ON THE GENERALIZATION OF THE ENSKOG EQUATION TO THE CASE OF STEEP REPULSIVE POTENTIALS

R. DER, S. FRITZSCHE and R. HABERLANDT
Zentralinstitut für Isotopen- und Strahlenforschung der AdW, Permoserstrasse 15, 7050 Leipzig, GDR

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For a classical homogeneous system of particles interacting via steeply repulsive potentials a generalization of the Enskog equation is proposed. This kinetic equation has the properties that it reduces to the usual Enskog equation in the limit of hard-sphere potentials and that the total instead of the kinetic energy is conserved in the system. The expression for the potential energy obtained is correct at arbitrary densities in equilibrium.

The generalized Boltzmann equation for hard-core systems as proposed by Enskog [1] is known to describe the kinetic properties of such systems nearly exactly up to half the closest packing density and to yield good approximations for transport coefficients even at liquid densities [2]. Also, equilibrium properties are obtained exactly at arbitrary densities. In view of the simplicity of the Enskog equation this is a very surprising, still not fully understood situation. Since a microscopic interpretation of the Enskog equation is very complicated even in the case of hard-sphere systems no generally accepted extension to the case of (short-ranged) soft-core potentials exists in the literature.

The philosophy underlying the EE is that spatial correlations between colliding particles are taken into account while momentum correlations are neglected altogether. These spatial correlations originate from the influence of the surrounding particles via the so-called screening effect [3] this effect being of a purely geometrical origin. Therefore, these correlations will play an important role also in a system of particles interacting via a steeply repulsive potential V. In an equilibrium system these correlations are represented by $y_2(1,2) = y_2(r_1 - r_2)$ where

$$g(r) = e^{-\beta V(r)} y_2(r) \,, \tag{1}$$

$g(r)$ being the pair correlation function, $\beta = 1/kT$ and $V(r)$ the pair interaction potential. In a hard-sphere system $y_2(r)$ is entirely independent of the temperature (i.e. on the kinetics) and represents just the screening correlations mentioned above. In a realistic system and in nonequilibrium the screening will be slightly dependent on the kinetics of the system so that $y_2(r)$ should actually be determined self-consistently. For simplicity of presentation we neglect these effects in the present paper and use the $y_2(r)$ of (1) in nonequilibrium, too.

To introduce these correlations into the desired kinetic equations for a classical homogeneous N-particle system we start from the first two equations of the BBGKY hierarchy which read for large N with given density n,

$$\frac{\partial}{\partial t} f_1(1;t) = -n \int \mathrm{d}2\, L_1(1,2) f_2(1,2;t) \,, \tag{2}$$

$$\left[\frac{\partial}{\partial t} + L(1,2)\right] f_2(1,2;t) = -n \int \mathrm{d}3\ [L_1(1,3) + L_1(2,3)] f_3(1,2,3;t) \,, \tag{3}$$

where

$$L = L_0 + L_1 , \qquad L_0(1,2) = \frac{p_1}{m}\frac{\partial}{\partial r_1} + \frac{p_2}{m}\frac{\partial}{\partial r_2} , \qquad L_1(i,j) = -\frac{\partial V(i,j)}{\partial r_i}\left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j}\right) .$$

These equations have to be equipped with an initial condition which we choose here in such a way as to take account of the screening correlations mentioned above, i.e.

$$f_2(1,2;0) = f_1(1;0)\, f_1(2;0)\, y_2(1,2) . \tag{4}$$

These correlations are formally introduced into the hierarchy, too, by rewriting (3) by means of (2) as

$$\left[\frac{\partial}{\partial t} + L(1,2)\right] f_2(1,2;t) - \frac{\partial}{\partial t} y_2(1,2) f_1(1;t) f_1(2;t)$$

$$= -n \int \mathrm{d}3 \{ L_1(1,3)[f_3(1,2,3;t) - y_2(1,2) f_2(1,3;t) f_1(2;t)]$$

$$+ L_1(2,3)[f_3(1,2,3;t) - y_2(1,2) f_2(2,3;t) f_1(1;t)]\}$$

$$\underset{\mathrm{Def}}{=} \Sigma(1,2;t) f_2(1,2;t) , \tag{5}$$

the latter equality sign simply defining a quantity Σ which depends on f_3, f_2 and f_1. It is interesting to evaluate Σ in equilibrium. Using

$$f_3^{\mathrm{eq}}(1,2,3) = \mathrm{e}^{-\beta V(1,2,3)} y_3(1,2,3)$$

and the hierarchy equations for the y functions, one immediately obtains

$$\Sigma^{\mathrm{eq}} f_2^{\mathrm{eq}} = \hat{\Sigma}_{\mathrm{eq}}(1,2) f_2^{\mathrm{eq}}(1,2) \underset{\mathrm{Def}}{=} \frac{\partial V^{\mathrm{av}}(r_1 - r_2)}{\partial r_1}\left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2}\right) f_2^{\mathrm{eq}}(1,2) ,$$

