Nonequilibrium Statistical Mechanics of Systems Interacting with Nonadditive Forces. III. Properties to First Order in the Density

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We obtain the transport coefficients up to first order in the density for a system of particles interacting with nonadditive forces. To zeroth order in the density we recover the usual results obtained from the Boltzmann equation. To first order in the density one finds that the transport coefficients consist of two parts: the value of the corresponding quantities for a system with only additive forces, plus a contribution due to nonadditive forces.

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1. INTRODUCTION

In two earlier-papers[1,2] (hereafter referred to as I and II; here we use the same notation as in these papers) we started the study of nonequilibrium statistical mechanics of systems interacting with nonadditive forces. In paper I we obtained the hydrodynamic equations for these systems and the explicit expressions for the contribution due to nonadditive forces to the stress tensor and the heat current. In paper II we set up the general kinetic equation using Bogolyubov's functional assumption. Furthermore, after linearizing in the gradients we solved this equation using a Chapman–Enskog method, and finally obtained the explicit expressions for the shear and bulk viscosities and thermal conductivity. It should be mentioned that all the results obtained in II were obtained without using series expansions in the density of the relevant quantities.

It is the purpose of this paper to discuss the density expansion of the transport coefficients, and obtain the explicit effect of the nonadditivity of the intermolecular potential on the triple collision part of these quantities. Therefore we restrict ourselves in this paper to quantities up to first order in the density.

In Section 2 we solve the generalization of the BBGKY hierarchy for systems with nonadditive forces obtained in paper II, as a power series in the density. We use, for this purpose, the ideas on the boundary conditions discussed elsewhere (Ref. 3; hereafter referred to as III). We also demonstrate in this section the fact that in our one-component system no diffusion is present. As was mentioned in Appendix B of II, we can only prove this by making density expansions of the two- and three-body distribution functions.

In Section 3 we find the explicit expressions for the transport coefficients. To zeroth order in the density the nonadditive potentials do not play any role, and we recover the usual Boltzmann results. To first order in the density we find that the transport coefficients consist of two parts; the contribution of the additive part of the potential, obtained in another paper (Ref. 4; hereafter referred to as IV), and an explicit contribution due to nonadditive forces.

2. THE TWO-BODY DISTRIBUTION FUNCTION

In this section we proceed to obtain from the generalization of the BBGKY hierarchy to systems that interact with nonadditive forces the two-body distribution function up to first order in the density.

The generalized BBGKY hierarchy was obtained in paper II and can be

written in terms of the reduced distribution functions in phase space F_s as

$$(\partial F_s/\partial t) + \mathfrak{H}_s F_s = \sum_{k=1}^{s} n \int dx_{s+1} \, [\nabla_{q_k}\varphi_{k,s+1}] \cdot \nabla_{p_k} F_{s+1}$$

$$+ \tfrac{1}{2}\sum_{k\neq j}^{s}\sum n \int dx_{s+1} \, [\nabla_{q_k} w_{k,j,s+1}] \cdot \nabla_{p_k} F_{s+1}$$

$$+ \sum_{k=1}^{s} n^2 \int dx_{s+1} \, dx_{s+2} \, [\nabla_{q_k} w_{k,s+1,s+2}] \cdot \nabla_{p_k} F_{s+2},$$

$$s = 1, 2,... \quad (1)$$

where

$$\mathfrak{H}_s = \sum_{k=1}^{s} (\mathbf{p}_k/m)\cdot\nabla_{p_k} - \sum_{k\neq j}^{s}\sum [\nabla_{q_k}\varphi_{kj}]\cdot\nabla_{p_k}$$

$$- \tfrac{1}{2}\sum_{k\neq j\neq l}^{s}\sum\sum [\nabla_{q_k} w_{kjl}]\cdot\nabla_{p_k} \equiv \mathscr{H}_s + \Delta_s \quad (2)$$

Here $\mathscr{H}_s$ is the additive hamiltonian operator given in Eq. (4) of III, and Δ_s is the nonadditive part of $\mathfrak{H}_s$. Furthermore, we have taken the thermodynamic limit $(N \to \infty, \ V \to \infty, \ N/V = n, \ \text{finite})$. Equation (1) can be rewritten in a more convenient form as follows:

$$(\partial F_s/\partial t) + \mathfrak{H}_s F_s = \sum_{k=1}^{s} n \int dx_{s+1} \, \theta_{k,s+1} F_{s+1}$$

$$+ \tfrac{1}{2}\sum_{k\neq j}^{s}\sum n \int dx_{s+1} \, \zeta_{k,j,s+1} F_{s+1}$$

