STATISTICAL T MATRIX IN THE THEORY OF DENSE GASES AND THE ENSKOG APPROACH

A. V. Bogdanov, Yu. E. Gorbachev, and I. D. Kaganovich

The pole approximation in the Kadanoff–Baym formalism for a dense gas is used in a systematic study to derive a kinetic equation that takes into account simultaneously "exact" convective transport and collisional transport.

1. Introduction

The intuitively most attractive approach in the kinetic theory of dense gases is the method based on the Enskog–Boltzmann equation [1]. Important evidence in its support is a result of Bogolyubov [2], who showed that for the hard-sphere system such an equation has solutions corresponding to the exact evolution. Moreover, the collision integral in the Enskog–Boltzmann equation describes exactly the transport of molecular characteristics by collisions and is a convenient theoretical model that contains all the main characteristic properties and symmetry properties of such integrals. Determining experimentally the value of just one parameter (the χ factor), one can describe very well the transport parameters as functions of the pressure on the basis of such an approach. The difficulties in describing the temperature dependence are associated with the inadequacy of the model of the potential in the Enskog–Boltzmann equation.

It is convenient to divide the attempts to go beyond the framework of the Enskog model into two main groups. In the effective-potential method [3] and its generalizations [4], the interaction is assumed to consist of two parts — the potential of a hard wall and a weak smooth attractive potential. On the right-hand side of the corresponding equations there is a sum of collision integrals that take into account the individual terms of the potential as well as their interference. The transparent physical meaning and simple structure of the Enskog–Boltzmann integral are lost in this approach.

In the second group of approaches [5–8], a realistic smooth potential is taken as the basis, and a kinetic equation is derived from the exact equations of statistical mechanics [5] using an expansion with respect to a small parameter of the theory.

This leads to a kinetic equation of the Landau–Boltzmann form describing evolution of quasiparticles, i.e., it takes into account renormalization of the energy of a particle due to its weak (attractive) interaction with other particles. This renormalization arises because of peripheral interactions, which determine the small-angle scattering [9]. It ensures that transport by collisions is taken into account; in particular, an equation of state of the van der Waals type can be obtained. Partial allowance for transport of molecular characteristics by collisions of this type, for which the contribution disappears in the limit of hard spheres, makes it impossible to use the obtained equations at fairly high pressures, although for fixed pressure the temperature dependence of the transport phenomena is correctly described.

The aim of this paper is to obtain a kinetic equation that makes it possible to describe both the self-consistent field effects and collisional transport due to short-range interactions. We note that the semiphenomenological approach that one might be tempted to use, namely, replacement of the collision integral in the kinetic equation of quasiparticle type [9] by the Enskog integral, does not work. The reason for this is that in a consistent derivation of the kinetic equation from the equation for the Green's functions the convective part of the kinetic equation of quasiparticle type is formed from both the convective and the collisional part of the Kadanoff–Baym equation (and the situation is the same for the collisional part).

A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences. Translated from Teoreticheskaya i Matematicheskaya Fizika, Vol. 87, No. 2, pp. 241-253, May, 1991. Original article submitted January 5, 1990.

with the same remarks as in (3.3) with regard to the integration over the momentum and energy variables and standard indexing of the distribution functions in accordance with their momentum dependence.

To transform the obtained expressions, it is convenient to represent $\nabla_{\mathbf{p}}$ as a combination of products with respect to the relative momentum $\mathbf{p}-\mathbf{p}'$ and the total momentum $\mathbf{p}+\mathbf{p}'\equiv\mathbf{P}$ of a colliding pair. Then for short-range potentials, which is what we shall consider below and for which the total momentum occurs only in the energy variable, one gradient can be calculated explicitly:

$$\nabla_{\mathbf{P}}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\,|\mathcal{T}_{\mathbf{P}}(z)\,|\mathbf{k}\right\rangle=\nabla_{\mathbf{P}}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}\left(z-\frac{P^2}{4m}\right)\left|\,\mathbf{k}\right\rangle=\frac{\mathbf{P}}{2m}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\,|\mathcal{T}'|\mathbf{k}\right\rangle. \tag{3.5}$$

