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Nonequilibrium Statistical Mechanics of Systems Interacting with Nonadditive Forces. I. Hydrodynamical Equations

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The hydrodynamical equations for a system of particles interacting with nonadditive forces are obtained. General properties of these forces are discussed and explicit expressions for the contribution of these nonadditive forces to the stress tensor and heat current are given.

I. INTRODUCTION

In the last decades the attention of many authors has been centered in the development of nonequilibrium statistical mechanics for dense media. The aim was to start from Liouville's equation and develop from it the general description of a macroscopic system in a nonequilibrium state. Thus, the equations of hydrodynamics were derived[1,2] and expressions for the stress tensor and heat current densities in terms of molecular variables obtained. Furthermore, Bogolyubov[3] set up a program for the foundation of the kinetic theory of dense gases. In this program a method was proposed to generalize the well-known Boltzmann kinetic equation to describe the approach to equilibrium of a dense gas. Pursuing this method, various authors[4–6] showed that a kinetic equation can be obtained by a cluster expansion of the nonequilibrium distribution functions. This procedure leads to an expansion of the transport coefficients in powers of the density.

On the other hand, the generalized Boltzmann equation was solved[7] without making any reference to a density expansion, and in this way general expressions for the transport coefficients were obtained.

Another method for obtaining transport coefficients in dense gases has been developed.[8] In this method general expressions for the transport coefficients are obtained in terms of equilibrium time-correlation functions. It was also shown that the results obtained using this method are equivalent to those obtained using the kinetic equation.

It should be mentioned, however, that all the work done has been based on the assumption that the potential energy of the system of particles is pairwise additive, i.e., is of the form

$$\frac{1}{2}\sum_{i\neq j}\sum \varphi(|\vec{q}_i - \vec{q}_j|),$$

where $\varphi(|\vec{q}_i - \vec{q}_j|)$ is the intermolecular potential between the molecules situated at the points $\vec{q}_i$ and $\vec{q}_j$.

The calculation of nonadditive corrections to the energy of systems of interacting molecules has been done by several authors.[9] For example, the He-He-He system was studied by Rosen,[10] who used valence-bond theory, and by Shostak,[11] who used a linear-combination-of-atomic-orbitals molecular-orbital (LCAO MO) analysis. Recent calculations made by Bader, Novaro, and Beltrán-López[12] and by Novaro and Beltrán-López,[13] which seem to be correct to the Hartree-Fock limit, show that nonadditive three-body effects may be appreciable for small distances between the molecules.

Therefore, it one tries to develop explicit expressions for triple collision effects on transport coefficients,[14-16] one has to take into account nonadditive intermolecular forces between the particles of a dense system.

It is the purpose of this series of papers to develop the nonequilibrium statistical mechanics of systems that interact with nonadditive forces. In this paper we obtain the corresponding hydrodynamical equations. In Sec. II we discuss general properties of the nonadditive forces. In Sec. III we obtain the hydrodynamic equations, and by so doing we derive the expressions for the stress tensor and heat current densities in terms of the interaction potential. We give the explicit contributions due to nonadditive forces between the particles.

II. NONADDITIVE FORCES

In this sections we present some general properties of the nonadditive forces. Let us consider three particles which we call 1, 2, and 3 (see Fig. 1). The potential energy u of the interaction of these three particles is given by the expression

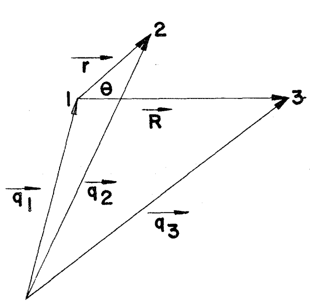

FIG. 1. Positions of particles 1, 2, and 3.

$$u = \varphi(|\vec{q}_1 - \vec{q}_2|) + \varphi(|\vec{q}_1 - \vec{q}_3|) + \varphi(|\vec{q}_2 - \vec{q}_3|) + w(\vec{q}_1, \vec{q}_2, \vec{q}_3). \quad (2.1)$$

Here $\varphi(|\vec{q}_i - \vec{q}_j|)$ is the pair potential between the particles situated at $\vec{q}_i$ and $\vec{q}_j$, and $w(\vec{q}_1, \vec{q}_2, \vec{q}_3)$ is the nonadditive potential between the three particles. It is the properties of the function $w(\vec{q}_1, \vec{q}_2, \vec{q}_3)$ and its derivatives which we now discuss.

