ON THE KINETIC THEORY OF GASES WITH ROTATIONAL DEGREES OF FREEDOM

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Abstract

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E. G. KOLESNICHENKO, V. F. BAIBUZ

ON THE KINETIC THEORY OF GASES WITH ROTATIONAL DEGREES OF FREEDOM

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In the present work we consider several questions in the kinetic theory of gases with nonspherical molecules, whose interaction can be approximated by the potential of rigid bodies. The kinetic equation for such gases was obtained from heuristic considerations by Curtiss ([1]), and subsequently more rigorously, though in a rather cumbersome form, by Curtiss and Dahler ([2]). Quite a number of works have been devoted to the formal generalization, to this case, of the solution methods developed for the Boltzmann equation describing the motion of monatomic gases; however, the mathematical structure of these equations has so far scarcely been studied.

We begin by giving a simple derivation of the kinetic equation. In the first approximation with respect to the gas density n, for an arbitrary potential with finite radius of action it has the form ([3]):

$$\frac{\partial F(x_1,t)}{\partial t} + \mathcal{H} F(x_1,t) = n \int dx_2\, \theta(P)\, [\mathcal{H}_2^{(0)} I - I \mathcal{H}_2^{(0)}] F(x_1,t) F(x_2,t). \quad (1)$$

Here x is the set of generalized coordinates and momenta of a molecule: $x = \{r, p, \alpha, M_\alpha\}$, where r and p are the coordinates and momenta of the center of mass, and α and M_α are the Euler angles and the conjugate momenta. $\mathcal{H}$ is the Liouville operator for one particle, $\mathcal{H}_2^{(0)} = \mathcal{H}(x_1) + \mathcal{H}(x_2)$ is the Liouville operator for two noninteracting particles, $\mathcal{H}_2$ is the Liouville operator for two interacting particles, and $I = \exp(-t\mathcal{H}_2)\exp(t\mathcal{H}_2^{(0)})$. Let us denote $q = \{r, \alpha\}$, $p = \{p, M_\alpha\}$. Then $P(q_1, q_2)$ is the function defining the region G in which the interaction potential is nonzero, by the formulas $P(q_1, q_2) > 0$ for $q_1, q_2 \in G$ and $P(q_1, q_2) < 0$ outside G. θ is the Heaviside function, so that $\theta(P)$ is the characteristic function of the region G.

Multiplying both sides of (1) by an arbitrary differentiable function $\varphi(x_1)$ and integrating with respect to x_1, and integrating by parts in the first term on the right-hand side, we obtain that it is equal to

$$\int dx_1 dx_2 [-\mathcal{H}_2^{(0)} P] \delta(P) \varphi(x_1) I F(x_1) F(x_2)$$

$$-\int dx_1 dx_2 \theta(P) [\mathcal{H}_2^{(0)} \varphi(x_1)] I F(x_1) F(x_2) - \int dx_1 dx_2 \theta(P) \varphi(x_1) I \mathcal{H}_2^{(0)} F(x_1) F(x_2), \tag{2}$$

We shall regard the interaction potential of two rigid bodies as the limit of a sequence of smooth repulsive potentials of finite radius of action. Then, in passing to the limit along this sequence, the integration in the last two terms will in fact be performed over an infinitely thin layer surrounding the excluded volume, so that in the limit both of them will become 0 because the integrand is finite. It then follows from the fundamental lemma of the calculus of variations that the kinetic equation for rigid bodies has the form:

$$\frac{\partial F(x_1,t)}{dt} + \mathcal{H} F(x_1,t) = n \int dx_2 [-\mathcal{H}_2^{(0)} P] \delta(P) I F(x_1,t) F(x_2,t). \tag{3}$$

Let us pass from integration with respect to r_2 to the integral with respect to $r_{21} = r_2 - r_1$. Following Curtiss and Dahler ([2]), we shall specify r_{21} in curvilinear coordinates

