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SOME COMMENTS ON A RECENT METHOD FOR DERIVING KINETIC EQUATIONS

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ABSTRACT: The purpose of this note is a twofold one, namely, to show how one can formally obtain a class of kinetic equations from the BBGKY hierarchy together with Bogoliubov's functional assumption for the one particle distribution function, and to show how a naive procedure leads to results which can hardly be interpreted as kinetic equations.

The aim of this note is to illustrate how it is formally possible to obtain a description of the time evolution of a fluid, in the so-called kinetic stage, through equations which, if not carefully analyzed, may lead to inconsistent and even false interpretation of the results generated by them.

We take as our starting point the first of the well known B.B.G.K.Y. hierarchy of equations[1] for the reduced distribution functions of a fluid under the action of an external force $\mathbf{F}$. Thus,

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$$\frac{\partial F_1}{\partial t} + \frac{p_1}{m} \cdot \frac{\partial F_1}{\partial q_1} + \frac{\mathbf{F}}{m} \cdot \frac{\partial F_1}{\partial p_1} = \frac{1}{v} \iint dq_2\, dp_2\, \frac{\partial \phi(r_{12})}{\partial r_{12}} \cdot \frac{\partial F_2}{\partial p_1} \qquad (1)$$

where F_1 and F_2 are the first two distributions functions, $\phi(r_{12})$ is the intermolecular potential and $v = V/N$.

Let us now introduce two assumptions, namely

a):

$$F_2(x_1, x_2; t) \rightarrow F_2(x_1, x_2 \,|\, F_1(\,;t)) \qquad (2)$$

which is the so-called Bogoliubov's functional assumption for the two particle distribution function. Here $x_i \equiv (q_i, p_i)$, $i = 1,2$.

b):

$$\lim_{t \to \infty} S_{-t}^{(2)}(x_1, x_2)\, F_2\left(x_1, x_2 \,|\, S_t^{(1)} F_1\right) =$$

$$= \lim_{t \to \infty} S_{-t}^{(2)}(x_1, x_2) \prod_{i=1}^{2} S_t^{(1)}(x_i)\, F_1(x_i; t), \qquad (3)$$

which is essentially the condition whereby one introduces the direction of time in the kinetic equations[2]. The meaning to the time evolution operators S has been fully discussed in the literature[1], so we shall not worry about them here.

Let us now write the two-particle distribution functional in terms of a pair correlation functional $X(x_1, x_2 \,|\, F_1)$ by requiring that[3]

$$F_2(x_1, x_2 \,|\, F_1) = \mathcal{S}^{(2)}(x_1, x_2) \left[X(x_1, x_2 \,|\, F_1)\, F_1(x_1; t)\, F_1(x_2; t) \right] \qquad (4)$$

where

$$\mathcal{S}^{(2)}(x_1, x_2) = \lim_{t \to \infty} S_{-t}^{(2)}(x_1, x_2) \prod_{i=1}^{2} S_t^{(1)}(x_i) \,. \qquad (5)$$

Eq. (4) is nothing else that the non-equilibrium generalization of the equilibrium expression for the two-particle correlation function.

Substituting Eq. (4) back into Eq. (1), yields

$$\frac{\partial F_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial F_1}{\partial \mathbf{q}_1} + \frac{\mathbf{F}}{m} \cdot \frac{\partial F_1}{\partial \mathbf{p}_1} = \frac{1}{v} \int dx_2 \, \frac{\partial \phi(r_{12})}{\partial r_{12}} \times$$

$$\times \, \mathcal{S}^{(2)}(x_1, x_2) \cdot \left[\mathrm{X}\left(x_1, x_2 \,\middle|\, F_1\right) F_1(x_1; t)\, F_1(x_2; t) \right] \; . \qquad (6)$$

Eq. (6) is the source of a wide variety of kinetic equations depending on the very particular form we choose for the pair correlation function. As it is well known, taking $\mathrm{X} = 1$ we get Boltzmann's equation in the low density limit[2] and taking $\mathrm{X} = \mathrm{X}(\mathbf{q}_1, \mathbf{q}_1 + \sigma \mathbf{k})$ for rigid spheres yields Enskog's equation[3].