Because of translational invariance, this function is of the form

$$w(\vec{q}_1, \vec{q}_2, \vec{q}_3) = w(\vec{q}_2 - \vec{q}_1, \vec{q}_3 - \vec{q}_1); \quad (2.2)$$

i.e., the function w depends on the vectors

$$\vec{r} = \vec{q}_2 - \vec{q}_1, \quad \vec{R} = \vec{q}_3 - \vec{q}_1. \quad (2.3)$$

In fact, it depends on $|\vec{r}|$, $|\vec{R}|$, and θ, the angle between $\vec{r}$ and $\vec{R}$. Therefore, we have that

$$w(\vec{r}, \vec{R}) = w(\vec{R}, \vec{r}). \quad (2.4)$$

Furthermore, we can also write

$$w(-\vec{r}, -\vec{R}) = w(\vec{r}, \vec{R}). \quad (2.5)$$

Now we consider the time derivative of the total momentum $\vec{P}$ of the system, in the absence of external forces. One finds that

$$\frac{d}{dt}\vec{P} = -\sum_{\text{all pairs}}\sum \vec{\nabla}_{q_i}\varphi(|\vec{q}_i - \vec{q}_j|) - \sum_{\text{all triplets}}\sum\sum \vec{\nabla}_{q_i} w(\vec{q}_i, \vec{q}_j, \vec{q}_k). \quad (2.6)$$

As is well known, the first term on the right-hand side vanishes. Consider any triplet of particles, say, 1, 2, and 3. Then in the second term on the right-hand side of Eq. (2.6) there appear terms of the form

$$\vec{\nabla}_{q_1} w + \vec{\nabla}_{q_2} w + \vec{\nabla}_{q_3} w. \quad (2.7)$$

But, using Eqs. (2.3), one finds that

$$\vec{\nabla}_{q_1} w = -\vec{\nabla}_r w - \vec{\nabla}_R w, \quad \vec{\nabla}_{q_2} w = \vec{\nabla}_r w, \quad \vec{\nabla}_{q_3} w = \vec{\nabla}_R w. \quad (2.8)$$

Therefore, we see that the terms of the form (2.7) vanish. Thus, in the absense of external forces, the total momentum of the system is conserved.

From Eqs. (2.8) we also see that the nonadditive force on any particle of the triplet, say, 1, is equal to the negative of the sum of the nonadditive forces on the other two particles:

$$(-\vec{\nabla}_{q_1} w) = -(-\vec{\nabla}_{q_2} w - \vec{\nabla}_{q_3} w). \quad (2.9)$$

This is a generalization of Newton's third law to the case of nonadditive forces.

From Eqs. (2.8) we see that the forces on the particles are given in terms of $\vec{\nabla}_r w$ and $\vec{\nabla}_R w$. These quantities can be written in the form

$$\vec{\nabla}_R w = \vec{R} h_1(\vec{r}, \vec{R}) + \vec{r} h_2(\vec{r}, \vec{R}) \tag{2.10}$$

and

$$\vec{\nabla}_r w = \vec{R} g_1(\vec{r}, \vec{R}) + \vec{r} g_2(\vec{r}, \vec{R}), \tag{2.11}$$

where h_1, h_2, g_1, and g_2 are scalar functions of $\vec{r}$ and $\vec{R}$. In Appendix A we calculate these functions explicitly in terms of the derivatives of w, and show that

$$h_1(\vec{r}, \vec{R}) = g_2(\vec{R}, \vec{r}) \tag{2.12}$$

and

$$h_2(\vec{r}, \vec{R}) = h_2(\vec{R}, \vec{r}) = g_1(\vec{r}, \vec{R}) = g_1(\vec{R}, \vec{r}). \tag{2.13}$$

With these properties we can now demonstrate the conservation of the total angular momentum. In fact, by taking the time derivative of the total angular momentum $\vec{L}$ of the system, in the absence of external forces, one finds that

$$\frac{d}{dt}\vec{L} = -\sum\sum_{\text{all pairs}} \vec{q}_i \times \vec{\nabla}_{q_i} \varphi(|\vec{q}_i - \vec{q}_j|) - \sum\sum\sum_{\text{all triplets}} \vec{q}_i \times \vec{\nabla}_{q_i} w(\vec{q}_i, \vec{q}_j, \vec{q}_k) . \tag{2.14}$$

The first term on the right-hand side vanishes. The second term is a sum of triplets of the form

$$\begin{aligned}
\vec{q}_1 \times \vec{\nabla}_{q_1} w + \vec{q}_2 \times \vec{\nabla}_{q_2} w + \vec{q}_3 \times \vec{\nabla}_{q_3} w
&= -\vec{q}_1 \times (\vec{\nabla}_r w + \vec{\nabla}_R w) + \vec{q}_2 \times \vec{\nabla}_r w + \vec{q}_3 \times \vec{\nabla}_R w \\
&= (\vec{q}_2 - \vec{q}_1) \times \vec{\nabla}_r w + (\vec{q}_3 - \vec{q}_1) \times \vec{\nabla}_R w \\
&= \vec{r} \times (\vec{R} g_1 + \vec{r} g_2) + \vec{R} \times (\vec{R} h_1 + \vec{r} h_2) \\
&= \vec{r} \times \vec{R}(g_1 - h_2) = 0 .
\end{aligned}$$

Here use was made of Eqs. (2.3), (2.10), (2.11), and (2.13). Thus, in the absence of external forces, the total angular momentum of the system is conserved.