$$+ \sum_{k=1}^{s} n^2 \int dx_{s+1} \, dx_{s+2} \, \zeta_{k,s+1,s+2} F_{s+2}, \qquad s = 1, 2,... \quad (3)$$

where

$$\theta_{kj} \equiv [\nabla_{q_k}\varphi_{kj}]\cdot\nabla_{p_k} + [\nabla_{q_j}\varphi_{kj}]\cdot\nabla_{p_j} \quad (4)$$

and

$$\zeta_{kjl} = [\nabla_{q_k} w_{kjl}]\cdot\nabla_{p_k} + [\nabla_{q_j} w_{kjl}]\cdot\nabla_{q_j} + [\nabla_{q_l}\cdot w_{kjl}]\cdot\nabla_{q_l} \quad (5)$$

In particular, for $s = 1$ we find that

$$(\partial F_1/\partial t) + (\mathbf{p}/m)\cdot\nabla_q F_1 = n \int dx_2 \, \theta_{12} F_2(x_1, x_2; t)$$

$$+ n^2 \int dx_2 \, dx_3 \, \zeta_{123} F_3(x_1, x_2, x_3; t) \quad (6)$$

Here we have set $x \equiv x_1$.

As we have done in II, we now make Bogolyubov's functional assumption, namely that the distribution functions of more than one particle are time-independent functionals of the one-particle distribution function

$$F_s(x_1,...,x_s;t) = F_s(x_1,...,x_s|F_1(x;t)), \qquad s \geq 2 \tag{7}$$

This assumption is only valid in the kinetic stage of the evolution of the system toward its equilibrium state. Substitution Eq. (7) into Eq. (6), one obtains the kinetic equation in the form

$$\partial F_1/\partial t = B(x|F_1) \tag{8}$$

We now expand B and F_s in a power series in the density n,

$$F_s(\cdots|F_1) = \sum_{l=0}^{\infty} n_s{}^l F_s^{(l)}(\cdots|F_1) \tag{9}$$

and

$$B(x|F_1) = \sum_{l=0}^{\infty} n^l B_l(x|F_1) \tag{10}$$

Substituting Eq. (9) into Eq. (6) and Eq. (10) into Eq. (8) and comparing the coefficients of the same powers in the density, we obtain

$$B_0 = -(\mathbf{p}/m)\cdot\nabla_q F_1 \tag{11a}$$

$$B_1 = \int dx_2\, \theta_{12} F_2^{(0)} \tag{11b}$$

$$B_2 = \int dx_2\, \theta_{12} F_2^{(1)} + \int dx_2\, dx_3\, \zeta_{123} F_3^{(0)} \tag{11c}$$

$$\vdots$$

$$B_l = \int dx_2\, \theta_{12} F_2^{(l-1)} + \int dx_2\, dx_3\, \zeta_{123} F_3^{(l-2)}, \qquad l \geq 2 \tag{11d}$$

If we now substitute Eq. (9) into the hierarchy, Eq. (3), and separate different orders in the density, we find that

$$\mathscr{D}_0 F_s^{(0)} + \mathfrak{H}_s F_s^{(0)} = 0 \tag{12a}$$

$$\mathscr{D}_0 F_s^{(1)} + \mathfrak{H}_s F_s^{(1)} = -\mathscr{D}_1 F_s^{(0)} + \sum_{k=1}^{s} \int dx_{s+1}\, \theta_{k,s+1} F_{s+1}^{(0)}$$

$$+ \tfrac{1}{2} \sum_{k \neq j}^{s} \sum \int dx_{s+1}\, \zeta_{k,j,s+1} F_{s+1}^{(0)} \equiv \mathfrak{P}_s^{(1)} \tag{12b}$$

$$\vdots$$

$$\mathscr{D}_0 F_s^{(l)} + \mathfrak{H}_s F_s^{(l)} = -\sum_{r=1}^{l} \mathscr{D}_r F_s^{(l-r)} + \sum_{k=1}^{s} \int dx_{s+1}\, \theta_{k,s+1} F_{s+1}^{(l-1)}$$

$$+ \tfrac{1}{2} \sum_{k \neq j}^{s} \sum \int dx_{s+1}\, \zeta_{k,j,s+1} F_{s+1}^{(l-1)}$$

$$+ \sum_{k=1}^{s} \int dx_{s+1}\, dx_{s+2}\, \zeta_{k,s+1,s+2} F_{s+2}^{(l-2)} \equiv \mathfrak{P}_s^{(l)}, \quad l \geq 2 \tag{12c}$$

Here we have defined the operator $\mathscr{D}_k$ as

$$\mathscr{D}_k \psi(\cdots|F_1) = [\delta\psi/\delta F_1, B_k(\cdots|F_1)] \tag{13}$$

where $(\delta\psi/\delta F_1)$ denotes the functional derivative of ψ with respect to F_1, and B_k is given by Eqs. (11a)–(11d).