4. Collision Integral in a Dense Gas with Short-Range Interaction

In accordance with (2.1) and (2.5), the collision integral I_{coll} can be expressed on the basis of the results of Sec. 3 in the form

$$\begin{aligned}I_{\text{coll}}=\int\Big\{&\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}\left(\omega+\omega'-\frac{(\mathbf{p}+\mathbf{p}')^2}{4m}+i0\right)\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\times\\
&\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}\left(\omega+\omega'-\frac{(\mathbf{p}+\mathbf{p}')^2}{4m}-i0\right)\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle(\bar{f}\bar{f}'-ff')+\\
&\mathrm{Im}\left(\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}^*\left(\omega+\omega'-\frac{(\mathbf{p}+\mathbf{p}')^2}{4m}+i0\right)\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\times\right.\\
&\left.\nabla_{\mathbf{p}-\mathbf{p}'}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}\left(\omega+\omega'-\frac{(\mathbf{p}+\mathbf{p}')^2}{4m}+i0\right)\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\right)\times\\
&(\nabla_{\mathbf{r}}\bar{f}f'-2f\nabla_{\mathbf{r}}f)+\mathrm{Im}\left(\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}\left(\omega+\omega'-\frac{(\mathbf{p}-\mathbf{p}')^2}{4m}+i0\right)\right|\times\\
&\left.\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\nabla_{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}\left(\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}\left(\omega+\omega'-\frac{(\mathbf{p}-\mathbf{p}')^2}{4m}+i0\right)\right|\times\\
&\left.\left.\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\right)\right)(\bar{f}'\nabla_{\mathbf{r}}f-\bar{f}\nabla_{\mathbf{r}}\bar{f}')-\frac{\mathbf{p}+\mathbf{p}'}{2m}\nabla_{\mathbf{r}}f'f\,\mathrm{Im}\left(\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}^*\left(\omega+\omega'-\right.\right.\\
&\left.\frac{(\mathbf{p}+\mathbf{p}')^2}{4m}+i0\right)\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\mathcal{T}'\left(\omega+\omega'-\frac{(\mathbf{p}+\mathbf{p}')^2}{4m}+i0\right)\right|\times\\
&\left.\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\right)\Big\}(2\pi)^4\delta(\omega+\omega'-\bar{\omega}-\bar{\omega}')\,\delta(\mathbf{p}+\mathbf{p}'-\bar{\mathbf{p}}-\bar{\mathbf{p}}')\,AA'\bar{A}\bar{A}'d\Gamma,\end{aligned} \tag{4.1}$$

where we have made the assumption of a short-range nature of the interaction between the particles, and the integration $d\Gamma$ is over all energies ω, ω', $\bar{\omega}$, $\bar{\omega}'$ and momentum variables of the particles $1'$, $\bar{1}$, $\bar{1}'$. The indices of the spectral functions relate both the momentum and the energy variables. The integration over the energies can be performed in the pole approximation of Sec. 2. However, as was noted in [8], there is no need for this, and in the calculation of the non-Boltzmann collision integral we can use the approximation $\Gamma = 0$,

$$A(\mathbf{p},\omega)=(2\pi)^{-1}\delta(\omega-p^2/2m).$$

In this approximation, the non-Boltzmann part of the collision integral I_{coll} (i.e., all the terms in the integrand of (4.1) except the first) together with the third and fifth terms from the convective part (2.5) can be naturally divided into a sum of four terms:

$$I'_{\text{coll}}\equiv K=K_1+K_2+K_3+K_4,$$

$$\begin{aligned}K_1=\int d\mathbf{p}'\,\frac{\mathbf{p}+\mathbf{p}'}{2m}\,\nabla_{\mathbf{r}}\Big\{&ff'\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\,|\,\mathrm{Re}\,T'\,|\,\frac{\mathbf{p}-\mathbf{p}'}{2}\right\rangle-\\
\int d\bar{\mathbf{p}}d\bar{\mathbf{p}}'\bar{f}\bar{f}'\Bigg[&\frac{1}{2}\,\frac{\mathcal{P}}{E_{\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}}}\left|\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\,|T(E_{\frac{\mathbf{p}+\mathbf{p}'}{2}}+i0)|\,\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\right|^2+\\
&\pi\delta\left(E_{\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}}\right)\mathrm{Im}\left(\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\,|T\,(E_{\frac{\mathbf{p}+\mathbf{p}'}{2}}+i0)|\,\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle^*\times\right.\end{aligned}$$

