Journal of Statistical Physics, Vol. 11, No. 6, 1974

A New Closure Hypothesis for the BBGKY System of Equations[1]

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Received March 8, 1974

The first part of this paper deals with the Frey–Salmon irreversibility hypothesis, the kinetic equation that is deduced therefrom, and the comparison with experiment for the viscosity and thermal conductivity coefficients. The relaxation time which has been introduced is the average value of the duration of a collision. The second part deals with a new irreversibility hypothesis which leads to a kinetic equation of the same form as the first but in which the relaxation time is deduced from the interparticle potential.

KEY WORDS: Relaxation time τ; Frey–Salmon hypothesis of linear relaxation; B collision integral; new hypothesis of development; expression of transport coefficients; Frey–Salmon kinetic equation.

1. INTRODUCTION

The transport phenomena in dilute gases are generally studied by means of Boltzmann's equation. This is deduced from the BBGKY system of equations on introducing closure hypotheses that are well known.(1)

We have recently proposed a closure hypothesis which has allowed us to obtain a new kinetic equation(2–5) containing a relaxation time τ. We have

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determined simple expressions for viscosity and thermal conductivity coefficients as a function of τ. We then introduced a second hypothesis in which the time τ was the average value of the duration of a collision. This duration is defined as the crossing time of a molecule in the repulsive zone of the potential.

We thus arrived at expressions for transport coefficients which are simple functions of the molecular mass m, the temperature T, and the depth KT_i of the potential well (K being Boltzmann's constant), and in good agreement with experiment.[6,7]

This aim of this paper is to propose a new hypothesis as a substitute for the two preceding ones which will allow us to obtain more precise results.

In the first part, we shall briefly recall the two hypotheses whose association allowed us to obtain the first results.

In the second part, we shall deal with the new hypothesis and the expressions for the transport coefficients to which it leads and shall compare the new theoretical results with experiment.

In the last part, we shall extend the method to moderately dense gases.

2. FIRST SET OF HYPOTHESES

Our notation is as follows: t designates the time; m is the molecular mass of the gas; $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$, and $\mathbf{w}_1$, $\mathbf{w}_2$, $\mathbf{w}_3$ designate the position and velocity vectors of particles numbered 1, 2, 3; $\mathbf{X}_1$ and $\mathbf{X}_2$ designate the external forces; $\mathbf{X}_{12}$, $\mathbf{X}_{23}$, and $\mathbf{X}_{13}$ designate the central interaction forces; f_1, f_2, and f_3 are the single distribution functions; f_{12}, f_{23}, and f_{13} are the double distribution functions; and f_{123} is the triple distribution function.

The first two equations of the BBGKY system are written as

$$\frac{\partial f_1}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial f_1}{\partial \mathbf{x}_1} + \frac{\mathbf{X}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{w}_1} + \int \frac{\mathbf{X}_{12}}{m} \cdot \frac{\partial f_{12}}{\partial \mathbf{w}_1} \, d\mathbf{x}_2 \, d\mathbf{w}_2 = 0 \tag{1}$$

$$\begin{aligned} &\frac{\partial f_{12}}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial f_{12}}{\partial \mathbf{x}_1} + \mathbf{w}_2 \cdot \frac{\partial f_{12}}{\partial \mathbf{x}_2} + \frac{\mathbf{X}_1 + \mathbf{X}_{12}}{m} \cdot \frac{\partial f_{12}}{\partial \mathbf{w}_1} + \frac{\mathbf{X}_2 + \mathbf{X}_{21}}{m} \cdot \frac{\partial f_{12}}{\partial \mathbf{w}_2} \\ &\qquad + \cdots + \int \left[\frac{\mathbf{X}_{13}}{m} \cdot \frac{\partial f_{123}}{\partial \mathbf{w}_1} + \frac{\mathbf{X}_{23}}{m} \cdot \frac{\partial f_{123}}{\partial \mathbf{w}_2} \right] d\mathbf{x}_3 \, d\mathbf{w}_3 = 0 \end{aligned} \tag{2}$$