Equations (12a)–(12c) are the differential equations satisfied by $F_s^{(l)}$. The solution is obtained in the same way as is done in the case of systems with purely additive forces.[3,5] We shall only write down the solutions. From Eq. (12a) one finds that

$$F_s^{(0)}(\cdots|F_1) = \mathfrak{S}_s^{-\tau}F_s^{(0)}(\cdots|\mathfrak{S}_1^{\tau}F_1) \tag{14a}$$

and in general from Eq. (12c)

$$F_s^{(l)}(\cdots|F_1) = \mathfrak{S}_s^{-\tau}F_s^{(l)}(\cdots|\mathfrak{S}_1^{\tau}F_1) + \int_0^{\tau} d\tau\, \mathfrak{S}_s^{-\tau}\mathfrak{P}_s^{(l)}(\cdots|\mathfrak{S}_1^{\tau}F_1), \quad l \geq 1 \tag{14b}$$

Here we have introduced the streaming operator of s particles as

$$\mathfrak{S}_s^{\tau}(x_1,\ldots,x_s) = \exp\{\tau\mathfrak{H}_s(x_1,\ldots,x_s)\} \tag{15}$$

with $\mathfrak{H}_s$ given by Eq. (2).

We now proceed to consider the right-hand sides of Eqs. (14a) and (14b) in the usual way.[3,5] Due to the fact that the left-hand sides of Eqs. (14a) and (14b) do not depend on τ, the right-hand sides do not depend on τ either. Therefore we can take $\tau \to \infty$ in Eqs. (14a) and (14b). At this point we introduce, following the ideas advanced in III, the following boundary conditions:

$$\lim_{\tau\to\infty} \mathfrak{S}_s^{-\tau}F_s^{(0)}(\cdots|\mathfrak{S}_1^{\tau}F_1) = (1 - \mathfrak{g}_s^{(0)}) \lim_{\tau\to\infty} \mathfrak{S}_s^{-\tau} \prod_{i=1}^{s} \mathfrak{S}_1^{\tau}(x_i)F_1(x_i) \tag{16a}$$

and

$$\lim_{\tau\to\infty} \mathfrak{S}_s^{-\tau}F_s^{(l)}(\cdots|\mathfrak{S}_1^{\tau}F_1) = \mathfrak{g}_s^{(l)} \lim_{\tau\to\infty} \mathfrak{S}_s^{-\tau} \prod_{i=1}^{s} \mathfrak{S}_1^{\tau}(x_i)F_1(x_i), \quad l \geq 1 \tag{16b}$$

Here we have introduced the s-body local equilibrium correlation function $\mathfrak{g}_s$, given by its series expansion

$$\mathfrak{g}_s = \sum_{l=0}^{\infty} n^l \mathfrak{g}_s^{(l)} \tag{17}$$

As was done in III, we take the local equilibrium value of the correlation function because we are interested in evaluating the distribution functions in the hydrodynamic regime, in order to calculate transport coefficients.

As we discussed in III and IV, the use of the boundary conditions given by Eqs. (16a) and (16b) will ensure the existence of a bona fide virial expansion for the transport coefficients.

It is now a straightforward matter to manipulate the right-hand sides of Eqs. (14a) and (14b) with the aid of Eqs. (16a) and (16b). Since this manipulation is the same as the one done for a system with additive forces,[3,5,6] we do not repeat it here. We will just quote the final results. To zeroth order in the density one obtains from Eqs. (14a) and (16a) that

$$F_s^{(0)}(x_1,...,x_s|F_1) = \Gamma_s(\mathbf{q}_1,...,\mathbf{q}_s)\mathfrak{W}_s(x_1,...,x_s)\prod_{i=1}^{s} F_1(x_i) \qquad (18)$$

where

$$\Gamma_s(\mathbf{q}_1,...,\mathbf{q}_s) \equiv 1 - \mathfrak{g}_s^{(0)} = 1 - \exp\left\{-\beta\left[\tfrac{1}{2}\sum_{i\neq j}^{s}\varphi_{ij} + \tfrac{1}{6}\sum_{i\neq j\neq k}^{s}w_{ijk}\right]\right\} \quad (19)$$

$$\mathfrak{W}_s(x_1,...,x_s) = \lim_{\tau\to\infty} \mathfrak{S}_s^{-\tau}(x_1,...,x_s)\prod_{i=1}^{s}\mathfrak{S}_1^{\tau}(x_i) \qquad (20)$$

and $\beta = (kT)^{-1}$, k being Boltzmann's constant and T the local temperature.

