^{2} \sum_{i=1}^{N_\lambda} \frac{1}{2} m_\lambda |\mathbf{v}_{\lambda i}|^2 + U(\Gamma)$$  \hspace{1cm} (2)

where

$$U(\Gamma) = \sum_{\lambda, \nu, i, j}^{'} \frac{1}{2} \varphi_{\lambda \nu}(|r_{\lambda i} - r_{\nu j}|).$$  \hspace{1cm} (3)

Here $\varphi_{\lambda \nu}$ are the pair potentials and the summation $\sum^{'}$ is restricted to exclude self-interaction of the particles, i.e. to exclude the cases where both $\lambda = \nu$ and $i = j$. For isotopic mixtures, $\varphi_{12} = \varphi_{11} = \varphi_{22}$. The equations of motion are thus given by

$$\dot{r}_{\lambda i} = \mathbf{v}_{\lambda i}$$  \hspace{1cm} (4)

$$\dot{\mathbf{v}}_{\lambda i} = - \frac{1}{m_\lambda} \frac{\partial U}{\partial r_{\lambda i}}.$$  \hspace{1cm} (5)

Before proceeding we introduce a few more quantities for later convenience. The local mass densities are given by $\rho_\lambda = m_\lambda n_\lambda$. Here and below when the spatial and temporal arguments of a local quantity are not denoted, it is implied that they are taken at position $r$ and time $t$. The local total number and mass densities are, respectively, $n = n_1 + n_2$ and $\rho = \rho_1 + \rho_2$. We furthermore define the local mole fractions as $x_\lambda = n_\lambda / n$ and the mass fraction of component 1 as $c = \rho_1 / \rho$. The mass fraction of component 2 is simply $1 - c$. The local mass currents of the two components in the laboratory frame are given by ($\lambda = 1, 2$)

$$\mathbf{j}_\lambda^* = N_\lambda m_\lambda \langle \mathbf{v}_{\lambda 1}(t) \delta(r - r_{\lambda 1}(t)) \rangle_{ne}$$  \hspace{1cm} (6)
Using these definitions the local mass velocity of the fluid can be written as

\[ u = (j_1^* + j_2^*)/\rho. \] (7)

Finally, we define the diffusive currents of the two components in the local frame (i.e. co-moving with the local velocity \( u \)) as

\[ j_\lambda = j_\lambda^* - \rho_\lambda u = N_\lambda m_\lambda ([v_{\lambda 1}(t) - u] \delta(\mathbf{r} - \mathbf{r}_{\lambda 1}(t)))_{ne} \] (8)

so that by definition we have

\[ j_1 + j_2 = 0. \] (9)

2.2. Thermodynamics, hydrodynamics and Green-Kubo formula

For classical isotopic mixtures and ideal mixtures, many thermodynamic equilibrium properties take on a particularly simple form — which is in fact the main reason we consider these systems here. In particular, for the current case of mass transport investigated in this paper, we will need \( (\partial \mu/\partial c)_T p \) and \( (\partial \rho/\partial c)_T p \) where \( T \) is the temperature, \( p \) is the pressure and \( \mu \) is the chemical potential of component \( \lambda \). These thermodynamic properties can be found from the form of chemical potential for isotopic systems [11, §93]:

\[ \mu_\lambda = k_B T \log x_\lambda + \mu_{0\lambda}; \quad \mu_{01} = \mu_{02} - \frac{3}{2} k_B T \log \frac{m_1}{m_2}, \] (11)

where \( \mu_{0\lambda} \) is the chemical potential of the pure isotope \( \lambda \) at the same temperature \( T \) and pressure \( p \) as those for which \( \mu_\lambda \) is evaluated. Equation (11) implies that

\[ \left( \frac{\partial \mu_\lambda}{\partial x_\lambda} \right)_T p = \frac{k_B T}{x_\lambda}; \quad \left( \frac{\partial \mu_1}{\partial p} \right)_{T x} = \left( \frac{\partial \mu_2}{\partial p} \right)_{T x}. \] (12)

We can use the Gibbs-Duhem relation [12, §8.7]

\[ N_1 d\mu_1 + N_2 d\mu_2 = V dp - S dT \] (13)

to derive that \( N_1(\partial \mu_1/\partial p)_{Tx} + N_2(\partial \mu_2/\partial p)_{Tx} = V \). Combined with \( (\partial \mu_1/\partial p)_{Tx} = (\partial \mu_2/\partial p)_{Tx} \) (cf. equation (12)) this yields

\[ \left( \frac{\partial \mu_1}{\partial p} \right)_{Tx} = \left( \frac{\partial \mu_2}{\partial p} \right)_{Tx} = \frac{1}{N}. \] (14)

We can write \( c \) as a function of \( x_1 \) as \( c = m_1 x_1 / [m_1 x_1 + m_2 (1 - x_1)] \), which gives \( dx_1/dc = \rho^2/(m_1 m_2 n^2) \). Using also equation (11), we get for equations (12) and (14) in terms of \( c \) and \( \mu \)

\[ \left( \frac{\partial \mu}{\partial c} \right)_{T p} = \frac{dx_1}{dc} \left( \frac{\partial \mu}{\partial x_1} \right)_{T p} = \frac{\rho k_B T}{c(1 - c)m_1 m_2 n} \] (15)

\[ \left( \frac{\partial \mu}{\partial p} \right)_{T c} = \left( \frac{\partial \mu}{\partial p} \right)_{T x} = \frac{m_2 - m_1}{m_1 m_2 n} \] (16)
From the fundamental relation for the Gibbs free energy \( dG = -SdT + Vdp + \mu_1dN_1 + \mu_2dN_2 \) [12, §8.7], one can deduce that \( (\partial \rho/\partial c)_{Tp} = -\rho^2(\partial \mu/\partial p)_{Tc} \), whence

\[
\left( \frac{\partial \rho}{\partial c} \right)_{Tp} = \frac{(m_1 - m_2)\rho^2}{m_1m_2n}. \tag{17}
\]

The quantities in equations (15) and (17) will be needed in the treatment of the long-time behaviour of the Green’s functions for mass transport in section 4. These are precisely of the form valid for ideal (“perfect”) mixtures [11, §92], which is the reason why our treatment is valid both for ideal mixtures and for isotopic binary mixtures.

Because in section 4 the results of the Green’s function approach for long times will be compared to those of hydrodynamics, we will now review the appropriate hydrodynamic equations and Green-Kubo formula for mass transport in ideal mixtures and in an isotopic binary mixture. Since we restrict ourselves in this paper to mass transport, the relevant conservation laws are only those for the local densities \( n_\lambda \), which follow from equations (1), (6) and (8):

\[
\frac{\partial n_\lambda}{\partial t} = -\nabla \cdot j^*_\lambda/m_\lambda = -\nabla \cdot (n_\lambda u + j_\lambda/m_\lambda). \tag{18}
\]

In terms of \( \rho = m_1n_1 + m_2n_2 \) and \( c = m_1n_1/\rho \), these equations become [1, ch. 2]

\[
\frac{D\rho}{Dt} = -\rho \nabla \cdot u \tag{19}
\]

\[
\rho \frac{Dc}{Dt} = -\nabla \cdot j_1 \tag{20}
\]

where we have used the material derivative \( D/Dt = \partial/\partial t + u \cdot \nabla \). To make these equations into a closed set, \( j_1 \) needs to be expressed as a function of \( \rho \) and \( c \) (as well as, in general, of \( u \) and \( T \), which will be assumed to be constant below). Near equilibrium one can use linear laws as closure relations. Following a widely used choice of currents and forces in the theory of irreversible thermodynamics [1, ch. 3], one has in general

\[
\dot{j}_1 = -\frac{L_{11}}{T}[(\nabla \mu)_T] - \frac{L_{1q}}{T} \nabla \ln T \tag{21}
\]

Here the gradient \( [\nabla \mu]_T \) is taken at constant temperature while the pressure \( p \) and the concentration \( c \) can vary. \( L_{11} \) and \( L_{1q} \) are called phenomenological coefficients.