$$V^{\mathrm{av}}(r_1 - r_2) = -kT \ln[y_2(r_1 - r_2)] ,$$

where $\hat{\Sigma}_{\mathrm{eq}}$ is seen to be just an interaction liouvillean defined in terms of the average force exerted by the surrounding medium via the screening effect on the particles in consideration. This force depends on the kinetics of the system only through the average kinetic energy and is easily interpreted as a kind of pressure driving the particles together. This easy physical picture arises from the fact that in equilibrium there are no momentum correlations between the particles.

In nonequilibrium this force is expected to be expressed by the operator

$$\hat{\Sigma}_1(1,2;t) = \frac{\partial V^{\mathrm{av}}(1,2;t)}{\partial r_1}\left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2}\right] , \tag{6}$$

where

$$V^{\mathrm{av}}(1,2;t) = -\tfrac{2}{3} E_{\mathrm{kin}}(t) \ln[y_2(1,2)] , \qquad E_{\mathrm{kin}}(t) = \int \mathrm{d}^3 p\,(p^2/2m) f_1(p;t)$$

so that (5) becomes

$$\left[\frac{\partial}{\partial t} + L - \hat{\Sigma}_1(t) - \Sigma_2(t)\right] f_2(1,2;t) - \frac{\partial}{\partial t} y_2 f_1(1;t) f_1(2;t) = 0 , \tag{7}$$

where $\Sigma_2 f_2 = (\Sigma - \hat{\Sigma}_1) f_2$ mainly contains effects due to the nonequilibrium momentum correlations between the particles. We have dropped indices where no misunderstanding is possible.

Now it is easily proved by differentiation that (7) together with (4) is equivalent to the integral equation

$$f_2(t) = y_2 f_1(1;t) f_1(2;t) - \int_0^t dt'\, e^{-(t-t')L} L y_2 f_1(1;t') f_1(2;t') + \int_0^t dt' e^{-(t-t')L} [\hat{\Sigma}_1(t') + \Sigma_2(t')] f_2(t') . \tag{8}$$

We use the identity

$$\int_0^t dt'\, e^{-(t-t')L} y_2 A(1,2;t') = \int_0^t dt'\, y_2 e^{-(t-t')L} A(1,2;t') - \int_0^t dt'\, e^{-(t-t')L} (L_0 y) \int_0^{t'} dt''\, e^{-(t'-t'')L} A(1,2;t'') \tag{9}$$

which is most easily proved in Laplace representation by using $L = L_0 + L_1$ is a linear differentiation operator and L_1 commutes with y. Introducing (9) into (8) and iterating as

$$f_2^{(0)}(t) = y_2 f_1(1;t) f_1(2;t) - \int_0^t dt'\, y_2\, e^{-(t-t')L} L_1 f_1(1;t') f_1(2;t') \underset{\text{Def}}{=} \int_0^t dt'\, K^{(0)}(t-t') f_1(1;t') f_1(2;t') , \tag{10a}$$

$$f_2^{(1)}(t) = f_2^{(0)}(t) + \int_0^t dt'\, e^{-(t-t')L} [\hat{\Sigma}_1(t') y_2 + \Sigma_2(t') y_2 - (L_0 y_2)] f_1(1;t') f_1(2;t')$$

$$- \int_0^t dt' \int_0^{t'} dt''\, e^{-(t-t')L} [\hat{\Sigma}_1(t') y_2 + \Sigma_2(t') y_2 - (L_0 y_2)] e^{-(t'-t'')L} L_1 f_1(1;t'') f_1(2;t'')$$

$$\underset{\text{Def}}{=} \int_0^t dt'\, K^{(1)}(t,t') f_1(1;t') f_1(2;t') , \tag{10b}$$

$$\vdots$$

and for $t \to \infty$ (in the abelian sense) we see that in equilibrium $f \to f_{eq}$, $f_2^{(0)}$ yields the exact equilibrium function $f_{2\,eq}$ while the higher order corrections are equal to zero, i.e.

$$f_{2\,eq}^{(k)} = f_{2\,eq}^{(0)} , \quad \forall k = 1, 2, \ldots .$$

Hoping that (10) in nonequilibrium rapidly converges, we may obtain a kinetic equation by introducing (10b) into (2).