As is shown in Section 3, it will be necessary, insofar as transport coefficients to first order in the density are concerned, to obtain only the two-body distribution function to first order in the density $F_2^{(1)}$. This is found to be

$$F_2^{(1)}(x_1, x_2|F_1) = \mathfrak{g}_2^{(1)}(\mathbf{q}_1, \mathbf{q}_2)\mathfrak{W}_2(x_1, x_2)F_1(x_1)F_1(x_2)$$

$$+ \int dx_3\,\mathscr{L}(x_1, x_2, x_3)F_1(x_1)F_1(x_2)F_1(x_3) \qquad (21)$$

where the operator $\mathscr{L}(x_1, x_2, x_3)$ is given by

$$\mathscr{L}(x_1, x_2, x_3) = \int_0^{\infty} d\tau\,\mathfrak{S}_2^{-\tau}(x_1, x_2)$$

$$\times \{(\theta_{13} + \theta_{23} + \zeta_{123})\Gamma_3(x_1, x_2, x_3)\mathfrak{W}_3(x_1, x_2, x_3)$$

$$- \Gamma_2(x_1, x_2)\mathfrak{W}_2(x_1, x_2)[\theta_{13}\Gamma_2(x_1, x_3)\mathfrak{W}_2(x_1, x_3)$$

$$+ \theta_{23}\Gamma_2(x_2, x_3)\mathfrak{W}_2(x_2, x_3)]\} \qquad (22)$$

We will now rewrite the operator $\mathscr{L}$ in a more convenient form. For this purpose, we notice that, with the aid of Eq. (2), the streaming operator $\mathfrak{S}_s^{\tau}$ [Eq. (15)] is

$$\mathfrak{S}_s^{\tau} = \exp\{\tau\mathfrak{S}_s\} = \exp\{\tau(\mathscr{H}_s + \Delta_s)\} = (e^{\tau(\mathscr{H}_s+\Delta_s)} - e^{\tau\mathscr{H}_s}) + e^{\tau\mathscr{H}_s}$$

$$= (e^{\tau(\mathscr{H}_s+\Delta_s)}e^{-\tau\mathscr{H}_s} - 1)e^{\tau\mathscr{H}_s} + e^{\tau\mathscr{H}_s}$$

$$= (\mathfrak{S}_s^{\tau}S_s^{-\tau} - 1)S_s^{\tau} + S_s^{\tau} \qquad (23)$$

where

$$S_s^{\tau} \equiv \exp\{\tau \mathcal{H}_s\} \tag{24}$$

is the streaming operator of a system with additive forces. Due to the fact that [see Eq. (2)]

$$\mathfrak{H}_i = \mathcal{H}_i \qquad i = 1, 2 \tag{25}$$

we have that

$$\mathfrak{S}_i^{\tau} = S_i^{\tau} \qquad i = 1, 2 \tag{26}$$

Therefore, from the definition of $\mathfrak{W}_s$, given by Eq. (20), we find that

$$\mathfrak{W}_s = \mathfrak{R}_s \mathcal{S}_s + \mathcal{S}_s \tag{27}$$

where

$$\mathfrak{R}_s = \lim_{\tau \to \infty} (\mathfrak{S}_s^{\tau} S_s^{-\tau} - 1) \tag{28}$$

and

$$\mathcal{S}_s(x_1, ..., x_s) = \lim_{\tau \to \infty} S_s^{-\tau}(x_1, ..., x_s) \prod_{i=1}^{s} S_1^{\tau}(x_i) \tag{29}$$

is the operator corresponding to a system with additive forces.

From Eq. (19) we can write

$$\Gamma_3 = \Gamma_{3ad} + (\Gamma_a - \Gamma_{3ad}) \tag{30}$$

where

$$\Gamma_{3ad} = 1 - g_{3ad}^{(0)} = 1 - \exp\left\{-\tfrac{1}{2}\beta \sum_{i \neq j}^{3} \varphi_{ij}\right\} \tag{31}$$

Further, we notice from Eq. (19) that Γ_2 does not have nonadditive contributions, i.e., it is the same function as the one corresponding to a system with additive forces. Using Eqs. (27) and (30) in Eq. (22), it can be shown in a straightforward way that

$$\mathcal{L}(x_1, x_2, x_3) = \mathcal{O}_3(x_1, x_2, x_3) + \mathcal{Q}(x_1, x_2, x_3) \tag{32}$$

where $\mathcal{O}_3$ is the operator for a system with additive forces, and is given by Eq. (30) of III. The operator $\mathcal{Q}$ is the contribution to $\mathcal{L}$ due to nonadditive forces, and is given by

$$\mathcal{Q}(x_1, x_2, x_3) = \int_0^{\infty} d\tau \, S_2^{-\tau}(x_1, x_2)(\theta_{13} + \theta_{23})$$
$$\times [\Gamma_3 \mathfrak{R}_3 + (\Gamma_3 - \Gamma_{3ad})] \mathcal{S}_3(x_1, x_2, x_3)$$
$$+ \int_0^{\infty} d\tau \, S_2^{-\tau}(x_1, x_2) \zeta_{123} [\Gamma_3 \mathfrak{R}_3 + \Gamma_3] \mathcal{S}_3(x_1, x_2, x_3) \tag{33}$$

