THE BOLTZMANN KINETIC EQUATION FOR AN IMPERFECT GAS

Yu. L. KLIMONTOVICH

Moscow State University

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To derive the Boltzmann kinetic equation, one employs the pair-collision approximation. However, in the framework of this model the interaction is not fully taken into account. It only defines the nature of dissipative processes in the kinetic equation. The contribution of the interaction to the thermodynamic functions is not taken into account and hence the kinetic equation is valid only for ideal gases. The kinetic equation for an imperfect gas is obtained in the pair-collision approximation. It contains in the collision integral two additional terms which are proportional to the time and coordinate derivatives of the first distribution function. The kinetic equation is used to derive the equations of gas dynamics for an imperfect gas in which the contribution of the interaction to the internal energy and pressure is taken into account. For the model of spherical molecules with weak attractive interactions, additional terms are expressed in terms of the Van der Waals constants.

1. THE BOLTZMANN EQUATION FOR A SPATIALLY HOMOGENEOUS IMPERFECT GAS

IN the monographs[1-5], different methods are described for the statistical derivation of kinetic equations and, in particular, of the Boltzmann kinetic equation. In the Boltzmann equation the two-particle interaction is not fully taken into account. Indeed, the effect of collisions is manifested only in the process of the establishment of equilibrium, i.e., in dissipative processes. The contribution of the interaction to the thermodynamic functions (internal energy, pressure, entropy) is not taken into account. Thus, the Boltzmann kinetic equation is valid only for an ideal gas.

In the present paper we derive the kinetic equation for an imperfect gas in the pair-collision approximation. On the basis of this equation, we obtain the equations of gas dynamics for an imperfect gas.

Let us denote by $f_N(x_1, \ldots, x_N, t)$ the particle coordinate and momentum distribution function, $x_i = (\mathbf{r}_i, \mathbf{p}_i)$ and $f_1(x_1, t) \equiv f_1(\mathbf{r}_1, \mathbf{p}_1, t)$ is the distribution function for one particle. The basic assumption in the Bogolyubov method for the derivation of the kinetic equations is as follows. With an arbitrary initial distribution function f_N, the system after some time—"synchronization time"—reaches the "kinetic stage" in which the entire subsequent time evolution of the system is completely determined by the time dependence of the distribution function $f_1(x_1, t)$. This dependence is determined by an equation of the type

$$\partial f_1 / \partial t = A(x_1, f_1(x_1, t)). \tag{1}$$

The quantity A clearly does not depend on time. The higher distribution functions in the kinetic stage depend on time only via the function $f_1(x_1, t)$, i.e.,

$$f_s = f_s(x_1, \ldots, x_s, f_1(x_1, t), \ldots, f_1(x_s, t)), \quad s \geqslant 2. \tag{2}$$

It is shown in[1], that for a spacially homogeneous gas the Boltzmann kinetic equation in the first approximation with respect to density is given by

$$\frac{\partial f_1(\mathbf{p}_1, t)}{\partial t} = I(\mathbf{p}_1, t), \quad \int f_1(\mathbf{p}_1, t)\, d\mathbf{p}_1 = 1. \tag{3}$$

Here $I(\mathbf{p}_1, t)$ is the Boltzmann collision integral. Let us write it in the form obtained in[1] (below, $\Phi(1, 2) = \Phi(|\mathbf{r}_1 - \mathbf{r}_2|)$, etc.),

$$I(\mathbf{p}_1, t) = n \int \frac{\partial \Phi(1,2)}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{p}_1} [f_1(\mathbf{P}_1(-\infty), t) f_1(\mathbf{P}_2(-\infty), t)]\, d\mathbf{r}_2\, d\mathbf{p}_2, \tag{4}$$

where $\mathbf{P}_1(x_1, x_2, -\infty)$, $\mathbf{P}_2(x_1, x_2, -\infty)$ are the "initial" momenta of two particles which collide at the moment of time t, and Φ is the interaction potential. The expression (4), as has been shown in Bogolyubov's paper, differs only by the form in which it has been written from the Boltzmann collision integral. The collision integral, as is well known, has the properties

$$\int \varphi(\mathbf{p}) I(\mathbf{p}, t)\, d\mathbf{p} = 0 \quad \text{for} \quad \varphi = 1,\ \mathbf{p},\ \mathbf{p}^2/2m. \tag{5}$$

The first property ensures the fulfillment of the law of conservation of the number of particles, the second—the law of conservation of momentum, and the third—of the kinetic energy of the particles of the gas. The first two conservation laws for a one-component gas in the absence of external forces are exact in the sense that their validity does not depend on the approximations made in the derivation of the Boltzmann equation from the Liouville equation. In contrast, the law of conservation of kinetic energy is an approximate law. It is valid only when the interaction potential energy is totally neglected, i.e., only for an ideal gas. Interaction then occurs only in processes leading to the establishment of equilibrium. These processes are determined by the Boltzmann collision integral.