We will only consider here the case in which there is only a gradient in the concentration \( c \), while gradients in temperature \( T \), pressure \( p \) and fluid velocity \( u \) are zero. In that case, one can write equation (21) as

\[
\dot{j}_1 = -\frac{L_{11}}{T} \left( \frac{\partial \mu}{\partial c} \right)_{Tp} \nabla c = -\rho D \nabla c. \tag{22}
\]

Here the mutual diffusion constant \( D = (\partial \mu/\partial c)_{Tp}L_{11}/(\rho T) \), or, with equation (14) for binary isotopic mixtures and ideal mixtures,

\[
D = \frac{k_B L_{11}}{c(1-c)m_1m_2n}. \tag{23}
\]
The Green-Kubo formula for the phenomenological coefficient $L_{11}$ for mutual diffusion in a fluid is [3, 4]:

$$L_{11} = \frac{1}{3k_B V} \int_0^\infty \! dt' \langle \tilde{J}_1(0) \cdot \tilde{J}_1(t') \rangle$$

(24)

where the average is over a grand canonical ensemble in the thermodynamic limit and $\tilde{J}_\lambda$ is the microscopic expression for the total current in the centre of mass frame given by

$$\tilde{J}_\lambda(t) = m_\lambda \sum_{i=1}^{N_\lambda} [\mathbf{v}_{\lambda i}(t) - \bar{\mathbf{v}}]$$

(25)
in which $\bar{\mathbf{v}}$ is the centre of mass velocity, i.e.

$$\bar{\mathbf{v}} = (m_1 N_1 + m_2 N_2)^{-1} \sum_{\lambda=1}^{2} \sum_{i=1}^{N_\lambda} m_\lambda \mathbf{v}_{\lambda i}.$$  

(26)

The Green-Kubo formulae for $L_{1q}$ and other transport coefficients are more complicated and not needed here; for these we refer to the literature [3, 4].

Note that $\bar{\mathbf{v}}$ is not an ensemble average but an average over particles taken per ensemble member, and that it is a constant of the motion for that ensemble member.

With the inclusion of $\bar{\mathbf{v}}$ we have on a microscopic level the analogue of equation (9) i.e. $\tilde{J}_1 + \tilde{J}_2 = 0$. This relation can be used to find an alternative representation of $L_{11}$:

$$L_{11} = -\frac{1}{3k_B V} \int_0^\infty \! dt' \langle \tilde{J}_1(0) \cdot \tilde{J}_2(t') \rangle$$

(27)

Using equations (25) and (27) in equation (23) for $D$, and that particles of the same component are indistinguishable, we find that

$$D = -\frac{1}{3c(1-c)nV} \int_0^\infty \! dt' \langle N_1 N_2 [\mathbf{v}_{11}(0) - \bar{\mathbf{v}}] \cdot [\mathbf{v}_{21}(t') - \bar{\mathbf{v}}] \rangle.$$  

(28)

In the thermodynamic limit ($N_1, N_2, V \to \infty$ keeping $N_1/V$ and $N_2/V$ fixed and finite) we may factor the averages to leading order, so that we get

$$D = -\frac{\rho^2}{m_1 m_2 n^2} f_{12},$$

(29)

where [13]

$$f_{12} = \frac{1}{3} \int_0^\infty \! dt' \langle N[\mathbf{v}_{11}(0) - \bar{\mathbf{v}}] \cdot [\mathbf{v}_{21}(t') - \bar{\mathbf{v}}] \rangle.$$  

(30)

Similarly, for future use, one can also define, following reference [13]

$$f_{\lambda \alpha \beta} = \frac{1}{3} \int_0^\infty \! dt' \langle N[\mathbf{v}_{\lambda 1}(0) - \bar{\mathbf{v}}] \cdot [\mathbf{v}_{\lambda 2}(t') - \bar{\mathbf{v}}] \rangle$$

(31)

$$D_{\lambda} = \frac{1}{3} \int_0^\infty \! dt' \langle [\mathbf{v}_{\lambda 1}(0) - \bar{\mathbf{v}}] \cdot [\mathbf{v}_{\lambda 1}(t') - \bar{\mathbf{v}}] \rangle.$$  

(32)

Note that the subscript $\alpha \beta$ does not denote indices but instead signifies that correlations between different particles are involved and that we added a factor $N$ in equations (30) and (31) compared to the definition of $f_{12}$ and $f_{\lambda \alpha \beta}$ in reference [13] to get a well-defined
thermodynamic limit. Due to the subtraction terms $-\bar{v}$ and the conservation of total momentum, one has the relations [13]

\[ f_{12} = -\frac{m_1}{m_2 x_2} (D_1 + x_1 f_{1\alpha\beta}) \quad (33) \]

\[ f_{12} = -\frac{m_2}{m_1 x_1} (D_2 + x_2 f_{2\alpha\beta}) \quad (34) \]

Using these, one can rewrite the right hand side of equation (29) as [13–15]

\[ D = x_2 D_1 + x_1 D_2 + x_1 x_2 (f_{1\alpha\beta} + f_{2\alpha\beta} - 2 f_{12}) \quad (35) \]

The first part of this relation, i.e. the part involving only the self or intrinsic diffusion constants $D_\lambda$, is often used as if it were the full expression for $D$, which goes under the name of the Darken [16] or Hartley-Crank equation [17]. Douglas and co-workers were apparently the first to have shown that corrections to the Darken-Hartley-Crank equation involve the cross correlations given by the $f_{\lambda\alpha\beta}$ and $f_{12}$ [13, 14].

3. Green’s functions for mass transport in mixtures

3.1. General formulation

The hydrodynamic treatment only works near (local) equilibrium. For other situations i.e. on small length and time scales, a new description is necessary. For self-diffusion the short time behaviour, as well as the long time behaviour, could be successfully described by using Green’s functions [6]. A similar description for heat transport gives good numerical agreement with simulations as well [7–9].

Analogous to the Green’s function approach for self-diffusion we want to write the $r$ and $t$ dependent densities $n_\lambda$ here as integrals over Green’s functions that give the probability for a representative particle of the appropriate component to be at position $r$ at time $t$ given that it was at position $r'$ at time 0. Starting from equation (1) we can write ($\lambda = 1, 2$)

\[ n_\lambda(r, t) = N_\lambda \langle \delta(r - r_\lambda(t)) \rangle_{ne} = \int_V d\mathbf{r}' G_\lambda(r, \mathbf{r}', t) n_\lambda(\mathbf{r}', 0), \quad (36) \]

where the Green’s function $G_\lambda$ is defined as

\[ G_\lambda(r, \mathbf{r}', t) = \langle \delta(r - r' - \Delta r_\lambda(t)) \rangle_{\mathbf{r}'r}. \quad (37) \]

Here $\Delta r_\lambda(t) = r_\lambda(t) - r_\lambda(0)$ is the displacement of particle 1 of component $\lambda$ while $\langle \rangle_{\mathbf{r}'r}$ is the average over initial conditions for which $r_\lambda(0) = r'$. For an arbitrary phase function $A(\Gamma)$, this conditional average is defined as

\[ \langle A(\Gamma) \rangle_{\mathbf{r}'r} = \frac{\langle A(\Gamma) \delta(r' - r_\lambda(0)) \rangle_{ne}}{\langle \delta(r' - r_\lambda(0)) \rangle_{ne}}. \quad (38) \]

We now make two remarks about this definition of the Green’s functions and the conditional average. First, for initial conditions where $n_\lambda(r', 0) = N_\lambda \langle \delta(r' - r_\lambda(0)) \rangle_{ne} = 0$ for some $r'$, the right-hand side of equation (38) seems ill defined. The way we choose to define it for such $r'$ will not matter since $\langle \delta(r' - r' - \Delta r_\lambda(t)) \rangle_{\mathbf{r}'r}$ is multiplied by
\( n_\lambda(r',0) = 0 \) in equation (36) anyway.‡ Second, equation (38) differs in normalization from the definition of \( \langle \rangle_{r'} \) in the heat pulse case of references [7–9], in which the conditional averages were only properly normalized when the system is initially of uniform density (which was the case in references [7–9]). In contrast, the definition of the conditional average in equation (38) is always normalized i.e. \( \langle 1 \rangle_{\lambda r'} = 1 \). This definition is also more analogous to the self-diffusion case [6] because of the appearance of \( n_\lambda(r',0) \) inside the integrals in equation (36) instead of a single factor of the average density \( N_\lambda / V \) in front of the integral.