$$\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T'(E_{\frac{\mathbf{p}-\mathbf{p}'}{2}}+i0)\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\Big)\delta(\mathbf{p}+\mathbf{p}'-\bar{\mathbf{p}}-\bar{\mathbf{p}}')\Big]\Big\},$$

$$K_2=\int d\mathbf{p}'\frac{\mathbf{p}-\mathbf{p}'}{2m}\nabla_{\mathbf{r}}\Big\{ff'\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|\operatorname{Re}T'\left|\frac{\mathbf{p}-\mathbf{p}'}{2}\right\rangle-$$

$$\frac{1}{2}\int d\mathbf{p}'d\mathbf{k}ff'\frac{\mathcal{P}}{E_{\mathbf{k}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}}}\left|\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T(E_{\mathbf{k}}+i0)|\mathbf{k}\rangle\right|^2\Big\},$$

$$K_3+K_4=\pi\int d\mathbf{p}'d\mathbf{k}'\delta(E_{\mathbf{k}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}})\times$$

$$\Big\{\frac{1}{2}\operatorname{Im}\Big[\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T(E_{\mathbf{k}}+i0)|\mathbf{k}\rangle^*\nabla_{\mathbf{k}}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T(E_{\frac{\mathbf{p}-\mathbf{p}'}{2}}+i0)|\mathbf{k}\rangle\Big]\times$$

$$[\bar{f}'\nabla_{\mathbf{r}}f'-f'\nabla_{\mathbf{r}}\bar{f}]+\operatorname{Im}\Big[\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T(E_{\mathbf{k}}+i0)|\mathbf{k}\rangle^*\times\nabla_{\mathbf{p}}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T(E_{\mathbf{k}}+i0)|\mathbf{k}\rangle\nabla_{\mathbf{r}}\bar{f}\bar{f}\Big\}. \quad (4.2)$$

In these last relations, $\mathcal{P}$ is the symbol of the principal value of an integral, and the index of E identifies the momentum used in the calculation of the kinetic energy $E_{\mathbf{k}}=k^2/2m$. For the $\mathcal{T}$ matrix on the energy shell, we use the symbol T. In addition, in the derivation of (4.2) one of the terms, proportional to $f\nabla_{\mathbf{r}}f'$, vanishes, since, as can be shown [12],

$$\int d\mathbf{k}\,\delta(E_{\mathbf{k}}-E_{\mathbf{p}})\operatorname{Im}(\langle\mathbf{p}|T|\mathbf{k}\rangle^*\nabla_{\mathbf{p}}\langle\mathbf{p}|T|\mathbf{k}\rangle)=0.$$

Using for the quasi-Boltzmann part of the collision integral the notation

$$I_B=\int d\mathbf{p}'\,d\bar{\mathbf{p}}\,d\bar{\mathbf{p}}'\left|\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T(\omega_0(\mathbf{p})-\omega_0(\mathbf{p}')+i0)\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\right|^2\times$$

$$\delta_{\mathbf{p}}\delta_E(ff'-\bar{f}'\bar{f}'),\quad \omega_0=\varepsilon(\mathbf{p})-i\frac{\Gamma}{2}, \quad (4.3)$$

where $\delta_{\mathbf{p}}=\delta(\mathbf{p}+\mathbf{p}'-\bar{\mathbf{p}}-\bar{\mathbf{p}}')$, $\delta_E=\delta(\varepsilon(\mathbf{p})+\varepsilon(\mathbf{p}')-\varepsilon(\bar{\mathbf{p}})-\varepsilon(\bar{\mathbf{p}}'))$ are the δ functions of the momentum and energy conservation laws for the quasiparticles, we write our kinetic equation in the final form

$$\Big(\frac{\partial}{\partial t}+\nabla_{\mathbf{p}}\varepsilon(\mathbf{p})\nabla_{\mathbf{R}}+\nabla_{\mathbf{R}}\varepsilon(\mathbf{p})\nabla_{\mathbf{p}}\Big)f(\mathbf{p},\mathbf{R},t)=\chi' I_B+I'_{\text{coll}},\quad \chi'=\Big(1-\frac{\partial\operatorname{Re}\Sigma}{\partial\omega}\Big)^{-1}. \quad (4.4)$$

The collisional parts of this equation I'_{coll} and I_B are determined by the relations (4.2) and (4.3), respectively.