We give now the derivation of the generalized Boltzmann kinetic equation, which describes equilibrium as well as non-equilibrium processes in imperfect gas in the pair-collision approximation. To begin with, let us use the first two equations of Bogolyubov's chain of equations:

$$\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \frac{\partial f_1}{\partial \mathbf{r}_1} = n \int \frac{\partial \Phi(1,2)}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{p}_1} f_2(x_1, x_2, t)\, dx_2 \equiv I(x_1, t),$$

$$\left(\frac{\partial}{\partial t}+\mathbf{v}_1\frac{\partial}{\partial \mathbf{r}_1}+\mathbf{v}_2\frac{\partial}{\partial \mathbf{r}_2}-\frac{\partial\Phi}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}-\frac{\partial\Phi}{\partial \mathbf{r}_2}\frac{\partial}{\partial \mathbf{p}_2}\right)f_2 \tag{6}$$

$$=n\int\left[\frac{\partial\Phi(1,3)}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}+\frac{\partial\Phi(2,3)}{\mathbf{r}_2}\frac{\partial}{\partial \mathbf{p}_2}\right]f_3(x_1,x_2,x_3,t)\,dx_3. \tag{7}$$

The function f_3 may be represented in the form

$$f_3=f_1f_1f_1+f_1(x_1,t)g_2(x_2,x_3,t)+f_1(x_2,t)g_2(x_3,x_1,t)+f_1(x_3,t)g_2(x_1,x_2,t)+g_3. \tag{8}$$

In a spatially homogeneous gas the term $f(x_3)g_2(x_1, x_2)$ drops out when integrated over r_3. Its contribution is also negligibly small in the spatially inhomogeneous case.

Let us consider the pair-collision approximation. In this approximation, the three-particle correlation function is equal to zero, i.e., $g_3 = 0$. Moreover, in substituting expression (8) into the right hand side of (7), we must take into consideration only the correlation between pairs of the interacting particles. This means that when substituting f_3 into the first term of the right hand side of (7), we must discard the term $f_1(x_1)g_2(x_2, x_3)$, and when substituting into the second—the term $f_1(x_2)g_2(x_3, x_1)$.

As a result, in the pair collision approximation, the right hand side of Eq. (7) takes the form

$$n\int\left[\frac{\partial\Phi(1,3)}{\partial \mathbf{r}_1}\frac{\partial f_2(x_1,x_3)}{\partial \mathbf{p}_1}f_1(x_2)+\frac{\partial\Phi(2,3)}{\partial \mathbf{r}_2}\frac{\partial f_2(x_2,x_3)}{\partial \mathbf{p}_2}f_1(x_1)\right]dx_3. \tag{9}$$

Using Eq. (6), we may write this equation in the form

$$\left(\frac{\partial}{\partial t}+\mathbf{v}_1\frac{\partial}{\partial \mathbf{r}_1}+\mathbf{v}_2\frac{\partial}{\partial \mathbf{r}_2}\right)f_1(x_1,t)f_1(x_2,t). \tag{10}$$

Eq. (6) and Eq. (7) with its right hand side given by (10) constitute a closed system of equations for the functions f_1 and f_2 in the pair collision approximation.

Let us first consider the case of a spatially homogeneous distribution, when $f_1(x, t) = f_1(p, t)$. The system of equations for the functions f_1 and f_2 takes, under this condition, the form

$$\frac{\partial}{\partial t}f_1(\mathbf{p}_1,t)=n\int\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}f_2(x_1,x_2,t)\,dx_2\equiv I(\mathbf{p}_1,t), \tag{11}$$

$$\left(\frac{\partial}{\partial t}+\mathbf{v}_1\frac{\partial}{\partial \mathbf{r}_1}+\mathbf{v}_2\frac{\partial}{\partial \mathbf{r}_2}-\frac{\partial\Phi}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}-\frac{\partial\Phi}{\partial \mathbf{r}_2}\frac{\partial}{\partial \mathbf{p}_2}\right)f_2=\frac{\partial}{\partial t}f_1(\mathbf{p}_1,t)f_1(\mathbf{p}_2,t). \tag{12}$$

Let us write the solution of Eq. (12) for times $\tau = t - t'$ much larger than the attenuation time for the initial correlation at the moment t'. This permits us to neglect the initial correlation. In this approximation

$$f_2(x_1,x_2,t)=f_1(\mathbf{P}_1(-\tau),t-\tau)f_1(\mathbf{P}_2(-\tau),t-\tau)+\int_0^\tau\left[\frac{\partial}{\partial t}f_1f_1\right]_{\mathbf{P}_1(-\tau'),\,\mathbf{P}_2(-\tau'),\,t-\tau'}d\tau'. \tag{13}$$

Here $\mathbf{P}_1(-\tau)$, $\mathbf{P}_2(-\tau)$ are the initial momenta at the moment t', expressed in terms of x_1, x_2 at the moment t.