3.2. Expansion around Gaussian behaviour

Next the Green’s functions \( G_\lambda \) are Fourier transformed with respect to \( r - r' \), i.e. one considers

\[
F_\lambda(k, r', t) = \int_V dr \, e^{ik \cdot (r - r')} G_\lambda(r, r', t)
\]  

(39)

Using equation (37) and expanding in \( k \), this gives

\[
F_\lambda(k, r', t) = \langle \exp[i k \cdot \Delta r_\lambda(t)] \rangle_{\lambda r'} = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \mu_{\lambda n}(\hat{k}, r', t)
\]  

(40)

where \( k = |k|, \hat{k} = k/k \) and the moments are defined as

\[
\mu_{\lambda n}(\hat{k}, r', t) = \left\langle \left[ \hat{k} \cdot \Delta r_\lambda(t) \right]^n \right\rangle_{\lambda r'}.
\]  

(41)

Since divergences would occur if one would directly take the inverse Fourier transform term by term in equation (40), an alternative expansion will be used. For given direction \( \hat{k} \), \( F_\lambda \) is the generating function of the cumulants of the displacement of the particle in that direction, [18–20] so that one can write

\[
F_\lambda(k, r', t) = \exp \sum_{n=1}^{\infty} \frac{(ik)^n}{n!} \kappa_{\lambda n}(\hat{k}, r', t)
\]  

(42)

The cumulants \( \kappa_{\lambda n} \) and \( \mu_{\lambda n} \) are related through [20]

\[
\kappa_{\lambda n} = -n! \sum_{\{p_\ell \geq 0\}} \left( \sum_{\ell=1}^{\infty} p_{\ell} - 1 \right)! \prod_{\ell=1}^{\infty} \left[ -\mu_{\lambda \ell} / \ell! \right]^{p_{\ell}} / p_{\ell}!
\]  

(43)

where we dropped the arguments \( \hat{k}, r' \) and \( t \) of \( \mu_{\lambda \ell} \) and \( \kappa_{\lambda n} \), as we will do below as well. For instance, for the first few \( \kappa_{\lambda n} \), equation (43) becomes

\[
\kappa_{\lambda 1} = \mu_{\lambda 1}
\]  

(44)

\[
\kappa_{\lambda 2} = \mu_{\lambda 2} - \mu_{\lambda 1}^2
\]  

(45)

\[
\kappa_{\lambda 3} = \mu_{\lambda 3} - 3 \mu_{\lambda 1} \mu_{\lambda 2} + 2 \mu_{\lambda 1}^3
\]  

(46)

\[
\kappa_{\lambda 4} = \mu_{\lambda 4} - 4 \mu_{\lambda 1} \mu_{\lambda 3} - 3 \mu_{\lambda 2}^2 + 12 \mu_{\lambda 2}^2 \mu_{\lambda 1}^2 - 6 \mu_{\lambda 1}^4
\]  

(47)

‡ However, to have a proper definition everywhere, one could follow the convention that \( \langle A \rangle_{\lambda r'} = \langle A \rangle_{\lambda r'} \) for values of \( r' \) where \( n_\lambda(r',0) = 0 \). An alternative would be to introduce a “tracer particle” of component \( \lambda \) at \( r' \) but this works only in the thermodynamic limit.
The Fourier transform in equation (42) is first rearranged by factoring out a Gaussian expression [6–9]. This can be done in several ways, but here we write

$$F_\lambda(\mathbf{k}, \mathbf{r}', t) = f_\lambda(\mathbf{k}, \mathbf{r}', t) \left[ 1 + \sum_{n=3}^{\infty} b_{\lambda n}(ik)^n \right].$$

(48)

and we demand that the first correction term to the Gaussian $f_\lambda(\mathbf{k}, \mathbf{r}', t)$ in equation (48) is only $O(k^3)$, so that

$$f_\lambda(\mathbf{k}, \mathbf{r}', t) = \exp \left[ ik_\lambda k - \frac{1}{2} \kappa_{\lambda 2} k^2 \right]$$

(49)

with $\kappa_{\lambda 1}$ the mean of the displacement and $\kappa_{\lambda 2}$ its variance, explicitly given by

$$\kappa_{\lambda 1} = \langle \mathbf{k} \cdot \Delta \mathbf{r}_{\lambda 1}(t) \rangle_{\lambda'}$$

(50)

$$\kappa_{\lambda 2} = \langle (\mathbf{k} \cdot \Delta \mathbf{r}_{\lambda 1}(t) - \kappa_{\lambda 1}(\mathbf{k}, \mathbf{r}', t))^2 \rangle_{\lambda'}.$$ 

(51)

The coefficients $b_{\lambda n}$ in equation (48) can be determined by gathering terms of like order in $k$ in the $k$-expansion of $F_\lambda(\mathbf{k}, \mathbf{r}', t)/f_\lambda(\mathbf{k}, \mathbf{r}', t)$. This gives

$$b_{\lambda n} = \sum_{\{p\ell \geq 0\}} \prod_{\ell=3}^{\infty} \left[ \frac{1}{p!} \left( \frac{\kappa_{\lambda \ell}}{\ell!} \right)^{p_{\ell}} \right].$$

(52)

where the arguments $\mathbf{k}$, $\mathbf{r}'$ and $t$ of $b_{\lambda n}$ and $\kappa_{\lambda n}$ have been suppressed. The first few coefficients $b_{\lambda n}$ are given by

$$b_{\lambda 3} = \kappa_{\lambda 3}/3!$$

(53)

$$b_{\lambda 4} = \kappa_{\lambda 4}/4!$$

(54)

Up to a constant prefactor, the coefficients $\kappa_{\lambda 1}$ (mean), $\kappa_{\lambda 2}$ (variance), $b_{\lambda 3}$ (skewness), $b_{\lambda 4}$ (kurtosis) and $b_{\lambda 5}$ are pure cumulants, however starting from $n = 6$ the coefficients $b_{\lambda n}$ can only be written as combinations of cumulants, e.g. $b_{\lambda 6} = (\kappa_{\lambda 6} + 10\kappa_{\lambda 3}^2)/6!$.

Term by term the expression in equation (48) can be Fourier inverted. However, one has to keep the $\mathbf{k}$ dependence of the $\kappa_{\lambda n}$ in mind. For this $\mathbf{k}$ dependence, we can write, using equations (41), (43) and (52),

$$\mu_{\lambda n} = \hat{k}^n : M_{\lambda n}$$

(55)

$$\kappa_{\lambda n} = \hat{k}^n : K_{\lambda n}$$

(56)

$$b_{\lambda n} = \hat{k}^n : B_{\lambda n}$$

(57)

where $M_{\lambda n}$, $K_{\lambda n}$ and $B_{\lambda n}$ are $\mathbf{r}'$ and $t$ dependent tensors of rank $n$. Here a tensor notation is used. In this notation, "::" denotes a scalar product (summation over all $n$ indices), while powers of tensors are $A^n = A \otimes A \cdots \otimes A$ and yield symmetric tensors of rank $n$. The tensors $M_{\lambda n}$, $K_{\lambda n}$ and $B_{\lambda n}$ are chosen to be symmetric, and follow from equations (41), (43), (52) and equations (55–57):

$$M_{\lambda n} = \langle [\Delta \mathbf{r}_{\lambda 1}(t)]^n \rangle_{\lambda'}.$$ 

(58)

§ To avoid having to use explicit indices, we use here a symmetrized tensor product, such that $\mathbf{A} \mathbf{B} = [\mathbf{A} \otimes \mathbf{B}]_S$, where $[\mathbf{A}]_S$ denotes the symmetric part of a tensor e.g. $[\mathbf{A}]_{\lambda ij} = (\mathbf{A}_{\lambda j} + \mathbf{A}_{\lambda i})/2!$ for a rank two tensor, $[\mathbf{A}]_{\lambda ijk} = (\mathbf{A}_{\lambda jk} + \mathbf{A}_{\lambda kj} + \mathbf{A}_{\lambda ki} + \mathbf{A}_{\lambda ji} + \mathbf{A}_{\lambda kji} + \mathbf{A}_{\lambda jik})/3!$ for rank three, etc.
\[ K_{\lambda n} = -n! \sum_{\{p_\ell \geq 0\}} \left( \sum_{\ell=1}^{\infty} p_\ell - 1 \right)! \prod_{\ell=1}^{\infty} \frac{[-M_{\lambda\ell}/\ell!]^{p_\ell}}{p_\ell!} \]  
\[ B_{\lambda n} = \sum_{\{p_\ell \geq 0\}} \prod_{\ell=3}^{\infty} \left[ \frac{1}{p_\ell!} \left( \frac{K_{\lambda\ell}}{\ell!} \right)^{p_\ell} \right] \]  

Using these definitions, the Fourier inverse of \( f_\lambda \) of equation (49) is
\[ g_\lambda(r, r', t) = \frac{\exp\left[-\frac{1}{2}(r - r' - K_{\lambda 1}) \cdot (r - r' - K_{\lambda 1}) \right]}{\sqrt{\det(2\pi K_{\lambda 2})}} \]  

where
\[ K_{\lambda 1} = \langle \Delta r_{\lambda 1}(t) \rangle_{xy} \]  
\[ K_{\lambda 2} = \langle [\Delta r_{\lambda 1}(t) - K_{\lambda 1}]^2 \rangle_{xy}. \]

Using equations 18 and 57 and that the Fourier inverse of \( F_\lambda \) is \( G_\lambda \) and that of \( f_\lambda \) is \( g_\lambda \), we obtain
\[ G_\lambda(r, r', t) = \left[ 1 + \sum_{n=3}^{\infty} B_{\lambda n} : (-\nabla)^n \right] g_\lambda(r, r', t) \]  
\[ = \left[ 1 + \sum_{n=3}^{\infty} B_{\lambda n} : H_n \left( r - r' - K_{\lambda 1}, \frac{1}{2} K_{\lambda 2}^{-1} \right) \right] g_\lambda(r, r', t). \]

Here the \( H_n \) are polynomial tensors in \( s = r - r' - K_{\lambda 1} \) given (with \( A = \frac{1}{2} K_{\lambda 2}^{-1} \)) by
\[ H_n(s, A) = \sum_{m=0}^{\left\lfloor \frac{n}{2} \right\rfloor} \frac{(-1)^m n!}{m!(n-2m)!} A^m (2A \cdot s)^{n-2m}. \]

where \( \left\lfloor \frac{n}{2} \right\rfloor \) is the largest integer number less than or equal to \( \frac{n}{2} \). Explicitly, the first few polynomials \( H_{n \geq 3}(s, A) \) are given by
\[ H_3(s, A) = 4[2(A \cdot s)^3 - 3A(A \cdot s)] \]  
\[ H_4(s, A) = 4[4(A \cdot s)^4 - 12A(A \cdot s)^2 + 3A^2]. \]

The coefficients in the expressions of the right hand sides for these \( H_n \) are precisely those of the Hermite polynomials. They can in fact be related to the Hermite polynomials, in that the \( n \)th Hermite polynomial can be expressed as \( H_n(s_x) = H_n(s, 1) : \hat{A}^n \) (using Gradshteyn and Ryzhik 8.950.2 [21] with \( s = (s_x, s_y, s_z), \) the identity matrix, \( A : \hat{A}^n \) the (all) \( x \) component of \( A \), and noting that \( 2^m(2m-1)!/(2m)! = 1/m! \)).