Let us introduce the operators

$$\hat{S}_1 = \frac{\partial}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial}{\partial \mathbf{x}_1} + \frac{\mathbf{X}_1}{m} \cdot \frac{\partial}{\partial \mathbf{w}_1} \tag{3}$$

$$G_1 = -\int \frac{\mathbf{X}_{12}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_1} \, d\mathbf{x}_2 \, d\mathbf{w}_2 \tag{4}$$

$$\hat{S}_{12} = \frac{\partial}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial}{\partial \mathbf{x}_1} + \mathbf{w}_2 \cdot \frac{\partial}{\partial \mathbf{x}_2} + \frac{\mathbf{X}_1 + \mathbf{X}_{12}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_1} + \frac{\mathbf{X}_2 + \mathbf{X}_{21}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_2} \quad (5)$$

$$\hat{G}_{12} = -\int \left[\frac{\mathbf{X}_{13}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_1} + \frac{\mathbf{X}_{23}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_2}\right] d\mathbf{x}_3 \, d\mathbf{w}_3 \quad (6)$$

The system of equations (1) and (2) is written as

$$\hat{S}_1 f_1 = \hat{G}_1 f_{12} \quad (7)$$

$$\hat{S}_{12} f_{12} = \hat{G}_{12} f_{123} \quad (8)$$

In equilibrium at the temperature T, this system admits the solutions

$$f_{12} = f_1{}^M f_2{}^M \psi_{12} \quad (9)$$

$$f_{123} = f_1{}^M f_2{}^M f_3{}^M \psi_{123} \quad (10)$$

$$f^M = n(m/2\pi KT)^{3/2} \exp(-mw^2/2KT) \quad (11)$$

K is Boltzmann's constant and n is the density of a particle. ψ_{12} and ψ_{123} are the double and triple correlation functions at equilibrium. They are linked by the following formula:

$$KT\, \partial\psi_{12}/\partial\mathbf{x}_1 = \mathbf{X}_{12}\psi_{12} + \int \mathbf{X}_{13} n_3 \psi_{123}\, d\mathbf{x}_3 - \psi_{12} \int \mathbf{X}_{13} n_3 \psi_{13}\, d\mathbf{x}_3 \quad (12)$$

2.1. The Vlasov–BGK Equation

We can write f_{12} in the form

$$f_{12} = f_1 f_2 \psi_{12} + \chi_{12} \quad (13)$$

and introduce the hypothesis

$$\hat{G}_1 f_{12} = \hat{G}_1 f_1 f_2 \psi_{12} + [(f_1{}^M - f_1)/\Delta\tau] \quad (14)$$

where $\Delta\tau$ is a relaxation time of the order of magnitude of the average duration between two collisions.

On substituting (14) into (7), we obtain a kinetic equation containing the collective field term of Vlasov and the irreversibility term of BGK:

$$\frac{\partial f_1}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial f_1}{\partial \mathbf{x}_1} + \frac{\mathbf{X}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{w}_1} + \left[\int \frac{\mathbf{X}_{12}}{m} \psi_{12} n_2\, d\mathbf{x}_2\right] \cdot \frac{\partial f_1}{\partial \mathbf{w}_1} + \frac{f_1 - f_1{}^M}{\Delta\tau} = 0 \quad (15)$$

2.2. The Frey–Salmon (FS) Hypothesis in Isothermal Conditions

It is convenient to write f_{123} in the form

$$f_{123} = f_1 f_2 f_3 \psi_{123} + \chi_{123} \quad (16)$$

where χ_{123} designates the divergence between f_{123} and a form recalling that of equilibrium.

The FS hypothesis consists in stating that the action of the operator $\hat{G}_{12}$ on χ_{123} can be approximated by the formula

$$\hat{G}_{12}\chi_{123} = (f_1 f_2 \psi_{12} - f_{12})/\tau \tag{17}$$

where τ is a relaxation time of the order of magnitude of the average duration of a collision. In equilibrium, this term is zero. Away from equilibrium, it expresses the irreversibility.

Equation (5) is thus put in the following form:

$$\hat{S}_{12} f_{12} = \hat{G}_{12} f_1 f_2 f_3 \psi_{123} + [(f_1 f_2 \psi_{12} - f_{12})/\tau] \tag{18}$$

$$(1 + \tau\hat{S}_{12}) f_{12} = f_1 f_2 \psi_{12} + \tau\hat{G}_{12} f_1 f_2 f_3 \psi_{123} \tag{19}$$

By using an iterative method, we find that

$$(1 + \tau\hat{S}_{12})^{-1} = 1 - \tau\hat{S}_{12} + \tau^2(\hat{S}_{12})^2$$

It follows that, to first order in

$$f_{12} = f_1 f_2 \psi_{12} - \tau[\hat{S}_{12} f_1 f_2 \psi_{12} - \hat{G}_{12} f_1 f_2 f_3 \psi_{123}] \tag{20}$$

f_{12} has become a functional of f_1 and f_2.