Let us denote by $\tau_{\mathrm{rel}} = l/v_T$—the relaxation time of the distribution function—the mean collision interval; l—the mean free path, and $\tau_0 = r_0/v_T$—"the duration of the collision process," r_0 being the effective dimension of an atom. The time τ enters into formula (13) via the variables $\mathbf{P}_1(-\tau)$ and $\mathbf{P}_2(-\tau)$ and in the time argument of the functions f_1. Let us write expression (13) for the times τ:

$$\tau_0\ll\tau\ll\tau_{\mathrm{rel}}. \tag{14}$$

In the first approximation with respect to $\tau\partial f_1/\partial t$ it follows from (13) that

$$f_2=f_1(\mathbf{P}_1(-\tau),t)f_1(\mathbf{P}_2(-\tau),t)-\tau\frac{\partial}{\partial t}f_1(\mathbf{P}_1(-\tau),t)f_1(\mathbf{P}_2(-\tau),t)+\int_0^\tau\left[\frac{\partial}{\partial t}f_1f_1\right]_{\mathbf{P}_1(-\tau'),\,\mathbf{P}_2(-\tau'),\,t}d\tau'.$$

Let us integrate the second term by parts with respect to τ'. We obtain as a result, the expression

$$f_2=f_1(\mathbf{P}_1(-\tau),t)f_1(\mathbf{P}_2(-\tau),t)-\int_0^\tau\tau'\frac{\partial}{\partial t}\frac{d}{d\tau'}f_1(\mathbf{P}_1(-\tau'),t)f_1(\mathbf{P}_2(-\tau'),t)\,d\tau'. \tag{15}$$

Notice now that the derivative with respect to τ' in the integrand acts only on the dynamical variables. Indeed, let us use the equation for an arbitrary function of the dynamical variables $A(x)$:

$$dA(x)/dt=\{HA\}.$$

For

$$A=f_1(\mathbf{P}_1(-\tau))f_1(\mathbf{P}_2(-\tau)),\quad t=-\tau,$$

$$H=\frac{1}{2m}(\mathbf{p}_1^2+\mathbf{p}_2^2)+\Phi(1,2)$$

we obtain

$$\frac{d}{d(-\tau)}[f_1(\mathbf{P}_1(-\tau))f_1(\mathbf{P}_2(-\tau))]=-\left[\left(\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}+\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_2}\frac{\partial}{\partial \mathbf{p}_2}\right)f_1f_1\right]_{x_1(-\tau),\,x_2(-\tau)}. \tag{16}$$

The function $\Phi(|\mathbf{R}_1(-\tau) - \mathbf{R}_2(-\tau)|)$ decreases rapidly for $\tau > r_0/v_T$. Therefore we may, in accordance with the inequality (14), make the transition $\tau \to \infty$ in the expression (15). As a result, the solution (15) takes the form

$$f_2(x_1,x_2,t)=f_1(\mathbf{P}_1(-\infty),t)f_1(\mathbf{P}_2(-\infty),t)-\frac{\partial}{\partial t}\int_0^\infty\tau\frac{d}{d\tau}f_1(\mathbf{P}_1(-\tau),t)f_1(\mathbf{P}_2(-\tau),t)\,d\tau. \tag{17}$$

In Bogolyubov's paper[1] the distribution function is given by the first term on the right hand side. The additional term in (17) by order of magnitude is equal to $(\tau_0/\tau_{\mathrm{rel}})f_1f_1$. We shall see that this term determines the contribution of the interaction potential energy to the internal energy of an imperfect gas.