3.3. Reduction to one-dimensional Green’s functions

The somewhat cumbersome tensorial notation of the last section can be avoided in cases where the initial distribution \( P_{\text{ne}}(\Gamma) \) is only nonuniform in the \( x \) direction and
translation invariant in the $y$ and $z$ directions, such as in previous work on the Green’s functions [6–9]. In such a situation one can use the reduced Green’s function

$$G^\lambda_x(x, x', t) = \int dy' \int dz' G_\lambda(r, r', t) = \langle \delta(x - x' - \Delta x_\lambda(t)) \rangle_{\lambda r'}.$$

(69)

where $\Delta x_\lambda(t) = x_\lambda(t) - x_\lambda(0)$ is the displacement of particle 1 of component $\lambda$ in the $x$ direction. Note that the $y$ and $z$ dependence has dropped out because of the translation invariance of $P_{\text{ne}}(\Gamma)$ in those directions and the translation invariance of the dynamics i.e. of the Hamiltonian. In terms of the reduced Green’s function equation (66) becomes

$$n_\lambda(x, t) = \int dx' G^\lambda_x(x, x', t) n_\lambda(x', 0).$$

(70)

To see how the reduction works out for expansion (65), it is easier to start from the original expansion in equation (64). Noting that because of translation invariance the $K_{\lambda 1}(r', t)$ and consequently the $B_{\lambda n}(r', t)$ do not depend on $y'$ or $z'$, we can integrate equation (64) over $y'$ and $z'$ to find

$$G^\lambda_x(x, x', t) = \left[ 1 + \sum_{n=3}^{\infty} b_{\lambda n}^x \left( -\frac{\partial}{\partial x} \right)^n \right] g^\lambda_x(x, x', t)$$

(71)

where $b_{\lambda n}^x = B_{\lambda n} : \hat{\mathbf{x}}^n$ and

$$g^\lambda_x(x, x', t) = \int dy' \int dz' g_\lambda(r, r', t) = \frac{\exp \left[ -\frac{(x - x' - \kappa_\lambda^x)^2}{2\kappa_\lambda^2} \right]}{\sqrt{2\pi \kappa_\lambda^x}},$$

(72)

where $\kappa_\lambda^x = K_{\lambda n} : \hat{\mathbf{x}}^n$ and we used that the $xy$ and $xz$ components of the matrix $K_\lambda$ are zero by translation symmetry in the $y$ and $z$ direction (which also pertains to the inverse of this matrix). Working out the derivatives to $x$ in equation (71) gives

$$G^\lambda_x(x, x', t) = \left[ 1 + \sum_{n=3}^{\infty} \frac{b_{\lambda n}^x}{(2\kappa_\lambda^x)^{n/2}} H_n \left( \frac{x - x' - \kappa_\lambda^x}{\sqrt{2\kappa_\lambda^x}} \right) \right] g^\lambda_x(x, x', t),$$

(73)

where the $H_n$ are true Hermite polynomials.

We note that to obtain the $b_{\lambda n}^x$ and $\kappa_\lambda^x$, it is possible to avoid the tensors through which they have been defined, since by comparing the definitions $\kappa_\lambda^x = K_{\lambda n} : \hat{\mathbf{x}}^n$ and $b_{\lambda n}^x = B_{\lambda n} : \hat{\mathbf{x}}^n$ with the expressions in equation (56) and equation (57), one sees immediately that one only needs to set $\hat{\mathbf{k}}$ equal to $\hat{\mathbf{x}}$ in the expressions for $b_{\lambda n}$ and $\kappa_{\lambda n}$ to obtain $b_{\lambda n}^x$ and $\kappa_{\lambda n}^x$.

We note that the resummation of $G_\lambda$ leading to equations (65) and (73) is somewhat different from that used for the non-equilibrium heat transport case of references [7–9] where separate Gaussian factors were introduced for the even terms and the odd terms in $k$ (i.e. even and odd $n$), respectively, rather than a single overall Gaussian factor as we used in equation (68). A result was then found in terms of Sonine polynomials $S_n^{(n)}(x)$ [2]. The present formalism is nonetheless very similar since the Hermite polynomials are special cases of the Sonine (or Laguerre) polynomials (i.e. $H_{2n}(x) = (-1)^n 2^{2n} n! S^{(n)}_{\lambda - 1/2}(x^2)$ and $H_{2n+1}(x) = (-1)^n 2^{2n+1} n! x S^{(n)}_{\lambda 1/2}(x^2)$, see references [2, p. 127] and [21, 8.972]).
Leaving out the odd terms in equation (73) furthermore yields the exact same form as that in the self-diffusion result in equation (6) of reference [6] (with $\rho_1 = \frac{1}{2}K^{-1}_{\lambda_2}$, $\rho_2 = b^x_{\lambda_4}$ and $\rho_3 = b^x_{\lambda_6}$).

3.4. Practical considerations

Substituting the expression for $G_{\lambda}$ in equation (65) into expression (36) (or equation (73) into equation (70)) for the local densities $n_{\lambda}$ in terms of the Green's functions, leads to an expression for those densities involving an infinite sum over $n$. To make the Green's function approach practical the dynamical averages occurring in $M_{\lambda n}$ in equation (58) (and in $K_{\lambda n}$ and $B_{\lambda n}$ through equations (59) and (60)) need to be calculated, for instance by molecular dynamics. Since one can calculate only finitely many quantities in practice the infinite sum in equation (65) has to be truncated at some point.

Having chosen the Gaussian factor $g_{\lambda}$ in equation (48) such that corrections are at most $O(k^3)$, the Gaussian approximation

$$G_{\lambda}(r, r', t) \approx g_{\lambda}(r, r', t) = \frac{\exp\left[-\frac{1}{2}(r - r' - K_{\lambda 1}) \cdot K^{-1}_{\lambda 2} \cdot (r - r' - K_{\lambda 1})\right]}{\sqrt{\det(2\pi K_{\lambda 2})}}.$$ (74)

(cf. equation (61)) is expected to describe the correct long time limiting behaviour, similar to the self-diffusion case [6]. To confirm this expectation we will look in detail at the behaviour in the long time limit in section 3. For intermediate (non-infinitesimally small) times, it will be necessary to include some of the correction terms proportional to $B_{\lambda n}$ in equation (65) e.g. (using equations (58)–(60), (67) and (68))

$$G_{\lambda}(r, r', t) \approx g_{\lambda}(r, r', t) \left[1 + K_{\lambda 3} : (q^3_{\lambda} - 3K^{-1}_{\lambda 2} q_{\lambda}) + K_{\lambda 4} : (q^4_{\lambda} - 6K^{-1}_{\lambda 2} q^2_{\lambda} + 3[K^{-1}_{\lambda 2}]^2) + \ldots \right],$$ (75)

where $q_{\lambda} = K^{-1}_{\lambda 2} \cdot (r - r' - K_{\lambda 1})$. Checking whether these first few terms for the Green's functions describe the intermediate time behaviour accurately will be done in future numerical work.

3.5. Connection with the Van Hove self-correlation function

For equilibrium initial conditions (i.e. replacing $\langle \rangle_{\lambda r'}$ by $\langle \rangle$), the Green's function $G_{\lambda}(r, r', t)$ depends only on the difference $|r - r'|$ and reduces to the Van Hove self-correlation function [22,23]. Indeed, the self-part $G_s(r - r', t)$ of the Van Hove function also has the physical interpretation of the probability for a particle to be at position $r$ given that it was at position $r'$ a time $t$ earlier. Thus the Green's function $G_{\lambda}(r, r', t)$ can be seen as a nonequilibrium extension of $G_s(r - r', t)$. It is at present not clear whether this means that Green's functions could be observed in incoherent neutron scattering experiments like the Van Hove self-correlation function can [22].