III. HYDRODYNAMIC EQUATIONS

In this section we obtain the hydrodynamic equations for a system which interacts with nonadditive forces. We shall follow the method developed by Irving and Kirkwood.[1]

Let us consider a one-component gas consisting of N molecules of mass m enclosed in a volume V. The Hamiltonian of this system will be taken in the form

$$H = \sum_i^N \frac{p_i^2}{2m} + \frac{1}{2}\sum\sum_{i \neq j}^N \varphi(|\vec{q}_i - \vec{q}_j|) + \frac{1}{6}\sum\sum\sum_{i \neq j \neq k}^N w(\vec{q}_i, \vec{q}_j, \vec{q}_k) \equiv \sum_i^N \frac{p_i^2}{2m} + U , \tag{3.1}$$

where $\vec{p}_i$ is the momentum of the ith particle, U is the interaction potential of the system, and the rest of the symbols are defined in Sec. II.

Let $F_N(x_1, \ldots, x_N; t)$ be the distribution function of our system in phase space. $x_i \equiv (\vec{q}_i, \vec{p}_i)$ stands for the momentum $\vec{p}_i$ and position $\vec{q}_i$ of the ith particle. Then, the Liouville equation of the system is

$$\frac{\partial F_N}{\partial t} = \sum_i \left(-\frac{\vec{p}_i}{m} \cdot \vec{\nabla}_{q_i} F_N + \vec{\nabla}_{q_i} U \cdot \vec{\nabla}_{p_i} F_N \right). \tag{3.2}$$

As was shown in Ref. 1, the time derivative of the expectation value of any dynamical variable $\alpha(x_1, \ldots, x_N)$ is given by

$$\frac{\partial}{\partial t}\langle \alpha ; F_N \rangle = \sum_i \left\langle \frac{\vec{p}_i}{m} \cdot \vec{\nabla}_{q_i} \alpha - \vec{\nabla}_{q_i} U \cdot \vec{\nabla}_{p_i} \alpha ; F_N \right\rangle , \tag{3.3}$$

where the expectation value of α, $\langle \alpha; F_N \rangle$, is calculated by means of the expression

$$\langle \alpha; F_N \rangle = \int \alpha(x_1, \ldots, x_N) F_N(x_1, \ldots x_N; t)\, dx_1 \cdots dx_N, \tag{3.4}$$

with $dx_i \equiv d\vec{q}_i\, d\vec{p}_i$.

As is well known, the hydrodynamic equations are obtained by making α equal to

$$m\sum_i \delta(\vec{q}_i - \vec{q}),$$

$$\sum_i \vec{p}_i \delta(\vec{q}_i - \vec{q}) ,$$

$$\sum_i \frac{p_i^2}{2m}\delta(\vec{q}_i - \vec{q}) + \frac{1}{2}\sum\sum_{i \neq j} \varphi(|\vec{q}_i - \vec{q}_j|)\delta(\vec{q}_j - \vec{q}) + \frac{1}{6}\sum\sum\sum_{i \neq j \neq k} w(\vec{q}_i, \vec{q}_j, \vec{q}_k)\delta(\vec{q}_k - \vec{q})$$

successively. The first equation, the equation of continuity, is obtained by setting α equal to $m\sum_i \delta(\vec{q}_i - \vec{q})$ in Eq. (3.3). The result is

$$\frac{\partial}{\partial t}\rho(\vec{q}; t) = -\vec{\nabla}_q \cdot [\rho(\vec{q}; t)\vec{u}(\vec{q}; t)] , \tag{3.5}$$

where the mass density is

$$\rho(\vec{q}; t) = m\int d\vec{p} f_1(\vec{q}, \vec{p}; t) , \tag{3.6}$$

and the local velocity $\vec{u}$ at point $\vec{q}$ is given by

$$\rho(\vec{q}; t)\vec{u}(\vec{q}; t) = \int d\vec{p}\, \vec{p} f_1(\vec{q}, \vec{p}; t) . \tag{3.7}$$

Here we have used the following definitions of the reduced distribution functions in phase space

$$F_s(x_1, \ldots, x_s; t) = V^s \int dx_{s+1} \cdots dx_N F_N(x_1, \ldots, x_N; t) , \tag{3.8}$$

and in μ space

$$f_s = (1/v^s)F_s\,, \tag{3.9}$$

with $v = V/N$.