5. Hard-Sphere Limit

We now consider the obtained collision integral in the limit of hard spheres. In the semiclassical approximation, which is consistent with the approximation in which the kinetic equation has been derived, the amplitude for scattering by hard spheres is

$$f(\theta)=\frac{a}{2}\exp\Big\{\frac{i}{\hbar}S(\theta)\Big\}, \quad (5.1)$$

where a is the hard-sphere radius, $S(\theta)$ is the increment of the classical action,

$$S(\theta)=\int mvb(\theta)d\theta,$$

and $b(\theta)$ is the impact parameter. For absolutely elastic scattering $b(\theta)=a\cos(\theta/2)$, and therefore

$$S(\theta)=2mva\sin(\theta/2). \quad (5.2)$$

Note that $2mva/\hbar=\Lambda$ is the semiclassical parameter. Under normal conditions, $\Lambda\gg 1$, and therefore (5.1) is valid everywhere except at the smallest angles (grazing collisions), which do not contribute to the collision integral.

For the scattering amplitude (5.1)–(5.2) in the integral (4.2), the derivatives with respect to the momenta can be calculated explicitly. For this, we shall use the directly verified relation

$$\nabla_{\mathbf{p}} f(\mathbf{p},\theta)=\frac{\mathbf{p}}{p}\frac{\partial}{\partial p}f(\mathbf{p},\theta)+\frac{\mathbf{e}_\theta}{p}\frac{\partial}{\partial\theta}f(\mathbf{p},\theta)=ifa(\mathbf{e}_{\mathbf{p}}\sin\theta/2+\mathbf{e}_\theta\cos\theta/2)=ifa\mathbf{n}, \tag{5.3}$$

where e_γ is the unit vector in the direction of the γ axis, and $\mathbf{n}$ is the unit vector that joins the centers of mass of molecules moving with momenta $\mathbf{p}$ and $\mathbf{p}'$ at the time of the collision. Using (5.3), we can obtain

$$\nabla_{\mathbf{p}-\mathbf{p}'}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T(z)|\frac{\mathbf{p}-\mathbf{p}'}{2}\right\rangle\Big|_{z=E_{\mathbf{p}}}=\frac{1}{2}\left\{\left[ia\mathbf{n}-\frac{\mathbf{p}-\mathbf{p}'}{2m}\frac{\partial}{\partial z}\right]\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T(z)|\frac{\mathbf{p}-\mathbf{p}'}{2}\right\rangle\right\}_{z=E_{\mathbf{p}}} \tag{5.4}$$

and, similarly,

$$\nabla_{\mathbf{k}}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T|\mathbf{k}\right\rangle=\frac{1}{2}\left[-ia\mathbf{n}-\frac{\mathbf{k}}{m}\frac{\partial}{\partial z}\right]\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T|\mathbf{k}\right\rangle. \tag{5.5}$$

Note that under semiclassical conditions of the collisions exchange effects can be ignored.

We make a number of simplifications. By virtue of (5.4), we obtain for K_3 and K_4

$$K_3+K_4=\pi\int d\mathbf{p}'d\mathbf{k}\,\delta(E_{\mathbf{k}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}})\,a\mathbf{n}\,(\nabla_{\mathbf{r}}\bar{f}\bar{f}'+\bar{f}\nabla_{\mathbf{r}}\bar{f}'-\bar{f}'\nabla_{\mathbf{r}}\bar{f})\times$$
$$\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T|\mathbf{k}\right\rangle-\pi\int d\mathbf{p}'d\mathbf{k}\,\delta(E_{\mathbf{k}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}})\ \mathrm{Im}\left(\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T|\mathbf{k}\right\rangle^*\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T'|\mathbf{k}\right\rangle\right)\times$$
$$\left\{\frac{\mathbf{p}-\mathbf{p}'}{2m}\nabla_{\mathbf{r}}\bar{f}f'+\frac{\mathbf{k}}{m}(\bar{f}'\nabla_{\mathbf{r}}\bar{f}-\bar{f}\nabla_{\mathbf{r}}\bar{f}')\right\}. \tag{5.6}$$