Similar expansions as in equation (48) have been used for the Van Hove self-correlation function $G_s$ in a single component fluid in equilibrium [20,23–26], where odd terms in $k$ are absent. The Gaussian approximation to the Van Hove self-correlation
function turns out a good description in the very short and the long time limits. Non-Gaussian corrections are important for intermediate times, where including just the first correction term (involving the fourth moment) captures most of the physical behaviour [23–25]. For more information, we refer to chapter 4 of reference [23] which contains a nice overview of different approaches to $G_s$.

4. Limiting behaviour of the Green’s functions at long times

As a first approximation in investigating the large time and length scale behaviour of the Green’s functions, we realize that at long times gradients get small so that $O(k^3)$ terms become unimportant and the Gaussian approximation, found by neglecting the terms proportional to $B_{\lambda n}$ in equation (63), should capture all of the relevant dynamics for long times, since the hydrodynamic equations also contain at most second orders in gradients. This will now be checked.

Taking into account only the Gaussian term in the resummation in equation (65), we get the Gaussian approximation in (74), with $K_{\lambda 1}$ and $K_{\lambda 2}$ given in equations (62) and (63). We emphasize that the present approach differs from the self-diffusion case [6] where odd terms in $k$ existed. But in the mutual diffusion case odd terms such as $K_{\lambda 1}(r', t)$ cannot be neglected. These terms are of the form $\langle \Delta r_{\lambda 1}(t) \rangle_{\lambda r}$ so they represent net particle displacement or drift. In a diffusing system particles do move in a preferred direction, namely opposite to the gradient, so these terms will not be zero and will in fact be sensitive to the gradients.

Using the Gaussian approximation $G_{\lambda} \approx g_{\lambda}$ in equation (74), a diffusion-like equation can be derived for the Green’s function $G_{\lambda}$. The easiest way to derive this is by taking the time derivative on both sides of equation (49), thus obtaining an equation for the Fourier transform $F_{\lambda} \approx f_{\lambda}$, and then taking the inverse Fourier transform to get the corresponding equation for $G_{\lambda} \approx g_{\lambda}$. This leads to

$$\frac{\partial}{\partial t} G_{\lambda}(r, r', t) \approx - K_{\lambda 1} \cdot \nabla G_{\lambda}(r, r', t) + \frac{1}{2} \nabla \cdot \dot{K}_{\lambda 2} \cdot \nabla G_{\lambda}(r, r', t)$$

(76)

where $\dot{K}_{\lambda 1} = \partial K_{\lambda 1} / \partial t$ and $\dot{K}_{\lambda 2} = \partial K_{\lambda 2} / \partial t$. Using equation (58), which relates $G_{\lambda}$ to $n_{\lambda}$, this implies that

$$\frac{\partial n_{\lambda}}{\partial t} \approx - \nabla \cdot \left[ \int_V dr' K_{\lambda 1}(r', t) G_{\lambda}(r, r', t) n_{\lambda}(r', 0) \right] + \int_V dr' \frac{1}{2} \dot{K}_{\lambda 2}(r', t) \cdot \nabla G_{\lambda}(r, r', t) n_{\lambda}(r', 0).$$

(77)

In equation (77) we focus first on $\dot{K}_{\lambda 2}$. From equation (63) we have

$$\dot{K}_{\lambda 2}(r', t) = \frac{\partial}{\partial t} \langle [\Delta r_{\lambda 1}(t) - \langle \Delta r_{\lambda 1}(t) \rangle_{\lambda r'}]^2 \rangle_{\lambda r'}$$

$$= 2 \langle [v_{\lambda 1}(t) - \langle v_{\lambda 1}(t) \rangle_{\lambda r'}] [\Delta r_{\lambda 1}(t) - \langle \Delta r_{\lambda 1}(t) \rangle_{\lambda r'}] \rangle_{\lambda r'}$$

$$= 2 \int_0^t dt' \langle [v_{\lambda 1}(t) - \langle v_{\lambda 1}(t) \rangle_{\lambda r'}] [v_{\lambda 1}(t') - \langle v_{\lambda 1}(t') \rangle_{\lambda r'}] \rangle_{\lambda r'}. \quad (78)$$
(using the symmetrized tensor product explained in the footnote on page 10). Equation (78) looks surprisingly like a Green-Kubo formula for the self-diffusion coefficients except for the conditional average $\langle \rangle_{\lambda r'}$ and the integration to $t$. It seems reasonable to assume that for long times $t$ the condition that a particle was at some position $r'$ at time 0 should have a negligible effect on how fast it is diffusing at time $t$. In other words it seems reasonable that the limit of $t \to \infty$ of the above expression is independent of $r'$:

$$\lim_{t \to \infty} \dot{K}_{\lambda}(r', t) = \lim_{t \to \infty} 2 \int_0^t dt' \langle [v_{\lambda 1}(t) - \langle v_{\lambda 1}(t) \rangle] [v_{\lambda 1}(t') - \langle v_{\lambda 1}(t') \rangle] \rangle \quad (79)$$

For $t \to \infty$ the (closed) system will have reached equilibrium, so we can use the time translation invariance and isotropy of the equilibrium distribution and that $\langle v_{\lambda 1}(t) \rangle = 0$ for all $t$, to write

$$\lim_{t \to \infty} \dot{K}_{\lambda}(r', t) = \frac{2}{3} \int_0^\infty dt' \langle \vec{v}_{\lambda 1}(0) \cdot v_{\lambda 1}(t') \rangle \mathbb{1} = 2D_\lambda \mathbb{1}, \quad (80)$$

where we used the definition of $D_\lambda$ in equation (82). (Note that formally one needs to take the thermodynamic limit before taking $t \to \infty$.)

Assuming now that $\dot{K}_{\lambda 2}(r', t)$ attains its limiting value $2D_\lambda$ fast enough, we can replace $\dot{K}_{\lambda 2}(r', t)$ by that value in equation (77) for long times. It is then independent of $r'$ and can be taken outside of the integral in equation (77). (Another way to see that the $r'$ dependence of $\dot{K}_{\lambda 2}$ should drop out is by noting that this $r'$ dependence will just give additional gradients in $r$ if one expands around $r$, but the $\dot{K}_{\lambda 2}$ term in equation (77) is already of the highest order in gradients required for hydrodynamics, i.e. second order in the gradients.) Equation (77) then becomes

$$\frac{\partial n_\lambda}{\partial t} \approx - \vec{\nabla} \cdot \int_V dr' \dot{K}_{\lambda 1}(r', t) G_\lambda(r, r', t) n_\lambda(r', 0) + D_\lambda \nabla^2 n_\lambda. \quad (81)$$

Because the first expression on the right-hand side of equation (81) cannot be further calculated without additional assumptions, to see whether it describes long time behaviour in accordance with hydrodynamics, one next makes the essential assumption of local equilibrium (which is also used to derive hydrodynamics in other ways).

To keep the derivation of hydrodynamics from the Green’s functions simple we will also assume that the system is in mechanical equilibrium i.e. $\nabla p = 0$, and only has gradients in the concentration i.e. $\nabla T = 0$ and $\nabla u = 0$.

Within the context of local equilibrium, assumed to hold at time zero for now, we focus on the quantity $\dot{K}_{\lambda 1}$ in equation (81) for component $\lambda = 1$. According to equation (82),

$$\dot{K}_{11}(r', t) = \frac{\langle v_{11}(t) \delta(r' - r_{11}(0)) \rangle_{ne}}{\langle \delta(r' - r_{11}(0)) \rangle_{ne}} = \frac{\langle N_1 v_{11}(t) \delta(r' - r_{11}(0)) \rangle_{ne}}{n_1(r', 0)}, \quad (82)$$

where we have used that particles of the same component are indistinguishable. We will now evaluate $\dot{K}_{11}(r', t)$ with the local equilibrium distribution $P_L$ derived in appendix A (following Ernst’s treatment of a single component fluid [27]). Using equation (A.13) we can write $\dot{K}_{11}(r', t)$ as
where \( \langle A \rangle_0 \) is defined as \( \int A(\Gamma)\mathcal{P}_0(\Gamma)d\Gamma \) where \( \mathcal{P}_0 \) is the grand canonical distribution but with all velocities shifted over \( u \), and \( \tilde{n}_\lambda(\mathbf{r}''') \) is the microscopic expression for the number density of component \( \lambda \) at position \( \mathbf{r}'' \) (see appendix A for details). In appendix B it is shown that this gives to leading order in the gradients:

\[
\dot{K}_{11}(\mathbf{r}', t) = \mathbf{u} + \frac{\rho}{n_1} \left[ \frac{\langle N_1(N_1-1)\mathbf{v}_{11}(t)\mathbf{r}_{12}(0) \rangle}{cm^2nV} - \frac{\langle N_1N_2\mathbf{v}_{11}(t)\mathbf{r}_{21}(0) \rangle}{(1-c)m_1nV} \right] \cdot \nabla c. \tag{84}
\]

