A KINETIC EQUATION FOR DENSE GASES

J. BIEL

Departamento de Física Teórica, Universidad de Valencia, Spain

J. MARRO and L. NAVARRO

Departamento de Física Teórica, Universidad de Barcelona, Spain

We propose a kinetic equation for dense gases which does not diverge in the kinetic stage and allows us to establish some conclusions about the analyticity of the reduced n-particle distribution function and about the evaluation of transport coefficients.

Starting from the Liouville equation for the probability density in the phase space of N point molecules interacting through a two-body finite-range repulsive potential $\varphi_{jk} = \varphi(|r_j - r_k|)$, and using projection operator techniques as in ref. [1], we have obtained [2] the following equation for the rate of change of the n-particle momentum distribution function:

$$\frac{\partial f_n(t)}{\partial t} = \sum_{m=1}^{l} \rho^m \left\{ \int_0^t d\tau \frac{\partial K_{n,n+m}(\tau)}{\partial \tau} f_{n+m}(t-\tau) + K_{n,n+m}(t) h_{n+m}(0) \right\}$$
$$- i\rho^{l+1} \int_0^t d\tau K_{n,n+l}(\tau)(1-P_{n+l}) L_{n+l,n+l+1} h_{n+l+1}(t-\tau) . \tag{1}$$

This equation is *valid in the thermodynamic limit* and has been derived by iteration of eq. (22) of ref. [1] which follows from the BBGKY hierarchy without additional assumptions. Here $\rho = N/V$, where V is measured in units of molecular volumes and t is in units of τ_c (average duration of a collision between two particles);

$$K_{n,n+m}(t) = (-i)^m \lim_{V \to \infty} P_n L_{n,n+1}$$
$$\times \left\{ \prod_{k=1}^{m-1} \left[\int_{\tau_{k-1}}^t d\tau_k \exp(-i\tau_k L_{n+k})(1-P_{n+k}) L_{n+k,n+k+1} \exp(i\tau_k L_{n+k+1}) \right]_{\text{ord}} \right\} \exp(-itL_{n+m}) , \tag{2}$$

where $\tau_0 = 0$ and the index 'ord' denotes that the product (equal to 1 if $m = 1$) is ordered from left to right according to increasing values of k;

$$L_{m,m+1} = i \sum_{j=1}^{m} \iint dr_{m+1} dp_{m+1} \frac{\partial \varphi_{j,m+1}}{\partial r_j} \cdot \frac{\partial}{\partial p_j} ;$$

where L_m is the Liouville operator of the isolated set of m particles and P_m is the projection operator. From the reduced n-particle distribution function F_n one gets:

$$f_n(p^n;t) = P_n F_n(r^n, p^n; t) = \frac{1}{V^n} \int dr^n F_n(r^n, p^n; t) ; \qquad h_n(r^n, p^n; t) = (1-P_n) F_n(r^n, p^n; t) .$$

It can be shown [2] that eq. (1) may be written in Markovian from either (a) by developing $f_{n+m}(t-\tau)$ in a Taylor series around t and putting together the terms of the same power in ρ, or (b) by making a partial integration and substituting for the operators $K_{n,n+m}(\tau)$ their assymptotic values for large times. By means of procedure (a) the Choh—Uhlenbeck equation can be derived from (1); however this procedure does not provide exact compact equations but, instead, equations with *infinitely many terms*. Procedure (b) shows that the initial correlations decay for zero order in ρ, and the Boltzmann equation can be derived from (1) and its existence proved by considering the limit $\rho \to 0$, $t \to \infty$, ρt finite. The derivation of both the Boltzmann and the Choh—Uhlenbeck equations requires moreover the assumptions of initial spatial uniformity and initially finite-range correlations.

On the other hand, a study of each term in eq. (1), based on the generally-assumed "good-behaviour" of the functions $f_n(t)$ and $h_n(t)$ and of the operators $K_{n,n+m}(\tau)$, shows that the first l terms on the right-hand side of (1) and the remainder are respectively bounded by quantities of the order of $(\rho t)^l$, and $\rho(\rho t)^l$. Thus for gases far enough from condensation ($\rho \ll 1$), one can *neglect the last term* in eq. (1) which involves the contribution of collisions of more than $l+1$ particles. Our equation has no divergent terms for times such that $\rho t < 1$. A simple evaluation shows that such times cover the whole kinetic stage and therefore may be used in calculating the corrections to the Boltzmann term for *any order in the density*. For larger times ($\rho t > 1$) our equation does not converge. Because of the generality of eq. (1) and that of the hypothesis about the behaviour of f_n, h_n and $K_{n,n+m}$ we are allowed to think that the difficulties arising for large times are due to the fact that the reduced n-particle distribution function *is not analytic in the density* (except at $\rho = 0$). These difficulties are *not only* due, say, to Bogolubov's hypothesis. It is not possible, therefore, to calculate the corrections to the transport coefficients by means of the assumptions, say, of the Chapman—Enskog method; it is necessary to employ other procedures [e.g. 3], or to look for an expansion parameter other than the density.

References

[1] P. Mazur and J. Biel, Physica 32 (1966) 1633.
[2] J. Biel, J. Marro and L. Navarro, to be published.
[3] J. Albers and I. Oppenheim, Physica 59 (1972) 161, 187.