Next, we take in Eq. (3.3)

$$\vec{\alpha} = \sum_i \vec{p}_i\, \delta(\vec{q}_i - \vec{q})\,, \tag{3.10}$$

obtaining

$$\frac{\partial}{\partial t}\left[\rho(\vec{q};t)\vec{u}(\vec{q};t)\right] = -\vec{\nabla}_q \cdot \sum_i \left\langle \frac{\vec{p}_i\vec{p}_i}{m}\,\delta(\vec{q}_i - \vec{q});\ F_N \right\rangle - \sum_i \left\langle \left[\sum_{\substack{i\\ j\neq i}} \vec{\nabla}_{q_i}\, \varphi_{ij} + \frac{1}{2}\sum_{\substack{j\neq k\\ j,k\neq i}}\sum \vec{\nabla}_{q_i}\, w_{ijk}\right]\delta(\vec{q}_i - \vec{q});\ F_N\right\rangle. \tag{3.11}$$

Here $\varphi_{ij} \equiv \varphi(|\vec{q}_i - \vec{q}_j|)$ and $w_{ijk} \equiv w(\vec{q}_i, \vec{q}_j, \vec{q}_k)$. The first two terms on the right-hand side of Eq. (3.11) have already been worked out, so that we will just quote the result [see Eq. (3.20) below)]. The last term of Eq. (3.11) is

$$\begin{aligned}\vec{A} &= -\frac{1}{2}\left\langle \sum_{i\neq j\neq k}\sum\sum (\vec{\nabla}_{q_i}\, w_{ijk})\,\delta(\vec{q}_i - \vec{q});\ F_N\right\rangle \\ &= -\frac{1}{6}\left\langle \sum_{i\neq j\neq k}\sum\sum \left[(\vec{\nabla}_{q_i}\, w_{ijk})\,\delta(\vec{q}_i - \vec{q}) + (\vec{\nabla}_{q_j}\, w_{ijk})\,\delta(\vec{q}_j - \vec{q}) + (\vec{\nabla}_{q_k}\, w_{ijk})\,\delta(\vec{q}_k - \vec{q})\right];\ F_N\right\rangle \\ &= -\frac{1}{6}\left\langle \sum_{i\neq j\neq k}\sum\sum \left\{(\vec{\nabla}_{q_{ki}}\, w_{ijk})\left[\delta(\vec{q}_k - \vec{q}) - \delta(\vec{q}_i - \vec{q})\right] + (\vec{\nabla}_{q_{ji}}\, w_{ijk})\left[\delta(\vec{q}_j - \vec{q}) - \delta(\vec{q}_i - \vec{q})\right]\right\};\ F_N\right\rangle\,.\end{aligned} \tag{3.12}$$

Here we have symmetrized in the second line, set

$$\vec{q}_{ki} = \vec{q}_k - \vec{q}_i\,,\quad \vec{q}_{ji} = \vec{q}_j - \vec{q}_i\,, \tag{3.13}$$

and used Eqs. (2.8). Expanding the differences of δ functions, which appear in Eq. (3.12), as Taylor series in powers of $\vec{q}_{ki}$ and $\vec{q}_{ji}$, we find that

$$\begin{aligned}\vec{A} = -\vec{\nabla}_q \cdot \Bigg\{ -\frac{1}{6}\Bigg\langle \sum_{i\neq j\neq k}\sum\sum \Bigg[&\vec{q}_{ki}(\vec{\nabla}_{q_{ki}} w_{ijk})\left(1 - \tfrac{1}{2}\,\vec{q}_{ki}\cdot\vec{\nabla}_q + \cdots + \frac{1}{n!}\,(-\vec{q}_{ki}\cdot\vec{\nabla}_q)^{n-1} + \cdots\right)\delta(\vec{q}_k - \vec{q}) \\ &+ \vec{q}_{ji}(\vec{\nabla}_{q_{ji}}\, w_{ijk})\left(1 - \tfrac{1}{2}\,\vec{q}_{ji}\cdot\vec{\nabla}_q + \cdots + \frac{1}{n!}\,(-\vec{q}_{ji}\cdot\vec{\nabla}_q)^{n-1} + \cdots\right)\delta(\vec{q}_j - \vec{q})\Bigg];\ F_N\Bigg\rangle\Bigg\} \\ \equiv -\vec{\nabla}_q \cdot \left[\vec{P}_w^{(1)}(\vec{q};t) + \vec{P}_w^{(2)}(\vec{q};t)\right]&.\end{aligned} \tag{3.14}$$

The tensors $\vec{P}_w^{(1)}$ and $\vec{P}_w^{(2)}$ are the contributions to the stress tensor due to the nonadditive forces. Introducing two δ functions, $\delta(\vec{q}_{ki} - \vec{R})$ and $\delta(\vec{q}_{ji} - \vec{r})$, and two integrations in the definitions of the $\vec{P}$ tensors, and using the property given by Eq. (2.2) of the nonadditive potential, we obtain