$\mathbf{k}$ and ρ, where $\mathbf{k}$ is the normal to the surface of the excluded volume, and the coordinate surface $\rho = \text{const} = \rho_0$ is specified by the function $\rho_0 H(\mathbf{k})$. Then the volume element $d\mathbf{r}_{21}$ will be equal to $\rho^2 H(\mathbf{k}) S(\mathbf{k})\, d\mathbf{k}\, d\rho$, and the surface element $\rho = \text{const}$ will be $\rho^2 S(\mathbf{k})\, d\mathbf{k}$. In these variables one may put $P = \rho_0 - \rho$. Choosing the units so that the excluded volume is described by the function $H(\mathbf{k})$, i.e., for $\rho = 1$ we obtain the Kertiss-Dahler equation:

$$\frac{\partial F(x_1,t)}{\partial t} + \mathcal{H} F(x_1,t) = n \int_{(\mathcal{H}2^{(0)}\rho)>0} [I F(x_1,t) F(x_2,t)] [\mathcal{H}_2^{(0)} \rho]\, H(\mathbf{k}) S(\mathbf{k})\, d\mathbf{k}\, d\alpha_2\, d\mathbf{p}_2 +$$

$$+ n \int_{(\mathcal{H}2^{(0)}\rho)<0} F(x_1,t) F(x_2,t) [\mathcal{H}_2^{(0)} \rho]\, H(\mathbf{k}) S(\mathbf{k})\, d\mathbf{k}\, d\alpha_2\, d\mathbf{p}_2. \tag{4}$$

They showed that $[\mathcal{H}_2^{(0)} \rho] H(\mathbf{k}) = (\mathbf{k} \cdot \mathbf{g})$,

$$\mathbf{g} = \frac{1}{m}(\mathbf{p}_2 - \mathbf{p}_1) + [\omega_2 \times \sigma_2] - [\omega_1 \times \sigma_1],$$

where ω_i are the angular velocities of the molecules, and σ_i are vectors directed to the point of contact from the centers of the molecules.

Consider the integral $\int d\mathbf{k}\, S(\mathbf{k})(\mathbf{k} \cdot \mathbf{g})$. It is taken over the surface of the excluded volume for fixed orientations of the molecules. Transforming it into an integral over the volume, we obtain that it is equal to 0, since $\operatorname{div}\mathbf{p} = 0$, and $\operatorname{div}[\omega\times\sigma] = -(\omega\cdot\operatorname{rot}\sigma) = 0$, because

$$\sigma_i = \frac{1}{2}\operatorname{grad}[\rho H_i(\mathbf{k})]^2,$$

where $\rho H_i(\mathbf{k})$ is the function specifying the excluded volume of the i-th molecule. Consequently,

$$\int d\alpha_2\, d\mathbf{p}_2\, d\mathbf{k}\, S(\mathbf{k})(\mathbf{k}\cdot\mathbf{g})F(x_1,t)F(x_2,t) = 0. \tag{5}$$

Subtracting this integral from the right-hand side of (4), we obtain the kinetic equation in standard form:

$$\frac{\partial F(x_1,t)}{\partial t} + \mathcal{H}F(x_1,t) = n\int_{(\mathbf{k}\cdot\mathbf{g})>0} S(\mathbf{k})\, d\mathbf{k}\, d\alpha_2\, d\mathbf{p}_2\, (\mathbf{k}\cdot\mathbf{g})[I-1]F(x_1,t)F(x_2,t). \tag{6}$$

Let us now consider the equation linearized with the aid of the equilibrium distribution function $F_0(x) = Q^{-1}\exp(-E/kT)$: $F = F_0(1+\varphi)$. We shall restrict ourselves to the case where the molecules possess a center of symmetry. The equation for $\varphi(x_1)$ has the form:

$$\frac{\partial\varphi(x_1,t)}{\partial t} + \mathcal{H}\varphi(x_1,t) = n\int_{(\mathbf{k}\cdot\mathbf{g})>0} S(\mathbf{k})\, d\mathbf{k}\, d\alpha_2\, d\mathbf{p}_2\, (\mathbf{k}\cdot\mathbf{g})F_0(x_2)[I-1][\varphi(x_1,t)+ \\ +\varphi(x_2,t)] \equiv nL\varphi. \tag{7}$$