Using now that \( \langle \mathbf{v}_{11}(t)\mathbf{r}_{12}(0) \rangle = -\langle \mathbf{v}_{11}(0)\mathbf{r}_{12}(t) \rangle = \int_0^t dt' \langle \mathbf{v}_{11}(0)\mathbf{v}_{12}(t') \rangle \) and furthermore taking the thermodynamic limit and then the limit \( t \to \infty \), we get (cf. equations \([30]\) and \([31]\)) \( \dot{K}_{11}(\mathbf{r}', t) = \mathbf{u} + \frac{\rho^2}{m_1m_2n^2} (f_{12} - f_{\lambda\alpha\beta}) \nabla c \). By interchanging 1 and 2, which also implies that \( \nabla c \) be replaced by \( \nabla (1-c) = -\nabla c \), we find the corresponding result for component 2, i.e. \( \dot{K}_{21}(\mathbf{r}', t) = \mathbf{u} - \frac{\rho^2}{m_1m_2n^2} (f_{12} - f_{2\alpha\beta}) \nabla c \), so that

\[
\dot{K}_{11}(\mathbf{r}', t) = \mathbf{u} - (-1)^\lambda \frac{\rho^2}{m_1m_2n^2} (f_{12} - f_{\lambda\alpha\beta}) \nabla c. \tag{85}
\]

Substituting this result for \( \dot{K}_{11} \) from equation \((83)\) into equation \((31)\) and integrating over \( \mathbf{r}' \) results in

\[
\frac{\partial n_\lambda}{\partial t} = \nabla \cdot \left[ D_\lambda \nabla n_\lambda - n_\lambda \mathbf{u} + (-1)^\lambda \frac{\rho^2 x_\lambda}{m_1m_2n^2} (f_{12} - f_{\lambda\alpha\beta}) \nabla c \right]. \tag{86}
\]

Using equation \((18)\), we identify the right hand side as \( -\nabla \cdot (n_\lambda \mathbf{u} + j_\lambda/m_\lambda) \) and find that

\[
j_\lambda = - D_\lambda \nabla \rho_\lambda - (-1)^\lambda \frac{m_\lambda \rho^2 x_\lambda}{m_1m_2n^2} (f_{12} - f_{\lambda\alpha\beta}) \nabla c
\]

\[
= (-1)^\lambda \frac{m_\lambda \rho^2}{m_1m_2n^2} [D_\lambda - x_\lambda (f_{12} - f_{\lambda\alpha\beta})] \nabla c. \tag{87}
\]

where we have used equation \((17)\) to write \( \nabla \rho_1 \) at constant pressure and temperature (which is the case here) as \( \rho + c(\rho/\partial c)_{T_p} \nabla c = \rho^2/(m_2n) \nabla c \), and similarly \( \nabla \rho_2 = -\rho^2/(m_1n) \nabla c \). Since \( j_\lambda = (-1)^\lambda \rho D \nabla c \) (by definition), we see from equation \((87)\) that the mutual diffusion constant is given by

\[
D = \frac{m_\lambda \rho}{m_1m_2n} [D_\lambda - x_\lambda (f_{12} - f_{\lambda\alpha\beta})] = - \frac{\rho^2}{m_1m_2n^2} f_{12}. \tag{88}
\]

where in the last step we used equation \((33)\) for the case \( \lambda = 1 \) and equation \((34)\) for the case \( \lambda = 2 \). The Green’s function expression for the mutual diffusion in equation \((88)\) is therefore identical to the Green-Kubo result in equation \((29)\).

So far in this section the system was assumed to be in local equilibrium at time \( t = 0 \). We are really interested in systems that are initially far from equilibrium. If left unperturbed, such a system would still reach local equilibrium, after a time that we
shall denote by $t_L$ and which depends on the details of the initial condition (with no general way to determine it other than through measurement).

A natural question is therefore whether the Gaussian part of the Green’s function for such a far from equilibrium system is in agreement with hydrodynamics for times $t \gg t_L$ as well. We will now argue that this is indeed the case.

For this, we start from equation (81) for $\partial n / \partial t$. That equation was obtained by using 1) the Gaussian approximation for the Green’s function, and 2) that $t$ is large enough for $K_{\lambda_2}$ to have reached its long time value $2D_\lambda$. Since the assumption of local equilibrium was not needed for the derivation of equation (81), it holds also in cases where the system starts far from equilibrium. To obtain hydrodynamics from local equilibrium was not needed for the derivation of equation (81), it holds also in cases where the system starts far from equilibrium.

Using 1) the Gaussian approximation for the Green’s function, and 2) that $t$ be calculated using local equilibrium, since the condition involves time $t$ for such a far from equilibrium system is in agreement with hydrodynamics for times $t_L$ as well. The local equilibrium condition at time $t_L$ can be used by writing $\dot{K}_{\lambda_1}$ as (cf. equation (62))

$$K_{\lambda_1} = \langle v_{\lambda_1}(t) \rangle_{\lambda_1} = \int d\mathbf{r}'' (v_{\lambda_1}(t) \delta(\mathbf{r}'' - \mathbf{r}_{\lambda_1}(t_L))) \delta''(\mathbf{r}'' - \mathbf{r}_{\lambda_1}(t_L))$$  \hspace{1cm} (89)

Assuming now that all microscopic correlations between quantities at time 0 and at later times have died out before $t_L$, the condition that $\mathbf{r}_{\lambda_1}(0) = \mathbf{r}'$ in $\langle v_{\lambda_1}(t) \delta(\mathbf{r}'' - \mathbf{r}_{\lambda_1}(t_L)) \rangle_{\lambda_1}$ should not matter, i.e.

$$\langle v_{\lambda_1}(t) \delta(\mathbf{r}'' - \mathbf{r}_{\lambda_1}(t_L)) \rangle_{\lambda_1} \approx \langle v_{\lambda_1}(t) \delta(\mathbf{r}'' - \mathbf{r}_{\lambda_1}(t_L)) \rangle_2$$  \hspace{1cm} (90)

Using this in equation (89) gives

$$\dot{K}_{\lambda_1} = \int d\mathbf{r}'' \langle v_{\lambda_1}(t) \rangle_{\lambda_1} = \mathbf{r}'' \langle \delta(\mathbf{r}'' - \mathbf{r}_{\lambda_1}(t_L)) \rangle_1$$  \hspace{1cm} (91)

where the subscript appended to the average $\langle v_{\lambda_1}(t) \rangle_{\lambda_1} = \mathbf{r}''$ indicates that it is taken only over all configuration for which $\mathbf{r}_{\lambda_1}(t_L) = \mathbf{r}''$. The quantity $\langle v_{\lambda_1}(t) \rangle_{\lambda_1} = \mathbf{r}''$ can be calculated using local equilibrium, since the condition involves time $t_L$, at which time we assume local equilibrium to have been established. In fact, except for the time shift over $t_L$, it is precisely the same quantity $K_{\lambda_1}$ that was calculated for the case where local equilibrium was present at time zero, with the result (85), so that

$$\langle v_{\lambda_1}(t) \rangle_{\lambda_1} = \mathbf{u} - (-1)^\lambda \frac{\rho^2}{m_1 m_2 n^2} (f_{12} - f_{\lambda_0 \beta}) \nabla c.$$  \hspace{1cm} (92)

This expression for $\langle v_{\lambda_1}(t) \rangle_{\lambda_1} = \mathbf{r}''$ is independent of $\mathbf{r}''$, so that after its substitution into equation (81), the integration over $\mathbf{r}''$ can be performed giving

$$\dot{K}_{\lambda_1} = \mathbf{u} - (-1)^\lambda \frac{\rho^2}{m_1 m_2 n^2} (f_{12} - f_{\lambda_0 \beta}) \nabla c.$$  \hspace{1cm} (93)

This is identical to the case where local equilibrium was established at time zero, i.e. equation (85). Substituting equation (93) in equation (81) would thus lead, as before, to the hydrodynamic equation (86), with the right value for the mutual diffusion constant as given by equation (88).

In conclusion, the Gaussian approximation to the Green’s function for a far from equilibrium initial situation gives hydrodynamic behaviour for long times $t > t_L$ as long as local equilibrium is established at some finite time $t_L$ (not necessarily zero).
5. Discussion

In this paper we have shown that for binary diffusion in an isotopic or ideal mixture, the Green’s function theory is able to handle long time behaviour.

We remark that the very short time behaviour was discussed in a previous paper [20], using a recent theorem regarding particle displacements and their cumulants under the condition that the initial velocity distribution is Gaussian while the initial position distribution may be arbitrary.

The long time behaviour was checked here by expanding in gradients and using a local equilibrium assumption for long times. The latter assumption is natural because it is generally expected that local equilibrium is a condition for hydrodynamic behaviour.