It should be noted that if there are no contributions due to nonadditive forces, then $\mathcal{Q} = 0$, $\mathcal{L} = \mathcal{O}_3$, and we recover the theory for systems with additive forces developed in III and IV.

Substituting Eq. (32) into Eq. (21), we obtain

$$F_2^{(1)}(x_1, x_2 | F_1) = F_2^{(1)}(x_1, x_2 | F_1)_{\mathrm{ad}} + F_2^{(1)}(x_1, x_2 | F_1)_{na} \qquad (34)$$

where $F_2^{(1)}(x_1, x_2 | F_1)_{\mathrm{ad}}$ is the two-body distribution function to first order in the density corresponding to a system with additive forces, and is given by Eq. (29) of III. $F_2^{(1)}(x_1, x_2 | F_1)_{na}$ is the contribution due to nonadditive forces to the two-body distribution function to first order in the density, and is given by

$$F_2^{(1)}(x_1, x_2 | F_1)_{na} = (\mathfrak{g}_2^{(1)} - \mathfrak{g}_{2\mathrm{ad}}^{(1)}) \mathscr{S}_2(x_1, x_2) F_1(x_1) F_1(x_2)$$

$$+ \int dx_3 \, \mathscr{Q}(x_1, x_2, x_3) F_1(x_1) F_1(x_2) F_1(x_3) \qquad (35)$$

Here $\mathfrak{g}_{2\mathrm{ad}}^{(1)}$ is the term to first order in the density of the local equilibrium pair-correlation function of a system with additive forces.

Before proceeding to calculate the transport coefficients, we would like to turn the attention to a pending problem. It was mentioned in paper II that due to the fact that we are dealing with a one-component gas, no diffusion should be present. Therefore the vector $\mathbf{D}(\mathbf{p})$ defined by Eq. (3.20) of II should vanish. It was shown in Appendix B of paper II that in order to prove that $\mathbf{D}(\mathbf{p}) = 0$, it was enough to demonstrate that the quantities a, k, and j defined by Eqs. (B4) and (B5) of II are proportional to the single distribution function. It was also mentioned that without a density expansion of the two- and three-body distribution functions we had not been able to demonstrate this property of a, k, and j. We would like to show now this property of the functions a, k, and j. Since the proof is the same up to first order in the density as it is for any order, we proceed to present the proof in general.

One can obtain, in the same way as was done for $F_2^{(1)}$, any term in the density expansion of F_2 and F_3. It can be shown[7] that $F_s^{(l)}$ ($s = 2, 3; l \geqslant 1$) is of the form

$$F_s^{(l)}(\cdots | F_1) = \mathfrak{g}_s^{(l)} \mathfrak{W}_s F_1(x_1) \cdots F_1(x_s)$$

$$+ \sum_{r=s+1}^{r=l+s} \int dx_{s+1} \cdots dx_r \, \mathfrak{T}_{rl} \prod_{i=1}^{r} F_1(x_i), \qquad s = 2, 3; \quad l \geqslant 1 \quad (36)$$

where $\mathfrak{T}_{rl}$ is an operator. Therefore we can write from Eq. (9), with the aid of Eqs. (17), (18), and (36), that

$$F_s(\cdots | F_1) = (1 - 2\mathfrak{g}_s^{(0)} + \mathfrak{g}_s) \mathfrak{W}_s \prod_{i=1}^{s} F_1(x_i)$$

$$+ \sum_{l=1}^{\infty} n^l \sum_{r=s+1}^{r=l+s} \int dx_{s+1} \cdots dx_r \, \mathfrak{T}_{rl} \prod_{i=1}^{r} F_1(x_i), \qquad s = 2, 3 \quad (37)$$