We shall seek its solution in the Hilbert space $\mathcal{L}_2[F_0(x)]$ of functions that are square-integrable with weight $F_0(x)$ and vanish at the boundaries of the domain of variation of $\mathbf{r}$. Consider the expression

$$\langle\varphi L\varphi\rangle \equiv \int_{(\mathbf{k}\cdot\mathbf{g})>0} (\mathbf{k}\cdot\mathbf{g})S(\mathbf{k})\, d\mathbf{k}\, d\alpha_1\, d\alpha_2\, d\mathbf{p}_1\, d\mathbf{p}_2\, F_0(x_1)F_0(x_2)\varphi(x_1)[\varphi(x_1')+ \\ +\varphi(x_2') - \varphi(x_1) - \varphi(x_2)] = -\frac{1}{4}\int_{(\mathbf{k}\cdot\mathbf{g})>0} (\mathbf{k}\cdot\mathbf{g})S(\mathbf{k})\, d\mathbf{k}\, d\alpha_1\, d\alpha_2\, d\mathbf{p}_1\, d\mathbf{p}_2\, d\mathbf{p}_1'\, d\mathbf{p}_2'\times \\ \times F_0(x_1)F_0(x_2)[\varphi(x_1') + \varphi(x_2') - \varphi(x_1) - \varphi(x_2)]^2 - \{[\varphi(x_1') + \varphi(x_2')]^2 - \\ -[\varphi(x_1) + \varphi(x_2)]^2\}. \tag{8}$$

The transformation $x \to x' = Ix$ is canonical as a limit of canonical transformations. Since $q' = q$, it follows that $D(p_1', p_2') : D(p_1, p_2) = 1$. Therefore, passing in the penultimate integral to the integration variables p_1', p_2', and noting that for molecules with a center of symmet-

or $(\mathbf{k} \cdot \mathbf{g}) = -(\mathbf{k} \cdot \mathbf{g}')$, and, using equality (5), we obtain that the term in braces is equal to 0 and, consequently, $\langle \varphi L \varphi \rangle \leqslant 0$.

Let us now define the adjoint operator L^*. It is easy to see that the operator L can be written as

$$L\varphi = \lim_{\tau\to 0} \int dx_2\, (\mathbf{k} \cdot \mathbf{g})\, \delta(P)\, F_0(x_2)\, S_{-\tau}^{(2)}[\varphi(x_1) + \varphi(x_2)]. \tag{9}$$

Here $S_{-\tau}^{(2)} \equiv \exp(t\mathcal{H}_2)$. Then

$$\begin{aligned}\langle \psi L \varphi \rangle &= \lim_{\tau\to 0} \int dx_1 dx_2\, (\mathbf{k} \cdot \mathbf{g})\, \delta(P)\, \psi(x_1) F_0(x_1) F_0(x_2)\, S_{-\tau}^{(2)}[\varphi(x_1) + \varphi(x_2)] \\ &= \frac{1}{2} \lim_{\tau\to 0} \int dx_1 dx_2\, (\mathbf{k} \cdot \mathbf{g})\, \delta(P)\, F_0(x_1) F_0(x_2) [\psi(x_1) + \psi(x_2)]\, S_{-\tau}^{(2)}[\varphi(x_1) + \varphi(x_2)] \\ &= \frac{1}{2} \lim_{\tau\to 0} \int dx_1 dx_2\, [\varphi(x_1) + \varphi(x_2)]\, S_{\tau}^{(2)} (\mathbf{k} \cdot \mathbf{g})\, \delta(P)\, F_0(x_1) F_0(x_2) [\psi(x_1) + \psi(x_2)].\end{aligned} \tag{10}$$