Using the expression (17), we may write the collision integral in the form of a sum of two parts

$$I=I_1+I_2. \tag{18}$$

The expression for I_1 coincides with (4) and, consequently, differs only in notation from the Boltzmann collision integral:

$$I_2(\mathbf{p}_1,t)=-n\frac{\partial}{\partial t}\iint_0^\infty\tau\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}\frac{d}{d\tau}f_1(\mathbf{P}_1(-\tau),t)f_1(\mathbf{P}_2(-\tau),t)\,d\tau\,dx_2. \tag{19}$$

In the perturbation theory approximation, the expression (17) takes the form (here $\rho = |\mathbf{r}_1 - \mathbf{r}_2 - (\mathbf{v}_1 - \mathbf{v}_2)\tau|$),

$$f_2=f_1(\mathbf{p}_1,t)f_1(\mathbf{p}_2,t)+\int_0^\infty\frac{\partial\Phi(\rho)}{\partial \mathbf{r}_1}\left(1-\tau\frac{\partial}{\partial t}\right)d\tau\left(\frac{\partial}{\partial \mathbf{p}_1}-\frac{\partial}{\partial \mathbf{p}_2}\right)f_1(\mathbf{p}_1,t)f_1(\mathbf{p}_2,t). \tag{20}$$

The first term in (20) does not make any contribution to the collision integral. The second determines I_1. Expanding the integrand in terms of a Fourier integral with respect to $\mathbf{r}_1 - \mathbf{r}_2$, we write it in the form

$$I_1 = \frac{n}{8\pi^2}\frac{\partial}{\partial p_{1i}}\int k_i k_j \nu^2(k)\,\delta(\mathbf{k}\mathbf{v}_1 - \mathbf{k}\mathbf{v}_2)\left(\frac{\partial}{\partial p_{1j}} - \frac{\partial}{\partial p_{2j}}\right) f_1 f_1\, d\mathbf{k}\, d\mathbf{p}_2. \quad (21)$$

This is the Landau collision integral.

The expression for I_2 has the form

$$I_2 = \frac{n}{(2\pi)^3}\frac{\partial}{\partial p_{1i}}\int k_i k_j \nu^2(k)\int_0^\infty \cos[(\mathbf{k}\mathbf{v}_1 - \mathbf{k}\mathbf{v}_2)\tau]\tau\, d\tau \times \frac{\partial}{\partial t}\left(\frac{\partial}{\partial p_{1j}} - \frac{\partial}{\partial p_{2j}}\right) f_1 f_1 d\mathbf{k}\, d\mathbf{p}_2. \quad (22)$$

2. CONSERVATION LAWS

Let us consider the conservation laws for the kinetic equation with collision integral (18) and (19). Since the expression for I_1 coincides with the expression (4), then in accordance with (5)

$$\int \varphi(\mathbf{p}) I_1\, d\mathbf{p} = 0 \text{ for } \varphi = 1,\ \mathbf{p}, \mathbf{p}^2/2m. \quad (23)$$

It follows directly from expression (19) that

$$\int I_2 dp = 0. \quad (24)$$

Let us multiply expression (19) by $\mathbf{p}_1$ and integrate over $\mathbf{p}_1$. Then, let us integrate by parts with respect to $\mathbf{p}_1$. We obtain as a result

$$\int \mathbf{p}_1 I_2 d\mathbf{p}_1$$

$$= n\frac{\partial}{\partial t}\iint_0^\infty \tau\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{d}{d\tau} f_1(\mathbf{P}_1(-\tau), t) f_1(\mathbf{P}_2(-\tau), t)\, d\tau\, d\mathbf{p}_1\, d\mathbf{p}_2\, d\mathbf{r}_2.$$

Because of the spatial homogeneity, the integrand depends only on $\mathbf{r}_1 - \mathbf{r}_2$. Let us make a change of variables under the integral sign: $\mathbf{r}_1, \mathbf{p}_1 \rightleftarrows \mathbf{r}_2, \mathbf{p}_2$. The right hand side of the equality changes sign as a result. It follows from this that

$$\int \mathbf{p}_1 I_2 d\mathbf{p}_1 = 0. \quad (25)$$

Thus, on the basis of Eqs. (23)–(25), we have

$$\int \varphi(I_1 + I_2)\, d\mathbf{p} = 0 \text{ for } \varphi = 1, \mathbf{p}. \quad (26)$$

These properties guarantee the fulfillment of the laws of conservation of the number of particles and of momentum.