The functional derivative of F_s taken at point x' and evaluated for the

equilibrium distribution function $F_1{}^e$ is

$$F_s'(..., x' | F_1{}^e) F_1{}^e(\mathbf{p}') = (1 - 2\mathfrak{g}_s{}^{(0)} + \mathfrak{g}_s) \mathfrak{W}_s \prod_{i=1}^{s} F_1{}^e(\mathbf{p}_i) \sum_{j=1}^{s} \delta(x' - x_j)$$

$$+ \sum_{l=1}^{\infty} n^l \sum_{r=s+1}^{r=l+s} \int dx_{s+1} \cdots dx_r$$

$$\times \mathfrak{S}_{rl} \prod_{i=1}^{r} F_1{}^e(\mathbf{p}_i) \sum_{j=1}^{r} \delta(x' - x_i), \qquad s = 2, 3 \qquad (38)$$

Substituting this expression into Eqs. (B4) and (B5) of paper II, one finds that all the quantities a, b, c, d, e, f, j, and k are proportional to the single distribution function. Therefore we can conclude that $\mathbf{D(p)} = 0$ and for our system there is no diffusion.

In the next section we will obtain the explicit expressions of the transport coefficients up to first order in the density.

3. THE TRANSPORT COEFFICIENTS

In the last section we obtained the two-body distribution function up to first order in the density. With this function we can now proceed to construct the kernels of the integral equations for the $\mathscr{G}$, $\mathscr{A}$, and $\mathscr{B}$ functions which determine the transport coefficients (see paper II). For this purpose we make the following series expansions.

For the functional $\Psi(x|f_1)$ that determines the collisional term of the kinetic equation [see Eq. (2.7) of paper II]

$$\Psi = \sum_{l=0}^{\infty} n^{l+2} \Psi^{(l)} \qquad (39)$$

and

$$\mathscr{G} = (1/n)\mathscr{G}_B + \mathscr{G}_0 + n\mathscr{G}_1 + \cdots \qquad (40)$$

$$\mathscr{A} = (1/n)\mathscr{A}_B + \mathscr{A}_0 + n\mathscr{A}_1 + \cdots \qquad (41)$$

and

$$\mathscr{B} = (1/n)\mathscr{B}_B + \mathscr{B}_0 + n\mathscr{B}_1 + \cdots \qquad (42)$$

Substituting these expansions into Eqs. (3.32), (3.33), and (3.34) of II, and separating different orders in the density, one finds the following results.

Using Eq. (18) in the definition of the functional given by Eq. (2.7) of II, we can write

$$\Psi^{(0)}(x|F_1{}^e) = \Phi^{(0)}(x|F_1{}^e) \qquad (43)$$

where $\Phi^{(0)}(x|F_1^e)$ is the functional given in Section 4 of paper IV, i.e., is the same functional that corresponds to a system with only additive forces. Here we have used the relation between the reduced distribution functions in phase space F_s and in μ space f_s, namely $f_s = n^s F_s$. Further,

$$F_1^e(\mathbf{p}) = (2\pi m\theta)^{-3/2} \exp\{-(\mathbf{p} - m\mathbf{u})^2/2m\theta\} \tag{44}$$

and the rest of the symbols are defined elsewhere.[2]

Thus to zeroth order in the density one finds that there are no effects due to nonadditive forces; there are just contributions of binary collisions. To this order, $\mathscr{G}_B$ and $\mathscr{A}_B$ are the corresponding functions obtained from the linearized Boltzmann equation (see Section 3 of paper IV). Further, one finds that $\mathscr{B}_B = 0$. The transport coefficients are, to this order, precisely the ones obtained for dilute gases.[8]

To first order in the density one finds

$$\tfrac{1}{2}F_1^e(\mathbf{p})(\mathscr{P}/m)(d/d\theta)[\theta B_1(\theta)]$$

$$- \int \Psi''^{(0)}(x_1, x'|F_1^e(\mathbf{q}))F_1^e(\mathbf{p}')(\mathbf{q}' - \mathbf{q})(\mathscr{P}'^2/2m\theta - \tfrac{3}{2})\,dx'$$

$$+ \int \Psi''^{(1)}(x, \mathbf{p}'|F_1^e(\mathbf{q}))F_1^e(\mathbf{p}')\mathscr{P}'\mathscr{G}_B(\mathscr{P}')\,d\mathbf{p}'$$

$$= \int \Psi''^{(0)}(x, \mathbf{p}'|F_1^e(\mathbf{q}))F_1^e(\mathbf{p}')\mathscr{P}'\mathscr{G}_0(\mathbf{p}')\,d\mathbf{p}' \tag{45a}$$

$$\int \Psi''^{(1)}(x, \mathbf{p}'|F_1^e(\mathbf{q}))F_1^e(\mathbf{p}')\mathscr{P}'^0\mathscr{P}'\mathscr{A}_B(p')\,d\mathbf{p}'$$

$$- (1/\theta) \int \Psi''^{(0)}(x, x'|F_1^e(\mathbf{q}'))S^0 S F_1^e(p')\,dx'$$

$$= - \int \Psi''^{(0)}(x, \mathbf{p}'|F_1^e(\mathbf{q}))F_1^e(p')\mathscr{P}'^0\mathscr{P}'\mathscr{A}_0(p')\,d\mathbf{p}' \tag{45b}$$

In Eq. (45a) $B_1(\theta)$ is the second virial coefficient.