$$\begin{aligned}\vec{P}_w^{(1)}(\vec{q};t) &= -\frac{1}{6}\sum_{i\neq j\neq k}\sum\sum \Bigg\langle \iint d\vec{r}\,d\vec{R}\,\delta(\vec{q}_{ki} - \vec{R})\,\delta(\vec{q}_{ji} - \vec{r}) \\ &\qquad \times \vec{R}[\vec{\nabla}_R\, w(\vec{r},\vec{R})]\left(1 - \tfrac{1}{2}\,\vec{R}\cdot\vec{\nabla}_q + \cdots + \frac{1}{n!}\,(-\vec{R}\cdot\vec{\nabla}_q)^{n-1} + \cdots\right)\delta(\vec{q}_k - \vec{q});\ F_N\Bigg\rangle \\ &= -\iint d\vec{r}\,d\vec{R}\,\vec{R}[\vec{\nabla}_R\, w(\vec{r},\vec{R})]\left(1 - \tfrac{1}{2}\,\vec{R}\cdot\vec{\nabla}_q + \cdots + \frac{1}{n!}\,(-\vec{R}\cdot\vec{\nabla}_q)^{n-1} + \cdots\right) \\ &\qquad \times \left\langle \frac{1}{6}\sum_{i\neq j\neq k}\sum\sum \delta(\vec{q}_{ki} - \vec{R})\,\delta(\vec{q}_{ji} - \vec{r})\,\delta(\vec{q}_k - \vec{q});\ F_N\right\rangle \\ &= -\frac{1}{6}\iint d\vec{r}\,d\vec{R}\,d\vec{p}\,d\vec{p}_2\,d\vec{p}_3\,\vec{R}[\vec{\nabla}_R\, w(\vec{r},\vec{R})] \\ &\qquad \times \left(1 - \tfrac{1}{2}\,\vec{R}\cdot\vec{\nabla}_q + \cdots + \frac{1}{n!}\,(-\vec{R}\cdot\vec{\nabla}_q)^{n-1} + \cdots\right) f_3(\vec{q}, \vec{q} - \vec{R}, \vec{q} - \vec{R} + \vec{r}, \vec{p}, \vec{p}_2, \vec{p}_3; t)\,.\end{aligned} \tag{3.15}$$

In obtaining this last expression we used the definitions given by Eqs. (3.8) and (3.9).

The function $f_3(\vec{q}, \vec{q} - \vec{R}, \vec{q} - \vec{R} + \vec{r}, \vec{p}, \vec{p}_2, \vec{p}_3; t)$, considered as a function of the coordinates $\vec{q}$, $\vec{R}$, and $\vec{r}$, is a slow function of $\vec{q}$ but a sensitive function of the relative coordinates $\vec{R}$ and $\vec{r}$. Thus, we may write

$$\overleftrightarrow{P}_w^{(1)}(\vec{q};t) = -\tfrac{1}{6}\int d\vec{r}\, d\vec{R}\, d\vec{p}\, d\vec{p}_2\, d\vec{p}_3\, \vec{R}[\vec{\nabla}_R\, w(\vec{r},\vec{R})] \times f_3(\vec{q},\vec{q}-\vec{R},\vec{q}-\vec{R}+\vec{r},\vec{p},\vec{p}_2,\vec{p}_3;t)\ . \quad (3.16)$$

In an analogous way we can obtain an expression for $\overleftrightarrow{P}_w^{(2)}$, which turns out to be equal to $\overleftrightarrow{P}_w^{(1)}$:

$$\overleftrightarrow{P}_w^{(2)} = \overleftrightarrow{P}_w^{(1)}\ . \quad (3.17)$$

Thus the total contribution $\overleftrightarrow{P}_w$ to the stress tensor, due to nonadditive forces, is

$$\overleftrightarrow{P}_w = 2\,\overleftrightarrow{P}_w^{(1)}\ , \quad (3.18)$$

with $\overleftrightarrow{P}_w^{(1)}$ given by Eq. (3.16).

The equation of motion, Eq. (3.11), may then be written in the form

$$\rho(\vec{q};t)\ \frac{D\vec{u}(\vec{q};t)}{Dt} = -\vec{\nabla}_q\cdot\overleftrightarrow{P}(\vec{q};t)\ , \quad (3.19)$$

where the total stress tensor $\overleftrightarrow{P}(\vec{q};t)$ is given by

$$\overleftrightarrow{P} = \overleftrightarrow{P}_\kappa + \overleftrightarrow{P}_\varphi + \overleftrightarrow{P}_w\ , \quad (3.20)$$

with

$$\overleftrightarrow{P}_\kappa(\vec{q};t) = (1/m)\int d\vec{p}\ \vec{\mathcal{P}}\vec{\mathcal{P}} f_1(\vec{q},\vec{p};t)\ , \quad (3.21)$$

$$\overleftrightarrow{P}_\varphi(\vec{q};t) = -\tfrac{1}{2}\int d\vec{p}\, d\vec{p}_2\, d\vec{R}(\vec{R}\vec{R}/R)\ \varphi'(R) \times f_2(\vec{q},\vec{q}+\vec{R},\vec{p},\vec{p}_2;t)\ . \quad (3.22)$$

The total derivative D/Dt operator in Eq. (3.19) is given by

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{u}\cdot\vec{\nabla}_q\ , \quad (3.23)$$

and the thermal momentum by

$$\vec{\mathcal{P}} = \vec{p} - m\vec{u}\ . \quad (3.24)$$

In Appendix B, we show that the tensor $\overleftrightarrow{P}_w$ is a symmetric tensor. Thus, the total stress tensor is symmetric.