Let us consider the law of conservation of energy. Let us multiply the expression (19) by $\mathbf{p}_1^2/2m$ and integrate over $\mathbf{p}_1$. After that let us integrate by parts with respect to $\mathbf{p}_1$. We have as a result,

$$\int \frac{\mathbf{p}_1^2}{2m} I_2 d\mathbf{p}_1$$

$$= n\frac{\partial}{\partial t}\iint_0^\infty \tau v_1 \frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{d}{d\tau} f_1(\mathbf{P}_1(-\tau), t) f_1(\mathbf{P}_2(-\tau), t)\, d\tau\, d\mathbf{r}_2\, d\mathbf{p}_1\, d\mathbf{p}_2.$$

Let us symmetrize this expression with respect to the variables 1 and 2 and then make the change of variables $\mathbf{x}_2, \mathbf{x}_2 \to \mathbf{X}_1(-\tau), \mathbf{X}_2(-\tau)$. Using Liouville's theorem, we obtain

$$\int \frac{\mathbf{p}_1^2}{2m} I_2 d\mathbf{p}_1 = \quad (27)$$

$$= \frac{n}{2}\frac{\partial}{\partial t}\iint_0^\infty \tau\left[(\mathbf{v}_1 - \mathbf{v}_2)\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\right]_{\tau}\frac{d}{d\tau} f_1(\mathbf{P}_1(-\tau), t) f_1(\mathbf{P}_2(-\tau), t)$$

$$\times\, d\tau\, d(\mathbf{R}_1(-\tau) - \mathbf{R}_2(-\tau))\, d\mathbf{P}_1(-\tau)\, d\mathbf{P}_2(-\tau).$$

The brackets $[\ ]_\tau$ indicate that the expression enclosed in them is a function of τ and the integration variables $\mathbf{X}_1(-\tau)$, $\mathbf{X}_2(-\tau)$.

On the basis of (16), we conclude that the expression $d/d\tau \cdot f_1(\mathbf{P}_1(-\tau)) f_1(\mathbf{P}_2(-\tau))$ on the right hand side of (27) is a function of only the integration variables $\mathbf{X}_1(-\tau)$, $\mathbf{X}_2(-\tau)$ and does not, consequently, depend on the integration variable τ.

Let us in expression (27) carry out the integration with respect to τ by parts. As a result

$$\int_0^\infty\left[(\mathbf{v}_1 - \mathbf{v}_2)\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\right]_\tau \tau\, d\tau = -\int_0^\infty [\Phi(1,2)]_\tau d\tau. \quad (28)$$

Substituting this expression into the right hand side of (27) and making the inverse change of variables $\mathbf{X}(-\tau) \to \mathbf{x}$, we have

$$\int \frac{\mathbf{p}_1^2}{2m} I_2 d\mathbf{p}_1$$

$$= -\frac{n}{2}\frac{\partial}{\partial t}\iint_0^\infty \Phi(1,2)\frac{d}{d\tau} f_1(\mathbf{P}_1(-\tau), t) f_1(\mathbf{P}_2(-\tau), t)\, d\mathbf{r}_2\, d\mathbf{p}_1\, d\mathbf{p}_2\, d\tau.$$

Integrating with respect to τ, we finally obtain

$$\int \frac{\mathbf{p}_1^2}{2m} I_2\, d\mathbf{p}_1 = -\frac{n}{2}\frac{\partial}{\partial t}\int \Phi(1,2) f_1(\mathbf{P}_1(-\infty), t) f_1(\mathbf{P}_2(-\infty), t)\, d\mathbf{r}_2\, d\mathbf{p}_1\, d\mathbf{p}_2. \quad (29)$$

We took into account here the fact that for a spatially homogeneous particle distribution

$$\frac{\partial}{\partial t}\int f_1(\mathbf{p}_1, t) f_1(\mathbf{p}_2, t)\, d\mathbf{p}_1\, d\mathbf{p}_2 = 0.$$

Thus, the integral on the left hand side of (29) does not vanish and, hence, the integral

$$\int \frac{\mathbf{p}_1^2}{2m}(I_1 + I_2)\, d\mathbf{p}_1.$$

does not vanish also.

Let us multiply the kinetic equation (11), having (18) as its collision integral, by $\mathbf{p}_1^2/2m$ and integrate over $\mathbf{p}_1$. Taking (29) into account, we obtain the law of conservation of energy

$$\frac{\partial}{\partial t}\left\{n\int \frac{\mathbf{p}_1^2}{2m} f_1 d\mathbf{p}_1 + \frac{n^2}{4}\int \Phi(1,2) f_1(\mathbf{P}_1(-\infty), t) f_1(\mathbf{P}_2(-\infty), t)\, d(\mathbf{r}_1 - \mathbf{r}_2)\, d\mathbf{p}_1\, d\mathbf{p}_2\right\} = 0. \quad (30)$$