We do not consider the equation for $\mathscr{B}_0$, the function which appears in the bulk viscosity, because this latter quantity is at least of second order in the density.

For this order in the density we use Eq. (34) in the definition of the functional Ψ and find that

$$\Psi^{(1)}(x|F_1^e) = \Psi_{\mathrm{ad}}^{(1)}(x|F_1^e) + \Psi_{\mathrm{na}}^{(1)}(x|F_1^e) \tag{46}$$

Here $\Psi_{\mathrm{ad}}^{(1)}$ is the functional to first order in the density for a system with additive forces, and is given in paper IV; $\Psi_{\mathrm{na}}^{(1)}$ is the nonadditive contribution,

and is given by

$$\Psi_{\text{na}}^{(1)}(x_1|F_1{}^e) = \int dx_2\, \theta_{12}(\mathfrak{g}_2{}^{(1)} - g_{2\text{ad}}^{(1)})\mathscr{S}_2 F_1{}^e(x_1)F_1{}^e(x_2) + \int dx_2\, dx_3$$

$$\times\, [\theta_{12}\mathscr{Q}(x_1, x_2, x_3) + \zeta_{123}\Gamma_3(x_1, x_2, x_3)] \prod_{i=1}^{3} F_1{}^e(x_i) \quad (47)$$

Using Eqs. (43) and (46) in the integral equations (45a) and (45b), one finds that the unknown functions $\mathscr{G}_0$ and $\mathscr{A}_0$ can be written as

$$\mathscr{G}_0 = (\mathscr{G}_0)_{\text{ad}} + (\mathscr{G}_0)_{\text{na}} \quad (48)$$

$$\mathscr{A}_0 = (\mathscr{A}_0)_{\text{ad}} + (\mathscr{A}_0)_{\text{na}} \quad (49)$$

where $(\mathscr{G}_0)_{\text{ad}}$ and $(\mathscr{A}_0)_{\text{ad}}$ are the functions corresponding to a system of additive forces, and satisfy the integral equations given by Eqs. (24) and (30) of paper IV. The nonadditive contributions satisfy the following integral equations:

$$\int \Psi_{\text{na}}^{\prime(1)}(x, \mathbf{p}'|F_1{}^e)F_1{}^e(\mathbf{p}')\mathscr{P}'\mathscr{G}_B(\mathbf{p}')\, d\mathbf{p}'$$

$$= \int \Phi^{\prime(0)}(x, \mathbf{p}'|F_1{}^e)F_1{}^e(\mathbf{p}')\mathscr{P}'(\mathscr{G}_0)_{\text{na}}\, d\mathbf{p}' \quad (50a)$$

and

$$\int \Psi_{\text{na}}^{\prime(1)}(x, \mathbf{p}'|F_1{}^e)F_1{}^e(\mathbf{p}')\mathscr{P}'^0\mathscr{P}'\mathscr{A}_B(\mathbf{p}')\, d\mathbf{p}'$$

$$= -\int \Phi^{\prime(0)}(x, \mathbf{p}'|F_1{}^e)F_1{}^e(\mathbf{p}')\mathscr{P}'^0\mathscr{P}'(\mathscr{A}_0)_{\text{na}}\, d\mathbf{p}' \quad (50b)$$

Substituting the explicit expressions for $\Phi^{\prime(0)}$ and $\Psi_{\text{na}}^{\prime(1)}$ given by Eqs. (43) and (47) into Eqs. (50a) and (50b), one obtains the following integral equations for $(\mathscr{G}_0)_{\text{na}}$ and $(\mathscr{A}_0)_{\text{na}}$:

$$\int dx_2\, \theta_{12}(\mathfrak{g}_2{}^{(1)} - g_{2\text{ad}}^{(1)})\mathscr{S}_2(x_1, x_2)F_1{}^e(x_1)F_1{}^e(x_2) \sum_{i=1}^{2} \mathscr{P}_i\mathscr{G}_B(\mathscr{P}_i)$$

$$+ \int dx_2\, dx_3\, [\theta_{12}\mathscr{Q}(x_1, x_2, x_3) + \zeta_{123}\Gamma_3(x_1, x_2, x_3)]$$