To obtain the energy equation we put in Eq. (3.3)

$$\alpha = \sum_i \frac{p_i^{\,2}}{2m}\,\delta(\vec{q}_i-\vec{q}) + \frac{1}{2}\sum\sum_{i\neq j}\varphi_{ij}\delta(\vec{q}_j-\vec{q}) + \frac{1}{6}\sum\sum\sum_{i\neq j\neq k} w_{ijk}\ \delta(\vec{q}_k-\vec{q})\ . \quad (3.25)$$

After a lengthy, but straightforward, calculation analogous to the one made in obtaining the equation of motion, one finds the equation of energy in the form

$$\rho(\vec{q};t)\ \frac{D}{Dt}\left(\frac{\epsilon(\vec{q};t)}{\rho(\vec{q};t)}\right) = -\vec{\nabla}_q\cdot\vec{\mathcal{J}}(\vec{q};t) - \overleftrightarrow{P}(\vec{q};t) : \vec{\nabla}_q\vec{u}(\vec{q};t)\ . \quad (3.26)$$

In this equation, the energy density $\epsilon(\vec{q};t)$ is given by

$$\epsilon(\vec{q};t) = (1/2m)\int d\vec{p}\ \mathcal{P}^2 f_1(\vec{q},\vec{p};t) + \tfrac{1}{2}\int d\vec{p}\, d\vec{p}_2\, d\vec{R}\ \varphi(R)\, f_2(\vec{q},\vec{q}+\vec{R},\vec{p},\vec{p}_2;t) + \tfrac{1}{6}\int d\vec{p}\, d\vec{p}_2\, d\vec{p}_3\, d\vec{r}\, d\vec{R}\ w(\vec{r},\vec{R}) \times f_3(\vec{q},\vec{q}-\vec{R},\vec{q}-\vec{R}+\vec{r},\vec{p},\vec{p}_2,\vec{p}_3;t)\ . \quad (3.27)$$

The heat current $\vec{\mathcal{J}}$ is given by

$$\vec{\mathcal{J}} = \vec{\mathcal{J}}_\kappa + \vec{\mathcal{J}}_\varphi^{(1)} + \vec{\mathcal{J}}_\varphi^{(2)} + \vec{\mathcal{J}}_w^{(1)} + \vec{\mathcal{J}}_w^{(2)}\ , \quad (3.28)$$

with

$$\vec{\mathcal{J}}_\kappa(\vec{q};t) = \int d\vec{p}\ \frac{\vec{\mathcal{P}}}{m}\ \frac{\mathcal{P}^2}{2m}\ f_1(\vec{q},\vec{p};t)\ , \quad (3.29)$$

$$\vec{\mathcal{J}}_\varphi^{(1)}(\vec{q};t) = \frac{1}{2}\int d\vec{p}\, d\vec{p}_2\, d\vec{R}\ \frac{\vec{\mathcal{P}}}{m}\ \varphi(R)\, f_2(\vec{q},\vec{q}+\vec{R},\vec{p},\vec{p}_2;t), \quad (3.30)$$

$$\vec{\mathcal{J}}_\varphi^{(2)}(\vec{q};t) = -\frac{1}{4}\int d\vec{p}\, d\vec{p}_2\, d\vec{R}\ \varphi'(R)\ \frac{\vec{R}\vec{R}}{R}\cdot\left[\frac{\vec{\mathcal{P}}}{m}+\frac{\vec{\mathcal{P}}_2}{m}\right] \times f_2(\vec{q},\vec{q}+\vec{R},\vec{p},\vec{p}_2;t), \quad (3.31)$$

$$\vec{\mathcal{J}}_w^{(1)}(\vec{q};t) = \frac{1}{6}\int d\vec{p}\, d\vec{p}_2\, d\vec{p}_3\, d\vec{r}\, d\vec{R}\ \frac{\vec{\mathcal{P}}}{m}\ w(\vec{r},\vec{R}) \times f_3(\vec{q},\vec{q}-\vec{R},\vec{q}-\vec{R}+\vec{r},\vec{p},\vec{p}_2,\vec{p}_3;t)\ , \quad (3.32)$$

$$\vec{\mathcal{J}}_w^{(2)}(\vec{q};t) = -\frac{2}{9}\int d\vec{p}\, d\vec{p}_2\, d\vec{p}_3\, d\vec{r}\, d\vec{R} \times\vec{R}\,[\vec{\nabla}_R w(\vec{r},\vec{R})]\cdot\left[\frac{\vec{\mathcal{P}}}{m}+\frac{\vec{\mathcal{P}}_2}{m}+\frac{\vec{\mathcal{P}}_3}{m}\right] \times f_3(\vec{q},\vec{q}-\vec{R},\vec{q}-\vec{R}+\vec{r},\vec{p},\vec{p}_2,\vec{p}_3;t)\ . \quad (3.33)$$

The contribution to the heat current is given by the expressions (3.32) and (3.33).