In transforming K_2, it is convenient to use the identity

$$\int d\mathbf{k}\,\delta(E_{\mathbf{k}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}})\left\langle\mathbf{k}|T|\frac{\mathbf{p}-\mathbf{p}'}{2}\right\rangle\nabla_{\mathbf{p}}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T|\mathbf{k}\right\rangle=0$$

and obtain for the sum $K = K_1 + K_2 + K_3 + K_4$ the expression

$$K=2\pi\int d\mathbf{p}'d\mathbf{k}\,\delta(E_{\frac{\mathbf{p}-\mathbf{p}'}{2}}-E_{\mathbf{k}})\,a\mathbf{n}\,(f\nabla_{\mathbf{r}}f'+\bar{f}\nabla_{\mathbf{r}}\bar{f}')\times$$
$$\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T|\mathbf{k}\right\rangle^*\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T|\mathbf{k}\right\rangle+\int d\mathbf{p}'d\mathbf{k}\,\frac{\mathbf{p}}{2m}\nabla_{\mathbf{r}}(ff'-\bar{f}\bar{f}')\times$$
$$-\frac{1}{2}\frac{\mathscr{P}'}{E_{\mathbf{k}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}}}\left|\left\langle\mathbf{k}|T(E_{\mathbf{k}}+i0)|\frac{\mathbf{p}-\mathbf{p}'}{2}\right\rangle\right|^2+$$
$$\pi\int d\mathbf{p}'d\mathbf{n}\,\delta(E_{\mathbf{k}}-E_{\frac{\mathbf{p}-\mathbf{p}'}{2}})\,\mathrm{Im}\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}|T|\mathbf{k}\right\rangle\left\langle\mathbf{k}|T'|\frac{\mathbf{p}-\mathbf{p}'}{2}\right\rangle\times$$
$$\left\{\frac{\mathbf{p}-\mathbf{p}'}{2}\nabla_{\mathbf{r}}(ff'-\bar{f}\bar{f}')-\mathbf{k}(\bar{f}'\nabla_{\mathbf{r}}\bar{f}-\bar{f}\nabla_{\mathbf{r}}\bar{f}')\right\}, \tag{5.7}$$

where $\mathscr{P}'$ is the derivative of the operator $\mathscr{P}$ with respect to the variable E. The first term in this sum is the Enskog integral expanded in a series with respect to the weak nonlocality. Note that under the conditions of a consistent derivation the χ factor is not present in these terms, since they are themselves small corrections. In the approximation in which only the first terms of the expansion with respect to the spatial gradients are taken into account, the χ factor arises only in the Boltzmann part of the collision integral, and for it a microscopic representation can be obtained in the framework of the developed formalism. As a result, the collisional part of the kinetic equation can be rewritten in the form

$$\chi' I_B^0+\delta I+I'_{\mathrm{coll}}, \tag{5.8}$$

where I'_{coll} is determined from (5.7), I_B^0 is the Boltzmann integral obtained from I_B in (4.3) by replacement of $\varepsilon(\mathbf{p})$ by $p^2/2m$, and the question of the calculation of the χ factor and δI will be considered in more detail in the following section. For the part of the χ factor that describes the reduction in the volume accessible to the molecules on account of their size, we obtain

$$\chi'=\left(1-\frac{\partial\,\mathrm{Re}\,\Sigma}{\partial\omega}\right)^{-4}. \tag{5.9}$$

The remaining terms owe their origin to the specific way in which the interaction is introduced — by the process of going to the limit of hard spheres from a soft repulsive potential. This limit is singular [10], and when the amplitude is expanded there arise specific contributions corresponding to grazing waves and diffraction by the hard edge of the scatterer. The influence of these effects on the kinetics is reflected by the last terms in (5.9). It is important that in the other limiting process — from hard sphere with weak attraction — they do not appear, since in that case there are no diffraction effects. Since it also follows on physical grounds that the contribution of such collisions to the kinetics of hard spheres is small (because they do not lead to transport of molecular characteristics), it appears that their contribution can be ignored in an analysis of the kinetic equation.

6. Microscopic Models of the χ Factor

In the calculation of the corrections in the density ($\sim na^3$, where n is the density of the gas, and a is the interaction range of the particles), it is necessary to take into account triple collisions in the transport coefficients [13]. Enskog took them into account by means of the structure χ factor. This factor is introduced phenomenologically and consists of two parts. One describes the decrease in the volume accessible to the molecules on account of their finite size, while the second describes the screening of a collision of two particles by the particles of the medium. In the proposed approach, both these effects are contained in the self-energy function, and the estimate of them is associated with a calculation of the derivative $\partial\Sigma/\partial\omega$. The first effect is taken into account by the renormalization of the scattering amplitude [14] and is equal to the fourth power of the renormalization constant. In the pole approximation, this result is obtained automatically, and for the corresponding part of the χ factor we obtain the representation (5.9). In the framework of the T approximation,

$$\frac{\partial\Sigma}{\partial\omega}=T'(0)*f, \tag{6.1}$$

where the prime denotes the derivative with respect to the energy, and the symbol * denotes the convolution with respect to the momentum and energy variables. The argument (0) of the T matrix means that it corresponds to forward scattering.