$$+ \prod_{i=1}^{3} F_1{}^e(x_i) \sum_{j=1}^{3} \mathscr{P}_i\mathscr{G}_B(\mathscr{P}_i) = C_B(\mathscr{P}(\mathscr{G}_0)_{\text{na}}) \quad (51a)$$

and

$$-\int dx_2\, \theta_{12}(\mathfrak{g}_2{}^{(1)} - g_{2\text{ad}}^{(1)})\mathscr{S}_2(x_1, x_2)F_1{}^e(x_1)F_1{}^e(x_2) \sum_{i=1}^{2} \mathscr{P}_i^0\mathscr{P}_i\mathscr{A}_B(\mathscr{P}_i)$$

$$- \int dx_2\, dx_3\, [\theta_{12}\mathscr{Q}(x_1, x_2, x_3) + \zeta_{123}\Gamma_3(x_1, x_2, x_3)]$$

$$\times \prod_{i=1}^{3} F_1{}^e(x_i) \sum_{i=1}^{3} \mathscr{P}_i^0\mathscr{P}_i\mathscr{A}_B(\mathscr{P}_i) = C_B(\mathscr{P}^0\mathscr{P}(\mathscr{A}_0)_{\text{na}}) \quad (51b)$$

The operator C_B that appears in Eqs. (51a) and (51b) is the usual linearized Boltzmann operator which is given, in the usual notation, by[4,8]

$$C_B(h) = \iint d\mathbf{p}_2 \, d\Omega \, I(g, \epsilon) F_1{}^e(\mathbf{p}_2)[h(\mathbf{p}_1') + h(\mathbf{p}_2') - h(\mathbf{p}_1) - h(\mathbf{p}_2)] \quad (52)$$

The function $(\mathscr{G}_0)_{na}$ has to satisfy, additionally, the following subsidiary condition:

$$\int d\mathbf{p} \, F_1{}^e(\mathbf{p}) p^2 (\mathscr{G}_0)_{na} = 0 \quad (53)$$

There is no further condition on $(\mathscr{A}_0)_{na}$.

The general expressions for the transport coefficients corresponding to a system with nonadditive forces are given in paper II. These expressions were obtained without recourse to density expansions. If we now expand these expressions, we find to first order in the density the following results.

The shear viscosity is [see Eq. (4.15) of paper II]

$$(\eta)^{(1)} = (\eta)_{ad}^{(1)} + (\eta_\kappa)_{na}^{(1)} \quad (54)$$

where $(\eta)_{ad}^{(1)}$ is the shear viscosity of an additive system and is given by Eq. (38) of paper IV. The contribution of nonadditive forces is just kinetic, up to this order in the density, and is given by

$$(\eta_\kappa)_{na}^{(1)} = -(1/15m) \int d\mathbf{p} \, \mathscr{P}^4 F_1{}^e(\mathbf{p})(\mathscr{A}_0)_{na} \quad (55)$$

The coefficient of thermal conductivity is [see Eq. (4.29) of paper II]

$$(\lambda)^{(1)} = (\lambda)_{ad}^{(1)} + (\lambda_\kappa)_{na}^{(1)} \quad (56)$$

where $(\lambda)_{ad}^{(1)}$ is the thermal conductivity of an additive system, and is given by Eq. (34) of paper IV. The nonadditive contribution is also of kinetic origin, and is expressed as

$$(\lambda_\kappa)_{na}^{(1)} = -(1/6m^2\theta) \int d\mathbf{p} \, \mathscr{P}^4 F_1{}^e(\mathscr{P})(\mathscr{G}_0)_{na} \quad (57)$$

The coefficient of bulk viscosity vanishes to this order in the density. The demonstration of this fact is made using the same arguments as given by several authors (see, e.g., Ref. 9) and we do not repeat it here.

To summarize, we have obtained in this paper the transport coefficients, up to first order in the density, of a system interacting with nonadditive forces. It was found that to zeroth order in the density only the additive part of the potential plays a role, and we obtain the usual Boltzmann transport coefficients. To first order in the density one obtains the result that the

transport coefficients consist of two parts, the transport coefficients corresponding to just the additive potential, and a nonadditive contribution of kinetic origin. Therefore in the evaluation of the effects of triple collisions on the transport coefficients one has to take into account, not only those effects due to additive potentials,[10–12] but also the effects due to the nonadditive part of the potential. These latter effects are given by the expressions for $(\eta_\kappa)_{na}^{(1)}$ and $(\lambda_\kappa)_{na}^{(1)}$ given in Eqs. (55) and (57), respectively. In forthcoming publications we will obtain the explicit value of $(\eta_\kappa)_{na}^{(1)}$ and $(\lambda_\kappa)_{na}^{(1)}$ for different intermolecular models.

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