To summarize, we have obtained the hydrodynamical equations of a one-component system of particles that interact with nonadditive forces. The explicit contributions of these forces to the stress tensor and heat current were obtained.

In the following paper[17] we set up a kinetic equation for this system and by solving it we obtain the contribution of the nonadditive forces to the transport coefficients.

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APPENDIX A

In this Appendix we calculate explicitly, in terms

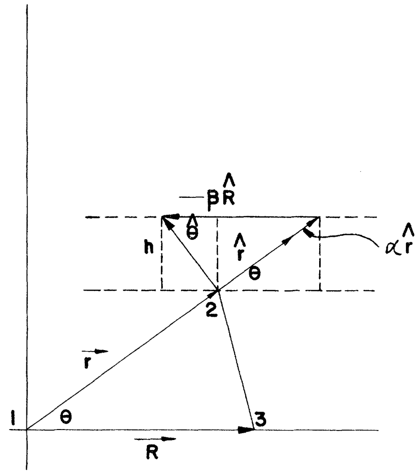

FIG. 2. Nonorthogonal base ($\vec{r}$, $\vec{R}$) and orthogonal base ($\hat{r}$, $\hat{\theta}$).

of the derivatives of w, the functions h_1, h_2, g_1, and g_2 given in the expressions

$$\vec{\nabla}_R w = \vec{R}\, h_1(\vec{r},\vec{R}) + \vec{r}\, h_2(\vec{r},\vec{R}) \tag{A1}$$

and

$$\vec{\nabla}_r w = \vec{R}\, g_1(\vec{r},\vec{R}) + \vec{r}\, g_2(\vec{r},\vec{R}). \tag{A2}$$

Consider three particles 1, 2, and 3 as shown in Fig. 2. The vectors $\vec{r}$ and $\vec{R}$ are also shown. They form a nonorthogonal base in the plane. The gradient $\vec{\nabla}_r w$ is

$$\vec{\nabla}_r w = \frac{\partial w}{\partial r}\,\hat{r} + \frac{1}{r}\frac{\partial w}{\partial \theta}\,\hat{\theta}, \tag{A3}$$

where $\hat{r}$ and $\hat{\theta}$ are unit vectors, forming an orthogonal base in plane polar coordinates. Therefore, to express $\vec{\nabla}_r w$ in the base $(\vec{r},\vec{R})$ we have to change the expression (A3) to that base. From Fig. 2 we see that

$$\hat{\theta} = \alpha\vec{r} - \beta\hat{R}, \tag{A4}$$

with $\hat{R}$ a unit vector in the direction of $\vec{R}$. We have

$$h = \cos\theta, \tag{A5}$$

and therefore

$$\alpha = \frac{h}{\tan\theta\,\cos\theta} = \cot\theta. \tag{A6}$$

Also,

$$\beta = \alpha\cos\theta + \sin\theta = \csc\theta. \tag{A7}$$

Thus

$$\hat{\theta} = \cot\theta\,\hat{r} - \csc\theta\,\hat{R}. \tag{A8}$$

Finally,

$$\vec{\nabla}_r w = \vec{r}\,\frac{1}{r}\left(\frac{\partial w}{\partial t} + \frac{\cot\theta}{r}\frac{\partial w}{\partial\theta}\right) - \vec{R}\,\frac{\csc\theta}{Rr}\frac{\partial w}{\partial\theta}. \tag{A9}$$

Analogously,

$$\vec{\nabla}_R w = \vec{R}\,\frac{1}{R}\left(\frac{\partial w}{\partial R} + \frac{\cot\theta}{R}\frac{\partial w}{\partial\theta}\right) - \vec{r}\,\frac{\csc\theta}{rR}\frac{\partial w}{\partial\theta}. \tag{A10}$$

Comparing Eqs. (A9) and (A10) with Eqs. (A1) and (A2), we see that

$$h_1(\vec{r},\vec{R}) = \frac{1}{R}\left(\frac{\partial w}{\partial R} + \frac{\cot\theta}{R}\frac{\partial w}{\partial\theta}\right), \tag{A11}$$

$$h_2(\vec{r},\vec{R}) = -\frac{\csc\theta}{rR}\frac{\partial w}{\partial\theta}, \tag{A12}$$

$$g_1(\vec{r},\vec{R}) = -\frac{\csc\theta}{rR}\frac{\partial w}{\partial\theta}, \tag{A13}$$

$$g_2(\vec{r},\vec{R}) = \frac{1}{r}\left(\frac{\partial w}{\partial r} + \frac{\cot\theta}{r}\frac{\partial w}{\partial\theta}\right). \tag{A14}$$

Using the property given by Eq. (2.4) we readily obtain Eqs. (2.12) and (2.13).

APPENDIX B

In this appendix we show that the tensor $\overleftrightarrow{P}_w$, the contribution to the stress tensor due to nonadditive forces, is a symmetric tensor.