To stay in the Enskog picture however we have to neglect any terms which are connected with momentum correlations extending beyond the range of the interaction potential V. This means dropping in $K^{(1)}$ the term containing $\hat{\Sigma}_2$ and all terms which do not decay on a time scale given by t_c, t_c being the duration of a single collision with respect to the potential V. This leads to the following equation (for details see ref. [4])

$$\frac{\partial}{\partial t} f_1(1;t) = n \int_0^t dt' \left[\int d2 \left\{ y_2 L_1\, e^{-t'L} L_1 f_1(1;t-t') f_1(2;t-t') - \int_0^{t-t'} dt'' L_1\, e^{-t'L} [(L_0 y_2) - \hat{\Sigma}_1(t-t') y_2] \right. \right.$$

$$\left. \left. \times\, e^{-t''L} L_1 f_1(1;t-t'-t'') f_1(2;t-t'-t'') \right\} \right] . \tag{11}$$

In the limit of hard-sphere potentials the first term is seen to yield the usual Enskog equation

$$\frac{\partial}{\partial t} f_1(1;t) = -n y(\sigma) \int d2\, \overline{T}_2(1,2) f_1(1;t) f_1(2;t) \tag{12}$$

and σ is the hard-sphere diameter, $\overline{T}$ being defined in ref. [5], while the second term may be shown to be equal to zero [4] and this term will therefore be small in systems with sufficiently steep repulsive potentials.

(11) does still contain the distribution functions at earlier times. Because of the afore mentioned decay properties of the kernels we may write

$$f_1(1;t-\tau)=f_1(1;t)-\tau\frac{\partial}{\partial t}f_1(1;t-\tau)\,, \tag{13}$$

$$\hat{\Sigma}_1(t-\tau)=\hat{\Sigma}_1(t)-\tau\frac{\partial}{\partial t}\hat{\Sigma}_1(t) \tag{14}$$

and anticipating the result (14) we may replace

$\hat{\Sigma}_1(t-t')$ by $\hat{\Sigma}_1(t-t'-t'')$

since the corresponding correcture term may be shown to be smaller than the terms retained by a factor of $U_{\mathrm{pot}}/E_{\mathrm{kin}}$. Introducing this into (11) and extending after introducing the usual damping factor the integrations to infinity one obtains in first order of retardation terms finally

$$\frac{\partial}{\partial t}f_1(1;t)=-n\lim_{\epsilon\to 0}\left[1+\frac{\partial}{\partial\epsilon}\frac{\partial}{\partial t}\right]\int \mathrm{d}2\left[yL_1\frac{1}{\epsilon+L}L_1-L_1\frac{1}{\epsilon+L}\left[(L_0y)-\hat{\Sigma}_1(t)\right]\frac{1}{\epsilon+L}L_1\right]f_1(1;t)f_1(2;t)\,. \tag{15}$$

(15) forms the central result of the present paper. Similarly as the Enskog equation, it contains only the dynamics of two particles, the effect of the medium being mainly represented by the factor y in the first term on the rhs of (15). The second term looks like a correcture term in Born approximation, the perturbation being $(L_0y)-\hat{\Sigma}_1$.

While $\hat{\Sigma}$ describes a force, driving the particles together, (L_0y) represents the tendency of the particles to diminish the correlations due to free streaming. In equilibrium, the two effects cancel each other, while in nonequilibrium these terms represent the influence of the medium on the course of a single binary collision.

In the limit of a hard-sphere system, the second term on the rhs of (15) is equal to zero, thus (15) reduces to the usual Enskog equation of a homogeneous system. By multiplying (15) with $p^2/2m$ and integrating one obtains [4]

$$\frac{\partial}{\partial t}E_{\mathrm{kin}}(t)=-\frac{\partial}{\partial t}U_{\mathrm{pot}}(t)\,,$$

$$U_{\mathrm{pot}}(t)=\lim_{\epsilon\to 0}-\tfrac{1}{2}n^2\int \mathrm{d}1\,\mathrm{d}2\left\{-V_y+V\frac{1}{\epsilon+L}\left[(L_0y)-\Sigma_1(t)\right]\right\}\frac{1}{\epsilon+L}L_1f_1(1;t)f_1(2;t) \tag{16}$$

and

$$U_{\mathrm{pot}}^{\mathrm{eq}}=\int \mathrm{d}^3r\,V(r)\,\mathrm{e}^{-\beta V(r)}y(r)=\int \mathrm{d}^3r\,V(r)\,g(r)\,.$$

Identifying $U_{\mathrm{pot}}(t)$ with the potential energy in the system we may say (15) conserves total energy. Since in a dense realistic system the potential energy cannot be neglected with respect to the kinetic energy this fact is nontrivial and serves as a serious test of any kinetic equation.

The details of the derivation will be presented elsewhere.

References

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