To calculate the derivative of the T matrix, we can proceed from the Lippmann–Schwinger equation, from which it follows that [5]

$$\langle\mathbf{p}|T'(\omega)|\mathbf{p}'\rangle=\langle\mathbf{p}|T|\mathbf{q}\rangle(\omega-q^2/2m)^{-2}\langle\mathbf{q}|T|\mathbf{p}'\rangle. \tag{6.2}$$

To calculate the object on the right-hand side of (6.2), it is convenient to use a mixed representation for the T matrix,

$$\langle\mathbf{p}|T(\omega)|\mathbf{r}\rangle=v(\mathbf{r})\exp\left\{-\frac{i}{\hbar}\mathbf{pr}+\frac{i}{\hbar}\int\limits_0^\infty v\left(\mathbf{r}-\frac{\mathbf{p}t}{m}\right)dt\right\}, \tag{6.3}$$

the last term being written down in the semiclassical approximation. Instead of (6.2) we then have

$$\langle\mathbf{p}|T'(\omega)|\mathbf{p}'\rangle=\int\limits_0^\infty dt\,tv(\mathbf{r}+\mathbf{v}t)v(\mathbf{r}-\mathbf{v}t)\exp\left\{-\frac{i}{\hbar v}\int\limits_{z-vt}^{z+vt}v(\mathbf{r})\,dz\right\}, \tag{6.4}$$

where the z axis is chosen in the direction of the asymptotic velocity $\mathbf{v}$, and in writing down the final exponential in (6.4) we have used the approximation of straight paths, which is sufficient for the hard-sphere potential and is valid for all potentials in the high-energy limit. Thus, for the hard-sphere model

$$\langle\mathbf{p}|T'|\mathbf{p}'\rangle=\pi a^3/3, \tag{6.5}$$

and for the χ' factor we have $(1+4\pi a^3/3)$, which corresponds to the result of the classical kinetic theory [1]. When the screening effect is taken into account, it is no longer sufficient to approximate the statistical T matrix by means of the ordinary collision amplitude (as is done in the case of a rarefied gas). In our formalism, it is necessary to take into account the finite lifetime of the quasiparticles [8] (the correction $-i\Gamma/2$ in the energy argument of the T matrix). Under the considered conditions, these corrections are small, and it is sufficient to take into account only the first two terms of the expansion in the "line width" Γ. In this way, we obtain

$$\left|\left\langle \mathbf{p}\left|T\left(\frac{p^2}{2m}-i\frac{\Gamma}{2}\right)\right|\mathbf{p}'\right\rangle\right|^2 \simeq |\langle\mathbf{p}|T(\varepsilon)|\mathbf{p}'\rangle|^2+\Gamma\,\mathrm{Im}[\langle\mathbf{p}|T^*|\mathbf{p}'\rangle\langle\mathbf{p}|T'|\mathbf{p}'\rangle]. \tag{6.6}$$

In the same approximation, it is necessary to use for the quasiparticle energy the formula $\omega_0(\mathbf{p})=\varepsilon(\mathbf{p})-i\Gamma(\mathbf{p})/2$, where $\varepsilon(\mathbf{p})$ is the ordinary real quasi-energy [8], and expand the δ function of the energy conservation law with respect to Γ.