From Eqs. (3.16) and (3.18) we see that

$$\begin{aligned}\overleftrightarrow{P}_w(\vec{q};t) &= -\tfrac{1}{3}\int d\vec{r}\,d\vec{R}\,d\vec{p}\,d\vec{p}_2\,d\vec{p}_3\,\vec{R}\,[\,\vec{\nabla}_R w(\vec{r},\vec{R})]\\ &\quad\times f_3(\vec{q},\vec{q}-\vec{R},\vec{q}-\vec{R}+\vec{r},\vec{p},\vec{p}_2,\vec{p}_3;t)\\ &= -\tfrac{1}{3}\int d\vec{r}\,d\vec{R}\,d\vec{p}\,d\vec{p}_2\,d\vec{p}_3\,\vec{R}\,[\,\vec{R}h_1(\vec{r},\vec{R}) + \vec{r}h_2(\vec{r},\vec{R})]\\ &\quad\times f_3(\vec{q},\vec{q}-\vec{R},\vec{q}-\vec{R}+\vec{r},\vec{p},\vec{p}_2,\vec{p}_3;t).\end{aligned} \tag{B1}$$

Here use was made of Eq. (2.10). The term containing h_1 is obviously symmetric. The other term is

$$-\tfrac{1}{3}\int d\vec{r}\,d\vec{R}\,d\vec{p}\,d\vec{p}_2\,d\vec{p}_3\,\vec{R}\vec{r}\,h_2(\vec{r},\vec{R}) \times f_3(\vec{q},\vec{q}-\vec{R},\vec{q}-\vec{R}+\vec{r},\vec{p},\vec{p}_2,\vec{p}_3;t)$$

and interchanging the integration variables $\vec{r}$ and $\vec{R}$, and using Eq. (2.13), it is found that this term is equal to

$$\begin{aligned}&-\tfrac{1}{3}\int d\vec{r}\,d\vec{R}\,d\vec{p}\,d\vec{p}_2\,d\vec{p}_3\,\vec{r}\vec{R}\,h_2(\vec{r},\vec{R})\\ &\quad\times f_3(\vec{q},\vec{q}-\vec{r},\vec{q}-\vec{r}+\vec{R},\vec{p},\vec{p}_2,\vec{p}_3;t)\\ &= -\tfrac{1}{3}\int d\vec{r}\,d\vec{R}\,d\vec{p}\,d\vec{p}_2\,d\vec{p}_3\,\vec{r}\vec{R}\,h_2(\vec{r},\vec{R})\\ &\quad\times f_3(\vec{q},\vec{q}-\vec{R},\vec{q}-\vec{R}+\vec{r},\vec{p},\vec{p}_2,\vec{p}_3;t)\end{aligned}$$

because the interchange of $\vec{r}$ and $\vec{R}$ from the first to the second line in f_3 means an interchange of identical particles. Therefore the second term in (B1) is also symmetric. Thus $\overleftrightarrow{P}_w$ is a symmetric tensor.

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Nonequilibrium Statistical Mechanics of Systems Interacting with Nonadditive Forces. II. Kinetic Equation and Transport Coefficients

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A kinetic equation is set up for a system of particles interacting with nonadditive intermolecular forces. Bogolyubov's functional assumption is used. After linearizing in the gradients, the kinetic equation is solved by a Chapman-Enskog method. Using the expressions for the stress tensor and heat current obtained in an earlier paper, the contributions of nonadditive forces to the shear and bulk viscosities and thermal conductivity are explicitly obtained. The results obtained are independent of density expansions.

I. INTRODUCTION

In an earlier paper[1] we obtained the hydrodynamical equations of a system of particles interacting with nonadditive intermolecular forces. Explicit expressions for the stress tensor and heat current were given, in terms of the intermolecular potential.

It is the purpose of this paper to obtain general expressions for the linear transport coefficients of a system of particles which interact with nonadditive forces. We obtain these expressions making Bogolyubov's assumption,[2] namely, that the distribution functions of more than one particle are functionals of the single-particle distribution. Thus, no expansion as power series in the density is used. Therefore the results that are obtained are independent of whether the density expansions exist or not. In this paper we generalize to our case the method proposed by García-Colín, Green, and Chaos[3] of obtaining linear transport coefficients without recourse to density expansions.

In Sec. II we start from Liouville's equation to obtain the generalization of the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy to the case of systems that interact with nonadditive forces. Taking the first equation of this hierarchy and making the Bogolyubov functional assumption, we obtain the kinetic equation. We then proceed to linearize the kinetic equation in the gradients of the system.

In Sec. III we solve the linearized kinetic equation by the usual Chapman-Enskog method.

In Sec. IV we use the expressions for the stress tensor and heat current obtained in I, together with Bogolyubov's functional assumption and the solution of the linearized kinetic equation, to compute the transport coefficient of this system, namely, the shear and bulk viscosities and thermal conductivity. We find the explicit contributions to these coeffi-