Given the form of the Green’s functions formula in equation (36), in which the density of component $\lambda$ at time $t$ is expressed solely in terms of that same density at time zero, it may be surprising that the Green’s functions do not produce only self-diffusion. In fact the Green’s functions reproduce mutual diffusion with the correct (Green-Kubo) expression for the mutual diffusion constant (see equation 35) with both the self (Darken-Hartley-Crank) terms and the necessary cross terms $f_{\lambda\alpha\beta}$ and $f_{12}$. Note that the cross terms found in equations 88 arose from the local equilibrium assumption applied to the drift terms $\dot{K}_{\lambda 1}(r', t)$, whereas the self-terms come from the rather simple approximation to the variance $\dot{K}_{\lambda 2}(r', t) \approx 2D_\lambda$. We can therefore conclude that although the Green’s functions seem to treat the system as self-diffusion, the sensitivity of the drift terms to local equilibrium restores the true mutual and hydrodynamic character of the binary diffusion.

We note that the Green’s function formalism presented here can be straightforwardly generalized to general classical multi-component mixtures with a non-equilibrium initial distribution, since the equations of the Green’s functions, equations (36)–(75), do not rely on the fact that there are only two components, nor on the fact that they are isotopic or ideal. It was mainly for the discussion of the approach to hydrodynamics in section 4 that we restricted ourselves to isotopic and ideal binary mixtures in order not to make the manipulations overly complicated.

We will end with a few questions to be addressed in the future.

Although we expect that the Green’s functions will also be able to reproduce hydrodynamics at long times in other systems, especially in general mixtures, this is at present an open problem.

The Green’s function formalism presented in section 3 only describes mass transport. Analogous to the treatment in references [7, 8], it would be desirable to extend the formalism presented here to include local currents and energy densities.

The intermediate time behaviour of the Green’s functions for mixtures — expected to be more relevant for nanoscale systems — is to be checked in computer simulations. Here, the correction terms $B_{\lambda n}$ in equation 65 will become important. If the situation is similar to that of the heat pulse studied in references [7–9], taking the Gaussian approximation alone would turn out not to suffice for the correct description of the
behaviour of the system, but that including just a few correction terms, such as in equation (75), should be enough to get good agreement with the simulations on the picosecond scale. Note that these correction terms represent non-Gaussian behaviour of the particle displacement; thus it is expected that non-Gaussian behaviour occurs on the time scale in between the initial infinitesimal and the long time, hydrodynamic behaviour.

These issues are currently under investigation.

Acknowledgments

We would like to thank Prof. J. M. Kincaid for useful discussions. We also acknowledge the support of the Office of Basic Energy Sciences of the US Department of Energy (grant no. DE-FG-02-88-ER13847) and of the National Science Foundation (grant no. PHY-0501315).

A. Local equilibrium

In this appendix we will formulate the local equilibrium distribution in an expansion in gradients following the method of Ernst [27] for a one-component fluid. For a one component system Ernst derived an expression for the (grand canonical-like) local equilibrium phase space distribution function at time $t$ expanded in gradients of the local thermodynamic fields $T$ (temperature), $u$ (fluid velocity) and $\mu$ (chemical potential), at a position $\mathbf{r}$ and time $t$ at which one wishes to calculate a local quantity. We will use a similar derivation here for a two component mixture, in which case there are two chemical potentials. As in the main text, we will consider a case with only gradients in the chemical potentials $\mu_\lambda$, while $\nabla p = 0$, $\nabla T = 0$ and $\nabla \mathbf{u} = 0$.

The local equilibrium distribution will be defined in analogy with the usual grand canonical equilibrium distribution function at temperature $T$, chemical potentials $\mu_1$ and $\mu_2$ and an average fluid velocity $\mathbf{u} = 0$, given by

$$ P(\Gamma) = \frac{\exp\{-[H(\Gamma) - \sum_{\lambda=1}^{2} \mu_\lambda N_\lambda]/k_B T\}}{N_1!N_2!h^{3N}Z}, \quad (A.1) $$

where the Hamiltonian is defined in equation (2) and the normalization $Z = \sum_{N_1} \sum_{N_2} \int d\Gamma \exp\{-[H(\Gamma) - \mu_1 N_1 - \mu_2 N_2]/k_B T\} / (N_1!N_2!h^{3N})$. For local equilibrium, we suppose that at a certain instant, taken to be time 0, one can define a uniform fluid velocity $\mathbf{u}$ and spatial varying chemical potentials of the two components, $\mu_1(\mathbf{r})$ and $\mu_2(\mathbf{r})$, while $p$ and $T$ are constant. The local equilibrium distribution is then

$$ P_L(\Gamma|\mu_\lambda) \equiv \frac{\exp\{-[H_p(\Gamma) - \int d\mathbf{r}' \sum_{\lambda=1}^{2} \mu_\lambda(\mathbf{r}')\tilde{n}_\lambda(\mathbf{r}')]/k_B T\}}{N_1!N_2!h^{3N}Z_L}, \quad (A.2) $$

where the normalization $Z_L$ is given by

$$ Z_L = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \int d\Gamma \frac{\exp\{-[H_p(\Gamma) - \int d\mathbf{r}' \sum_{\lambda=1}^{2} \mu_\lambda(\mathbf{r}')\tilde{n}_\lambda(\mathbf{r}')]/k_B T\}}{N_1!N_2!h^{3N}}. \quad (A.3) $$
Furthermore, in equations (A.2) and (A.3) the phase functions corresponding to the local number densities and the total peculiar energy are (cf. equations (1) and (2))

\[
\tilde{n}_\lambda(r') \equiv \sum_{i=1}^{N_\lambda} \delta(r' - r_{\lambda i})
\]

\[
H_p(\Gamma) \equiv \sum_{\lambda=1}^{2} \sum_{i=1}^{N_\lambda} \left[ \frac{1}{2} \rho_{\lambda i} |v_{\lambda i} - u|^2 + \sum_{\nu=1}^{N_\nu} \frac{1}{2} \rho_{\nu \nu} (|r_{\lambda i} - r_{\nu j}|) \right].
\]

We note that the requirement of constant pressure puts, through the Gibbs-Duhem relation (13), a restriction on the functions \(\mu_\lambda(r)\):

\[
\nabla \mu_2 = -n_1/n_2 \nabla \mu_1.
\]

Following Ernst we expand the distribution function as

\[
P_L(\Gamma|\mu_\lambda) = P_0(\Gamma|\mu_\lambda) + P_1(\Gamma|\mu_\lambda) + \ldots
\]

Here \(\mu_\lambda = \mu_\lambda(r,t)\) with \(r\) a specific position around which local quantities are to be evaluated. Furthermore, the leading term \(P_0(\Gamma|\mu_\lambda) = P_L(\Gamma|\mu_\lambda)|_{\mu_\lambda = \mu_\lambda(r,t)}\), which is a distribution of the form of a grand canonical equilibrium distribution in equation (A.1) at the (fixed) values \(\mu_\lambda = \mu_\lambda(r,t)\) and in terms of peculiar velocities i.e. with \(H\) replaced by \(H_p\).

Expanding equation (A.2) around \(\mu_\lambda \equiv \mu_\lambda(r,t)\), we find for the next-to-leading term in equation (A.7)

\[
P_1(\Gamma|\mu_\lambda) = \int dr' \sum_{\lambda=1}^{2} \left[ \frac{\partial P_L(\Gamma|\mu_\lambda)}{\partial \mu_\lambda(r')} \right]_{\mu_\lambda = \mu_\lambda(r,t)} (r' - r) \cdot \nabla \mu_\lambda(r,t) - t \frac{\partial}{\partial t} \mu_\lambda(r,t)
\]

where we used that \(\mu_\lambda(r',0) = \mu_\lambda(r,t) + (r' - r) \cdot \nabla \mu_\lambda(r,t) - t (\partial/\partial t) \mu_\lambda(r,t) + \ldots\).