Thus, with allowance for what was said in Sec. 5 (before Eq. (5.8)), the quasi-Boltzmann collision integral (4.3) decomposes into two terms $\chi' I_B = \chi' I_B^0 + \delta I$, where I_B^0 is exactly equal to the Boltzmann integral (see (5.8)), and the correction responsible for the screening effect has the form

$$\delta I=\frac{1}{2}\int\frac{d\bar{\mathbf{p}}\,d\mathbf{p}'\,d\bar{\mathbf{p}}'}{(2\pi)^9}2\pi\delta_{\mathbf{p}}\delta_{\varepsilon}\,\mathrm{Im}\left[\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T^*(\mathbf{p}'+\mathbf{p},\varepsilon+\varepsilon')\left|\frac{\mathbf{p}-\mathbf{p}'}{2}\right\rangle\times\right.$$

$$\left.\left\langle\frac{\mathbf{p}-\mathbf{p}'}{2}\right|T'(\mathbf{p}+\mathbf{p}',\varepsilon+\varepsilon')\left|\frac{\bar{\mathbf{p}}-\bar{\mathbf{p}}'}{2}\right\rangle\right]\ \{[\Gamma(\mathbf{p})+\Gamma(\mathbf{p}')]f(\mathbf{p})f(\mathbf{p}')-[\Gamma(\bar{\mathbf{p}})+\Gamma(\bar{\mathbf{p}}')]f(\bar{\mathbf{p}})f(\bar{\mathbf{p}}')\}. \tag{6.7}$$

Returning to the hard-sphere model, we must set

$$\varepsilon(\mathbf{p})=E(\mathbf{p})\equiv p^2/2m,\quad \Gamma(\mathbf{p})=a^2\int|\mathbf{p}-\mathbf{p}'|f(\mathbf{p}')d\mathbf{p}',$$

$$\langle\mathbf{p}|T'(\omega)|\mathbf{p}'\rangle|_{\omega=E(\mathbf{p})}=\frac{\partial}{\partial E(\mathbf{p})}\langle\mathbf{p}|T(E(\mathbf{p}))|\mathbf{p}'\rangle,$$

and we obtain for the additional collision integral (6.7) the explicit representation

$$\delta I=a^3\int d\mathbf{p}'\,d\bar{\mathbf{p}}\,d\bar{\mathbf{p}}'\,\delta_{\mathbf{p}}\delta_{E(\mathbf{p})}\frac{\sin\theta/2}{q}\{[\Gamma(\mathbf{p})+\Gamma(\mathbf{p}')]f(\mathbf{p})f(\mathbf{p}')-[\Gamma(\bar{\mathbf{p}})+\Gamma(\bar{\mathbf{p}}')]f(\bar{\mathbf{p}})f(\bar{\mathbf{p}}')\}, \tag{6.8}$$

where $q=|\mathbf{p}-\mathbf{p}'-\bar{\mathbf{p}}+\bar{\mathbf{p}}'|/2$, and θ is the angle between $\mathbf{p}-\mathbf{p}'$ and $\bar{\mathbf{p}}-\bar{\mathbf{p}}'$. It is worth noting that the assumption of a weak dependence of $\Gamma(\mathbf{p})$ on $\mathbf{p}$ (for example, replacement of $\Gamma(\mathbf{p})$ by its mean value) reduces I + δI to the Enskog form with an explicit representation for the χ factor. In fact, from this it is possible to obtain the limitations of the popular models of the χ factor.

As a result, the kinetic equation for the hard spheres will have the structure (4.4) with quasi-energy $\varepsilon = p^2/2m - i\Gamma/2$ and collisional part in the form

$$\chi' I_E^0+\delta I+I'_{\mathrm{coll}}. \tag{6.9}$$

where δI and I'_{coll} are determined by (6.8) and (5.7), respectively. Then $\chi' I_B^0$ and the first term in (5.7) give the first two terms in the expansion of the Enskog collision integral with respect to the small gradients.

It should be pointed out that the expansion with respect to the polarization diagrams [8] that is used to obtain the screening corrections for attractive potentials does not contribute in the hard-sphere model since the corresponding contributions to the transport properties appear only in the third order in na^3.

7. Connection with the Traditional Approach

To establish the connection between the employed approach and the traditional ones based on a system of coupled equations for the partial distribution functions, we consider in the framework of these approximations the right-hand side of the equation for the single-particle Green's function, which is expressed in terms of the convolution [5]

$$VG_2=\int_{-i\beta}^{0}T(1-\bar{1})*G(t_{\bar{1}},t_1)*G(t_{\bar{1}},t_2)\,dt_{\bar{1}}.$$

Transition to Fourier transforms, use of the convolution theorem, and elimination of the operators $T^{\gtrless}$ by means of the identity

$$T(z)=\mathscr{P}\int\frac{T^{>}(\omega)-T^{<}(\omega)}{z-\omega}\frac{d\omega}{2\pi}$$

gives to accuracy $(na^3)^2$

$$v(r_1-r_2)G_2(r_1r_2,r_1^+r_2^+)=\int T(\omega_1+\omega_2)*G(\omega_2)*G(\omega_1)\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}. \tag{7.1}$$