Thus, the conserving quantity is the sum of the kinetic and the potential energy of the pairs of colliding particles, i.e., the quantity

$$U = n\int \frac{\mathbf{p}_1^2}{2m} f_1 d\mathbf{p}_1 + \frac{n^2}{2}\int \Phi(1,2) f_1(\mathbf{P}_1(-\infty), t) f_1(\mathbf{P}_2(-\infty), t)\, d(\mathbf{r}_1 - \mathbf{r}_2)\, d\mathbf{p}_1\, d\mathbf{p}_2, \quad (31)$$

which is the internal energy density. In the equilibrium case, the expression (31) takes the form

$$U = n\frac{3}{2}\varkappa T + \frac{n^2}{2}\int \Phi(1,2)\exp\{-\Phi(1,2)/\varkappa T\}\, d(\mathbf{r}_1 - \mathbf{r}_2). \quad (32)$$

For the model of spheres with weak attractive interactions, when

$$\Phi(r) = \begin{cases} \infty & \text{for } r \leqslant r_0 \\ \Phi(r) < 0,\ |\Phi(r)|/\varkappa T \ll 1 & \text{for } r > r_0 \end{cases}, \quad (33)$$

from the formula (33) follows the expression

$$U = {}^3/_2 n\varkappa T - n^2 a.$$

Here

$$a = 2\pi \int_{r_0}^{\infty} |\Phi(r)| r^2 dr$$

is the Van der Waals constant.

3. SPATIALLY INHOMOGENEOUS DISTRIBUTION OF THE PARTICLES OF A GAS. EQUATIONS OF GAS DYNAMICS

To obtain the kinetic equation for a spatially inhomogeneous imperfect gas, we turn to the system of equations (6) and (7). In the pair-collision approximation, the right hand side of Eq. (7) is given by the expression (9) or (10).

Let us transform the right hand side of Eq. (6). Let us in the function f_2 change to the new variables: $(\mathbf{r}_1 - \mathbf{r}_2)$, $(\mathbf{r}_1 + \mathbf{r}_2)/2$. A characteristic length with respect to the variable $\mathbf{r}_1 - \mathbf{r}_2$ is the effective radius of interaction r_0, while with respect to, say, the variable $\mathbf{r}_1$, the mean free path l is a characteristic length. Since $r_0 \ll l$, we have in the first approximation with respect to r_0/l,

$$f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) = \left(1 - \frac{1}{2}(\mathbf{r}_1 - \mathbf{r}_2)\frac{\partial}{\partial \mathbf{r}_1}\right) f_2(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t).$$

When this expression is substituted into the right hand side of Eq. (6) a new term, proportional to the derivative with respect to $\mathbf{r}_1$, appears in the collision integral. Let us denote this part of the collision integral by I_3. We write the expression for I_3 in the form

$$I_3 = -\frac{n}{2}\int\left(\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}\right)$$
$$\times(\mathbf{r}_1 - \mathbf{r}_2)\frac{\partial}{\partial \mathbf{r}_1}\frac{1}{2}[f_2(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) + f_2(\mathbf{r}_1, -(\mathbf{r}_1 - \mathbf{r}_2), \mathbf{p}_1, \mathbf{p}_2, t)]\,d\mathbf{r}_2\,d\mathbf{p}_2. \qquad (34)$$

Here, we have used the fact that

$$f_2(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) = f_2(\mathbf{r}_1, -(\mathbf{r}_1 - \mathbf{r}_2), \mathbf{p}_1, \mathbf{p}_2, t) + O(r_0/l).$$

Let us write the equation for the function $f_2(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t)$. It follows from Eq. (7) with (10) as the right hand side and has the form

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1\frac{\partial}{\partial \mathbf{r}_1} + (\mathbf{v}_1 - \mathbf{v}_2)\frac{\partial}{\partial(\mathbf{r}_1 - \mathbf{r}_2)} - \frac{\partial\Phi}{\partial \mathbf{r}_1}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right)\right] f_2$$
$$= \left(\frac{\partial}{\partial t} + \mathbf{v}_1\frac{\partial}{\partial \mathbf{r}_1}\right) f_1(\mathbf{r}_1, \mathbf{p}_1, t) f_1(\mathbf{r}_1, \mathbf{p}_2, t). \qquad (35)$$

We solve this equation in the same manner as we solved Eq. (12). We obtain as a result

$$f_2(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) = f_1(\mathbf{r}_1, \mathbf{P}_1(-\infty), t) f_1(\mathbf{r}_1, \mathbf{P}_2(-\infty), t)$$
$$-\left(\frac{\partial}{\partial t} + \mathbf{v}_1\frac{\partial}{\partial \mathbf{r}_1}\right)\int_0^{\infty}\tau\frac{d}{d\tau} f_1(\mathbf{r}_1, \mathbf{P}_1(-\tau), t) f_1(\mathbf{r}_1, \mathbf{P}_2(-\tau), t)\,d\tau. \qquad (36)$$

In the spatially homogeneous case this expression coincides with (17).