The last equality follows from the unitarity of the operator $S_{-\tau}^{(2)}$. Noting that

$$S_{\tau}^{(2)} F_0(x_1) F_0(x_2) = F_0(x_1) F_0(x_2), \qquad \lim_{\tau\to 0} S_{\tau}^{(2)} \delta(P) = \delta(P), \qquad \lim_{\tau\to 0} S_{\tau}^{(2)} (\mathbf{k}\cdot\mathbf{g}) = -(\mathbf{k}\cdot\mathbf{g})$$

for $(\mathbf{k} \cdot \mathbf{g}) > 0$, and using equality (5), we obtain:

$$\begin{aligned}L^*\psi &= -\lim_{\tau\to 0} \int dx_2\, (\mathbf{k} \cdot \mathbf{g})\, \delta(P)\, F_0(x_2)\, S_{\tau}^{(2)} [\psi(x_1) + \psi(x_2)] \\ &= -\lim_{\substack{\tau\to 0 \\ (\mathbf{k}\cdot\mathbf{g})<0}} \int dx_2\, (\mathbf{k} \cdot \mathbf{g})\, \delta(P)\, F_0(x_2)\, [S_{\tau}^{(2)} - 1][\psi(x_1) + \psi(x_2)].\end{aligned} \tag{11}$$

Just as above, it is easy to prove the inequality $\langle \varphi L^* \varphi \rangle \leqslant 0$. Since $\langle \varphi \mathcal{H} \varphi \rangle = 0$, the operator $nL - \mathcal{H}$ and its adjoint turn out to be dissipative. Hence it follows that it generates a contracting semigroup of operators $U(t) = \exp[t(nL - \mathcal{H})]$, and the solution of the Cauchy problem for equation (7) is given by the formula $\varphi(t) = \bar{U}(t)\varphi(0)$ [4].

The last thing that we want to prove is the normality of the operator L. Write it in the form $L = L_1 + L_2$, where

$$L_1\varphi = \lim_{\tau\to 0}\int dx_2\,(\mathbf{k}\cdot\mathbf{g})\,\delta(P)\,F_0(x_2)\,S^{(2)}_{-\tau}\varphi(x_1),$$

$$L_2\varphi = \lim_{\tau\to 0}\int dx_2\,(\mathbf{k}\cdot\mathbf{g})\,\delta(P)\,F_0(x_2)\,S^{(2)}_{-\tau}\varphi(x_2). \tag{12}$$

If the operator $S^{(2)}_{-\tau}$ is represented formally as an integral operator with kernel $\Pi(x_1, x_2 \mid x_1', x_2'; -\tau)$, then L_1 and L_2 can also be regarded as integral operators with kernels

$$l_1(x_1 \mid x_1'; -\tau) = \int dx_2' dx_2\,(\mathbf{k}\cdot\mathbf{g})\,\delta(P)\,F_0(x_2)\,\Pi(x_1, x_2 \mid x_1', x_2'; -\tau),$$

$$l_2(x_1 \mid x_1'; -\tau) = \int dx_2' dx_2\,(\mathbf{k}\cdot\mathbf{g})\,\delta(P)\,F_0(x_2)\,\Pi(x_1, x_2 \mid x_2', x_1'; -\tau). \tag{13}$$

The kernels of the adjoint operators L_1^* and L_2^* can then be written as

$$l_1^*(x_1 \mid x_1'; -\tau) = l_1(x_1' \mid x_1; -\tau) = -l_1(x_1 \mid x_1'; \tau),$$

$$l_2^*(x_1 \mid x_1'; -\tau) = l_2(x_1' \mid x_1; -\tau) = -l_2(x_1 \mid x_1'; \tau). \tag{14}$$

The last equality follows from formula (11). Let $A(x_1 \mid x_1')$ be the kernel of the operator $L_1^* L_1$. Then

$$A(x_1 \mid x_1') = \int dx_2\, l_1^*(x_1 \mid x_2; -\tau)\, l_1(x_2 \mid x_1'; -\tau) = -\int dx_2\, l_1(x_1 \mid x_2; \tau)\times$$
$$\times\, l_1(x_2 \mid x_1'; -\tau) = -\int dx_2\, l_1(x_1' \mid x_2; \tau)\, l_1(x_2 \mid x_1; -\tau) = A(x_1' \mid x_1), \tag{15}$$

i.e., $L_1^* L_1 = L_1 L_1^*$. The normality of L_2 is proved similarly. Consequently, the operator L is normal, and there exists a spectral representation for the operator $nL - \mathcal{H}$, which makes it possible to obtain estimates for the rate of decay of solutions of equation (7).

Institute of High Temperatures
Academy of Sciences of the USSR
Moscow

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Note: Figure translations are in progress. See original paper for figures.