It is convenient to treat the matrix elements of the T operator that appear here in the mixed representation, in which there is a simple approximation for T in the semiclassical limit (6.3). However, for a dense gas, with allowance for the difference between $\varepsilon(\mathbf{p})$ and $p^2/2m$ and the finite width Γ, the phase of the exponential in (6.3) is replaced by the somewhat more complicated expression [12]

$$\eta(\mathbf{r},\mathbf{p})=\int_0^\infty v(\mathbf{r}+\mathbf{c}t)\exp(-\Gamma t)dt,\quad \mathbf{c}(\mathbf{p})=\partial\varepsilon(\mathbf{p})/\partial\mathbf{p}. \tag{7.2}$$

Substitution of these relations in (7.1) and integration over the frequencies give, after lengthy manipulations, a representation directly for the two-particle distribution function:

$$f_2(\mathbf{p}_1,\mathbf{p}_2,\mathbf{R}_1,\mathbf{R}_2)=f(\mathbf{P}_1,\mathbf{Q}_1)f(\mathbf{P}_2,\mathbf{Q}_2), \tag{7.3}$$

where $\mathbf{P}_1+\mathbf{P}_2=\mathbf{p}_1+\mathbf{p}_2$, $\mathbf{P}_1-\mathbf{P}_2=\mathbf{p}_1-\mathbf{p}_2-\partial\eta/\partial\mathbf{r}$, $\mathbf{Q}_1+\mathbf{Q}_2=\mathbf{R}_1+\mathbf{R}_2$, $\mathbf{Q}_1-\mathbf{Q}_2=\mathbf{R}_1-\mathbf{R}_2+\partial\eta/\partial\mathbf{p}$.

It is now clear that $\mathbf{P}_j$, $\mathbf{Q}_j$ are analogs of the limit coordinates of Bogolyubov, but they describe the evolution of a distinguished pair of particles in the semiclassical approximation in the effective mean field of the remaining particles with allowance for damping.

8. Conclusions

Thus, our analysis has enabled us, in the framework of a unified formalism, to give a description of two alternative transport mechanisms — the convective and the collisional. The kinetic description, which generalizes the advantages of the local quasiparticle approach and the nonlocal description of Enskog, is obtained in the framework of a model potential of Rice-Allnatt type [3], in which collisions occur on a hard core, and the quasiparticles are "dressed" on a long-range attractive potential. Such an approach makes it possible to reproduce correctly all the known limiting cases and approximations and can serve as a basis for the study of transport processes in gases in a wide range of pressures and densities.

LITERATURE CITED

1. D. Enskog, Ark. Mat. Astron. Fys., 21A, No. Bl, 1 (1928).
2. N. N. Bogolyubov, Teor. Mar. Fiz., 24, 242 (1975).
3. S. A. Rice and A. R. Allnatt, J. Chem. Phys., 34, 2144 (1961).
4. H. T. Davis, Adv. Chem. Phys., 24, 257 (1975).
5. L. P. Kadanoff and G. Baym, Quantum Statistical Mechanics, Benjamin, New York (1963).
6. J. C. Reinwater and R. F. Snider, Phys. Rev. A, 13, 1190 (1976).
7. K. Bauerwinkel and S. Grossman, Z. Phys., 198, 277 (1967).
8. A. V. Bogdanov and G. V. Dubrovskii, Teor. Mat. Fiz., 28, 80 (1976).
9. R. G. Newton, Scattering Theory of Waves and Particles, McGraw-Hill, New York (1966).
10. G. V. Dubrovskii and A. V. Bogdanov, Zh. Tekh. Fiz., 49, 1386 (1979).
11. P. M. Furtado, G. M. Mazenko, and S. Yip, Phys. Rev. A, 136, 1641 (1976).
12. K. Bauerwinkel, Z. Naturforsch. Teil A, 24, 22 (1969).
13. J. H. Ferziger and H. G. Kaper, Mathematical Theory of Transport Processes in Gases, Amsterdam (1972).
14. E. M. Lifshitz and L. P. Pitaevskii, Theoretical Physics, Vol. 9, Statistical Physics, Part 2 [in Russian], Nauka, Moscow (1978).