The functional derivatives are, using equation (A.2),

\[
\frac{\delta P_L(\Gamma|\mu_\lambda)}{\delta \mu_\lambda(r')} = P_L(\Gamma|\mu_\lambda) \left[ \frac{\tilde{n}_\lambda(r')}{k_B T} - \frac{\delta \ln Z_L}{\delta \mu_\lambda(r')} \right].
\]

The term \(\delta \ln Z_L/\delta \mu_\lambda(r')\) in equation (A.9) can be shown to be the average of \(\tilde{n}_\lambda(r')/k_B T\) taken with \(P_L\), so, as it occurs in equation (A.8),

\[
\left. \frac{\delta P_L(\Gamma|\mu_\lambda)}{\delta \mu_\lambda(r')} \right|_{\mu_\lambda = \mu_\lambda(r,t)} = \left. \frac{P_L(\Gamma|\mu_\lambda)}{k_B T} \frac{\tilde{n}_\lambda(r') - \langle \tilde{n}_\lambda(r') \rangle_L}{\mu_\lambda = \mu_\lambda(r,t)} \right|_{\mu_\lambda = \mu_\lambda(r,t)}
\]

\[
= \frac{P_0(\Gamma|\mu_\lambda)}{k_B T} \tilde{n}_\lambda(r') - n_\lambda,
\]

where we used that the average \(\langle \rangle_L \approx \langle \rangle_0\) is translation invariant so \(\langle \tilde{n}_\lambda(r') \rangle_0 = n_\lambda\). We substitute equation (A.10) into equation (A.8) and obtain

\[
P_1(\Gamma|\mu_\lambda) = \frac{P_0(\Gamma|\mu_\lambda)}{k_B T} \int dr' \sum_{\lambda=1}^{2} [\tilde{n}_\lambda(r') - n_\lambda] (r' - r) \cdot \nabla \mu_\lambda - t \frac{\partial}{\partial t} \mu_\lambda.
\]

In equation (A.11), we are only interested in \(\partial \mu_\lambda / \partial t\) to leading order in the gradients. This is given by the Euler equations which are just equations (19)–(20) without
dissipation terms i.e. $D\rho/Dt = Dc/Dt = 0$. The quantities $\mu_\lambda$ are just functions of $\rho$ and $c$ (and of $T$, which is constant), so that also $D\mu_\lambda/Dt = 0$ and equation (A.11) becomes

$$P_1(\Gamma|\mu_\lambda) = \frac{P_0(\Gamma|\mu_\lambda)}{kBT} \int dr' \sum_{\lambda=1}^2 [\tilde{n}_\lambda(r') - n_\lambda]\nabla \mu_\lambda \cdot (r' - r + ut). \quad (A.12)$$

As in the main text we use instead of $\mu_1$ the quantity $\mu = \mu_1/m_1 - \mu_2/m_2$. with the help of the Gibbs-Duhem relation (A.6), which gives $\nabla \mu_2 = -(n_1/n_2)\nabla \mu_1$, we find $\nabla \mu_1 = m_1(1-c)\nabla \mu$ and $\nabla \mu_2 = -m_2c\nabla \mu$. Substituting this into equation (A.12) and using equation (13) gives the result used in the main text:

$$P_1(\Gamma|\mu_\lambda) = \frac{P_0(\Gamma|\mu_\lambda)}{kBT} \int dr' [(1-c)m_1\tilde{n}_1(r') - cm_2\tilde{n}_2(r')]\nabla \mu \cdot (r' - r + ut)$$

$$= \left(\frac{\partial \mu}{\partial c}\right)_{Tp} \frac{P_0(\Gamma|\mu_\lambda)}{kBT} \int dr' [(1-c)m_1\tilde{n}_1(r') - cm_2\tilde{n}_2(r')] (r' - r + ut) \cdot \nabla c$$

$$= P_0(\Gamma|\mu_\lambda) \rho \int dr' \left[\frac{\tilde{n}_1(r')}{cm_2n} - \frac{\tilde{n}_2(r')}{(1-c)m_1n}\right] (r' - r + ut) \cdot \nabla c. \quad (A.13)$$

**B. Derivation of equation (84)**

The average $\langle \rangle_0$ in equation (83) is over a variant of the grand canonical ensemble where each particle has an additional velocity $u$ compared to the normal grand canonical equilibrium ensemble. Since each particle has the same velocity shift, this does not change the relative motion of the particles. Hence, we can replace $\langle \rangle_0$ in the above expression by a real canonical ($u = 0$) ensemble average $\langle \rangle$, if we replace $v_1(t)$ by $u + v_1(t)$ in equation (83):

$$M_{11}(r',t) = \frac{1}{n_1(r',0)} \langle N_1 \delta(r' - r_{11}(0))[u + v_{11}(t)] \rangle$$

$$\times \left\{ 1 + \rho \int dr'' \left[\frac{\tilde{n}_1(r'')}{cm_2n} - \frac{\tilde{n}_2(r'')}{(1-c)m_1n}\right] (r'' - r + ut) \cdot \nabla c \right\}. \quad (B.1)$$

The part of the average proportional to $u$ is precisely equal to $n_1(r',0)$, so

$$M_{11}(r',t) = u + \frac{\langle N_1 \delta(r' - r_{11}(0))v_{11}(t) \rangle}{n_1(r',0)}$$

$$+ \rho \langle N_1 \delta(r' - r_{11}(0))v_{11}(t) \rangle \int dr'' \left[\frac{\tilde{n}_1(r'')}{cm_2n} - \frac{\tilde{n}_2(r'')}{(1-c)m_1n}\right] (r'' - r + ut) \cdot \nabla c \quad (B.2)$$

To simplify this expression further we will apply the following trick, based on the fact that $\langle v_{11}(t) \rangle = 0$, several times. The term $\langle N_1 \delta(r' - r_{11}(0))v_{11}(t) \rangle$ can be shown to vanish as follows. Its only spatial dependence is through $r'$ but because of translation invariance it cannot really depend on $r'$ so we can integrate over $r'$ and divide by $V$. This leaves us with $\langle N_1v_{11}(t) \rangle/V$. Then $v_{11}(t)$ can be replaced by $v_{11}(0)$ because both the number of particles and the grand canonical distribution function are invariant under
time evolution and the average of it is then seen to be zero, i.e. \( \langle N_1 \nu_{11}(0) \rangle / V = 0 \). Thus
\[
\dot{\mathbf{M}}_{11}(r', t) = \mathbf{u} + \frac{\rho}{n_1} \int d\mathbf{r}'' \left( N_1 \delta(r' - r_{11}(0)) \nu_{11}(t) \left[ \frac{\tilde{n}_1(r'')}{cm_2 n} - \frac{\tilde{n}_2(r'')}{(1 - c)m_1 n} \right] \right) \\
\times (r'' - r + \mathbf{u} t) \cdot \nabla c,
\]
where we also replaced \( n_1(r', 0) \) by \( n_1(r, t) \), since the difference can be expressed in terms of gradients and would contribute only to second order in the gradients in equation (B.3). The term proportional to \((-r + \mathbf{u} t)\) can be integrated over \( r'' \). Using \( \int d\mathbf{r}'' \tilde{n}_\lambda(r'') = N_\lambda \), this yields factors of \( N_1^2 \) and \( N_1 N_2 \) times \( \nu_{11}(t) \delta(r' - r_{11}(0)) \). By the same reasoning as above this is zero, and we are left with
\[
\dot{\mathbf{M}}_{11}(r', t) = \mathbf{u} + \frac{\rho}{n_1} \int d\mathbf{r}'' \left( N_1 \delta(r' - r_{11}(0)) \nu_{11}(t) \left[ \frac{\tilde{n}_1(r'')}{cm_2 n} - \frac{\tilde{n}_2(r'')}{(1 - c)m_1 n} \right] \right) r'' \cdot \nabla c. \tag{B.4}
\]
The remaining integral over \( r'' \) can be performed by using the explicit forms of \( \tilde{n}_1(r'') \) and \( \tilde{n}_2(r'') \) in equation (A.4). This gives:
\[
\dot{\mathbf{M}}_{11}(r', t) = \mathbf{u} + \frac{\rho}{n_1} \left( N_1 \nu_{11}(t) \delta(r' - r_{11}(0)) \right) \left[ \frac{r'}{cm_2 n} + \sum_{i=2}^{N_1} \frac{r_{1i}(0)}{cm_2 n} - \sum_{i' = 1}^{N_2} \frac{r_{2i'}(0)}{(1 - c)m_1 n} \right] \cdot \nabla c.
\]
Here we have written out the term \( i = 1 \) explicitly. This term is in fact zero: once the factor of \( \nu' \) has been taken out of the average, we can use the above reasoning that the remainder by translation invariance does not depend on \( r' \) and can be integrated over \( r' \), after which we have an integral of a time invariant expression times \( \nu_{11}(t) \), which is zero. Using also that the particles of each component are indistinguishable, we find
\[
\dot{\mathbf{M}}_{11}(r', t) = \mathbf{u} + \frac{\rho}{n_1} \left[ \frac{\langle \delta(r' - r_{11}(0)) N_1 (N_1 - 1) \nu_{11}(t) r_{12}(0) \rangle}{cm_2 n} - \frac{\langle \delta(r' - r_{11}(0)) N_1 N_2 \nu_{11}(t) r_{21}(0) \rangle}{(1 - c)m_1 n} \right] \cdot \nabla c. \tag{B.5}
\]
This whole expression is independent of \( r' \). It may seem to change under translation over some fixed vector \( \mathbf{s} \) as this would change \( r_{\lambda i} \) to \( r_{\lambda i} + \mathbf{s} \). However, the prefactor in front of \( \mathbf{s} \) that results is itself independent of \( r' \), can therefore be integrated over \( r' \), and is then zero because of the factor \( \nu_{11}(t) \). Hence the expression is translation invariant and may be integrated over \( r' \) and divided by \( V \). This then gives equation (84).
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