Let us now represent the collision integral in the form of a sum of three parts

$$I = I_1 + I_2 + I_3. \qquad (37)$$

We obtain the expression for I_1 by substituting into $I(x_1, t)$ in Eq. (6) the first term of (36). Thus,

$$I_1(x_1, t) = n\int\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1} f_1(\mathbf{r}_1, \mathbf{P}_1(-\infty), t) f_1(\mathbf{r}_1, \mathbf{P}_2(-\infty), t)\,d\mathbf{r}_2\,d\mathbf{p}_2. \qquad (38)$$

In the spatially homogeneous case this expression coincides with (4).

The expression for I_2 is obtained as a result of the substitution of the symmetrized second term of (36) into the right hand side of Eq. (6):

$$I_2(x_1, t) = -\iint_0^{\infty}\frac{\partial\Phi(1,2)}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{p}_1}\left(\frac{\partial}{\partial t} + \frac{\mathbf{v}_1 + \mathbf{v}_2}{2}\frac{\partial}{\partial \mathbf{r}_1}\right)$$
$$\times\tau\frac{d}{d\tau} f_1(\mathbf{r}_1, \mathbf{P}_1(-\tau), t) f_1(\mathbf{r}_1, \mathbf{P}_2(-\tau), t)\,d\tau\,d\mathbf{r}_2\,d\mathbf{p}_2. \qquad (39)$$

In the spatially homogeneous case this expression coincides with (19).

The integral I_3 is given by the expression (34) if we substitute into it the first term of (36). In the spatially homogeneous state $I_3 = 0$.

Let us use the kinetic equation (6) with the collision integral (37) to derive the equations of gas dynamics for an imperfect gas. For this end, let us consider the contribution of the collision integrals I_1, I_2, I_3 to the transport equations. The integral I_1 again in the spatially inhomogeneous state has the properties given by expression (23) and does not therefore make a direct contribution to the transport equations. It contributes only to the stress tensor and the thermal flux-vector. The integral I_2, as in the spatially homogeneous case, has the properties

$$\int \varphi I_2 d\mathbf{p} = 0 \text{ for } \varphi = 1, \mathbf{p}$$

and, consequently, does not contribute directly to the transport equations for the particle number density and the momentum density. Thus, only the integral I_3 makes a contribution to the transport equation.

It follows from the expressions (34) and (36) that

$$n\int \mathbf{p}_{1i} I_3 d\mathbf{p}_1 = -\partial \mathbf{P}_{ij}/\partial r_j,$$

where

$$P_{ij}^{\text{int}} = -\frac{n^2}{2}\int\frac{r_i r_j}{r}\frac{\partial\Phi(r)}{\partial r} f_1(\mathbf{r}_1, \mathbf{P}_1(-\infty), t) f_1(\mathbf{r}_1, \mathbf{P}_2(-\infty), t)\,d\mathbf{r}\,d\mathbf{p}_1 d\mathbf{p}_2 \qquad (40)$$

is an addition to the stress tensor P_{ij} due to the interaction. This correction, naturally, differs from zero also in the local equilibrium approximation. In this approximation

$$P_{ij}^{\text{int}} = \delta_{ij} p_{\text{int}},$$
$$p_{\text{int}} = -\frac{n^2}{6}\int r\frac{\partial\Phi(r)}{\partial r} f_1^{(0)}(P_1(-\infty)) f_1^{(0)}(P_2(-\infty))\,d\mathbf{r}\,d\mathbf{p}_1\,d\mathbf{p}_2, \qquad (41)$$

where $f_1^{(0)}$ is the local Maxwell distribution. For the interaction potential (33), we find from the expression (41)

$$p_{\text{int}} = n^2(\varkappa T b - a),$$
$$b = \frac{2\pi}{3} r_0^3, \quad a = 2\pi\int_{r_0}^{\infty}|\Phi(r)| r^2 dr, \qquad (42)$$

where a and b are the Van der Waals constants.