One may proceed, however, in a rather more simplistic way. Indeed, let us assume that for X we take the first term of its equilibrium density expansion with a local equilibrium value for the temperature. Then,

$$\mathrm{X}\left(x_1, x_2 \,\middle|\, F_1\right) = \exp(-\phi(r)/k_B T) \; . \qquad (7)$$

Moreover, we perform a series expansion of the evolution operators $S_t^{(j)}$, $j = 1, 2$ in powers of t, neglecting all terms beyond the linear one. Thus,

$$S_t^{(2)}(x_1, x_2) = 1 + tH_2 + \ldots\ldots \qquad (8a)$$

$$S_t^{(1)}(x_1) = 1 + tH_1 + \ldots\ldots \qquad (8b)$$

Substitution of Eqs. (7) and (8) back into Eq. (6) yields, after some straightforward algebraic manipulations, the following result,

$$\frac{\partial F_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial F_1}{\partial \mathbf{q}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial F_1}{\partial \mathbf{p}_1} = \zeta_{\mathrm{F.S.}} \frac{\partial}{\partial \mathbf{v}_1} \cdot \left[\mathbf{c} f_1 + \frac{k_B T}{m} \frac{\partial f_1}{\partial \mathbf{v}_1} \right] , \qquad (9)$$

where

$$\zeta_{\text{F.S.}} = \frac{nk_BT}{2m}\, tB \qquad (10a)$$

$$B = \frac{8\Pi}{3}\,(k_BT)^{-2}\int_0^\infty \left(\frac{d\phi}{dr}\right)^2 \exp\left(-\frac{\phi(r)}{k_BT}\right) r^2 dr \qquad (10b)$$

and

$$f_1 = \frac{N}{V}\,F_1\,, \quad v_1 = \frac{p_1}{m}\,, \quad c = \frac{p_1}{m} - u$$

The quantities n, u and T are the usual average particle density, the hydrodynamic velocity and the temperature, respectively, calculated at the point r_1. This equation was derived following a different approach by J. Frey[4]. Notice that the equation itself has the same formal structure of a Fokker-Planck equation for the singlet distribution function as that derived by Kirkwood in his old paper on this subject[5,6].

From the physical point of view, however, Eq. (9) can hardly be identified with a kinetic equation. Indeed, the time expansions given by Eqs. (8a,b) are valid for very small values of t compared to the collision time. Thus, Eq. (9) describes the time evolution of two particles correlated at time $t = 0$, for values of t too small compared with the mean free time and, therefore, before they even leave their common region of interaction. It is not then surprising that we get a diffusion equation[7] and, moreover, one in which the medium does not exert any influence whatsoever in their motion. This last statement is supported by the fact that we only consider the singlet distribution function and also because if we calculate Kirkwood's friction coefficient on the basis of these results we obtain precisely Eq. (10a) provided we consider that there is no time correlation among the forces which the medium exerts on the particle. Indeed, from Kirkwood's formula

$$\zeta = (3mk_BT)^{-1}\int_0^\tau \langle F_1(t)\,F_1(t+s)\rangle_1\, ds\,, \qquad (11)$$

where $\langle\ \rangle_1$ indicates the average force exerted on particle one averaged over a local equilibrium ensemble, we get that

$$\zeta = \frac{\tau}{3mk_B T} \langle F_1 \rangle^2 \tag{12}$$

where τ is the average collision time, and

$$\langle F_1 \rangle^2 = 4\Pi n \int_0^\infty r^2 g(r) \left(\frac{d\phi}{dr}\right)^2 dr\,; \tag{13}$$

this is precisely $\zeta_{F.S.}$. In Eq. (13), $g(r)$ is the radial distribution function.

One may also mention the fact that the calculation of the kinetic contributions to the transport coefficients using an exact Fokker-Planck equation for the one particle distribution function has been discussed at length by Lebowitz et al[6]. Therefore we must conclude that Eq. (9) contains no new information, that the agreement between the corrections to transport coefficients obtained from it with experiments is merely fortitious and, what is more important, that it cannot be thought of as describing the time evolution of a system towards equilibrium, neither as a kinetic equation nor in Kirkwood's interpretation in terms of a diffusion equation.

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RESUMEN

El propósito de este trabajo es doble; mostrar por una parte como de la jerarquía BBGKY y la hipótesis funcional de Bogoliubov, se puede obtener toda una clase de ecuaciones cinéticas para la función de distribución de una partícula. Por otra parte, se demuestra como siguiendo procedimientos ingenuos pueden obtenerse resultados que difícilmente se pueden identificar como ecuaciones cinéticas.