The integrals I_2 and I_3 contribute to the energy balance equation. After making transformations similar to those carried out in Sec. 2 in the derivation of expression (29), we obtain from formula (39)

$$n\int\frac{\mathbf{p}_1^2}{2m} I_2 d\mathbf{p}_1 = -\frac{n^2}{2}\int\Phi(1,2)\left(\frac{\partial}{\partial t} + \frac{\mathbf{v}_1 + \mathbf{v}_2}{2}\frac{\partial}{\partial \mathbf{r}_1}\right)$$
$$\times f_1(\mathbf{r}_1, \mathbf{P}_1(-\infty), t) f_1(\mathbf{r}_1, \mathbf{P}_2(-\infty), t)\,d\mathbf{r}_2\,d\mathbf{p}_1\,d\mathbf{p}_2. \qquad (43)$$

In the spatially homogeneous state, this expression coincides with the expression (29).

In the local equilibrium approximation, expression (43) takes the form

$$n\int \frac{\mathbf{p}_1^2}{2m} I_2 d\mathbf{p}_1 = -\left(\frac{\partial U_{\text{int}}}{\partial t} + \frac{\partial \mathbf{u}}{\partial \mathbf{r}_1} U_{\text{int}}\right), \tag{44}$$

where

$$U_{\text{int}} = \frac{n^2}{2}\int \Phi(1,2) f_1^{(0)}\,(\mathbf{P}_1(-\infty)) f_1^{(0)}\,(\mathbf{P}_2(-\infty)) d(\mathbf{r}_1 - \mathbf{r}_2) d\mathbf{p}_1 d\mathbf{p}_2$$

$$= \frac{n^2}{2}\int \Phi(r) \exp\left\{-\frac{\Phi(r)}{\varkappa T}\right\} d\mathbf{r} \tag{45}$$

is the contribution to the internal energy density due to the interaction and **u** is the average velocity. For the interaction potential (33) $U_{\text{int}} = -n^2 a$.

Using the expression for I_3, we find

$$\int \frac{\mathbf{p}_1^2}{2m} I_3 d\mathbf{p}_1 = \frac{n^2}{4}\frac{\partial}{\partial r_j}\int (\mathbf{v}_1 + \mathbf{v}_2)_i \frac{r_i r_j}{r}\frac{\partial \Phi}{\partial r} f_2 d\mathbf{r} d\mathbf{p}_1 d\mathbf{p}_2.$$

It follows from this that in the local equilibrium approximation,

$$\int \frac{\mathbf{p}_1^2}{2m} I_3 d\mathbf{p}_1 = -\frac{\partial}{\partial \mathbf{r}_1}(\mathbf{u} p_{\text{int}}). \tag{46}$$

The quantity p_{int} is given by the expression (42).

The viscous stress tensor $\pi_{ij} = P_{ij} - \delta_{ij} p$ and the thermal flux vector S are calculated in the usual approximation using only the collision integral I_1. As a result, we obtain a system of equations of gas dynamics for an imperfect gas. This system differs from the system of equations of gas dynamics by the fact that the internal energy density and the pressure are given by the expressions

$$U(\mathbf{r}, t) = n(\mathbf{r}, t) \cdot {}^3/_2 \varkappa T(\mathbf{r}, t) + U_{\text{int}}(\mathbf{r}, t);$$
$$p(\mathbf{r}, t) = n(\mathbf{r}, t) \varkappa T(\mathbf{r}, t) + p_{\text{int}}(\mathbf{r}, t),$$

in which U_{int}, and p_{int} are contributions due to the fact that the gas is not an ideal gas (see the formulas (45), (41)).

In the above approximation, the equations of gas dynamics contain only terms which are linear in two small parameters: the density parameter $\epsilon = nr_0^3$ and the hydrodynamic parameter $\epsilon_h = l/L \sim \epsilon^{-1} r_0/L$.

It is possible to obtain generalized equations of gas dynamics to second order in ϵ and ϵ_h, i.e., to include terms of order ϵ^2, $\epsilon\epsilon_h$ and ϵ_h^2. The ϵ^2-order terms cannot be obtained from the above kinetic equation since they are determined not only by binary but also by ternary collisions. However, in the framework of gas dynamics, the ϵ^2-terms appear only in the thermodynamic functions p and U, and are given in p by the well-known second virial coefficient and the corresponding contribution to U. The ϵ_h^2-terms may be obtained on the basis of the Boltzmann equation, taking only the integral I_1 into account (equation with higher order derivatives). The $\epsilon\epsilon_h$-terms can be obtained only when the additional terms given above are taken into consideration in the Boltzmann equation. They determine the contribution of the interaction to the coefficients of viscosity and thermal conductivity.

In recent years a considerable number of papers have been published which deal with the possibility of taking into consideration in the framework of the kinetic equation ternary and higher collisions. A review of these papers is given in[6]. Naturally, as the density of the gas increases, the role of the additional contributions to the collision integral considered here (the integrals I_2 and I_3), increases.

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