We finally obtain

$$\begin{aligned} f_{12} = f_1 f_2 \psi_{12} &- \tau\left[f_2 \psi_{12}\left(\frac{\partial f_1}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial f_1}{\partial \mathbf{x}_1} + \frac{\mathbf{X}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{w}_1}\right) + f_2 \frac{\partial f_1}{\partial \mathbf{w}_1} \cdot \int \frac{\mathbf{X}_{13}}{m} n_3 \psi_{123}\, \mathbf{dx}_3 \right] \\ &- \tau\left[f_1 \psi_{12}\left(\frac{\partial f_2}{\partial t} + \mathbf{w}_2 \cdot \frac{\partial f_2}{\partial \mathbf{x}_2} + \frac{\mathbf{X}_2}{m} \cdot \frac{\partial f_2}{\partial \mathbf{w}_2}\right) + f_1 \frac{\partial f_2}{\partial \mathbf{w}_2} \cdot \int \frac{\mathbf{X}_{23}}{m} n_3 \psi_{123}\, \mathbf{dx}_3 \right] \\ &- \tau\left[f_1 f_2 \left(\frac{\partial \psi_{12}}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial \psi_{12}}{\partial \mathbf{x}_1} + \mathbf{w}_2 \cdot \frac{\partial \psi_{12}}{\partial \mathbf{x}_2}\right) + \psi_{12}\left(\frac{\mathbf{X}_{12}}{m} \cdot \frac{\partial f_1}{\partial \mathbf{w}_1} f_2 + \frac{\mathbf{X}_{21}}{m} \cdot \frac{\partial f_2}{\partial \mathbf{w}_2} f_1\right)\right] \end{aligned} \tag{20'}$$

$$\begin{aligned} &\frac{\partial f_1}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial f_1}{\partial \mathbf{x}_1} + \frac{\mathbf{X}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{w}_1} \\ &\qquad = -\frac{1}{m} \int \mathbf{X}_{12} \frac{\partial f_{12}}{\partial \mathbf{w}_1} \mathbf{dx}_2\, \mathbf{dw}_2 \\ &\qquad = -\int \frac{\mathbf{X}_{12}}{m} \frac{\partial}{\partial \mathbf{w}_1} [f_1 f_2 \psi_{12} - \tau(\qquad)]\, \mathbf{dx}_2\, \mathbf{dw}_2 \end{aligned}$$

On substituting into (20′) and only keeping the terms to first order in τ, it follows that

$$f_{12} = f_1 f_2 \psi_{12}$$
$$- \frac{\tau}{m} f_2 \frac{\partial f_1}{\partial \mathbf{w}_1} \cdot [\mathbf{X}_{12}\psi_{12} + \int \mathbf{X}_{13} n_3 \psi_{123} \, \mathbf{dx}_3 - \psi_{12} \int \mathbf{X}_{12} n_2 \psi_{12} \, \mathbf{dx}_2]$$
$$- \frac{\tau}{m} f_1 \frac{\partial f_2}{\partial \mathbf{w}_2} \cdot [\mathbf{X}_{21}\psi_{12} + \int \mathbf{X}_{23} n_3 \psi_{123} \, \mathbf{dx}_3 - \psi_{12} \int \mathbf{X}_{21} n_1 \psi_{12} \, \mathbf{dx}_2]$$
$$- \tau f_1 f_2 \left[\frac{\partial \psi_{12}}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial \psi_{12}}{\partial \mathbf{x}_1} + \mathbf{w}_2 \cdot \frac{\partial \psi_{12}}{\partial \mathbf{x}_2} \right]$$

Since

$$\int \mathbf{X}_{13} n_3 \psi_{13} \, \mathbf{dx}_3 = \int \mathbf{X}_{12} n_2 \psi_{12} \, \mathbf{dx}_2$$
$$\int \mathbf{X}_{23} n_3 \psi_{23} \, \mathbf{dx}_3 = \int \mathbf{X}_{21} n_1 \psi_{12} \, \mathbf{dx}_1$$

it becomes possible to use relation (12) and to obtain for F_{12} the form

$$f_{12} = f_1 f_2 \psi_{12} - \tau \left[f_1 f_2 \frac{\partial \psi_{12}}{\partial t} + f_2 \frac{\partial \psi_{12}}{\partial \mathbf{x}_1} \cdot \left(\mathbf{w}_1 f_1 + \frac{KT}{m} \frac{\partial f_1}{\partial \mathbf{w}_1} \right) + \cdots + f_1 \frac{\partial \psi_{12}}{\partial \mathbf{x}_2} \cdot \left(\mathbf{w}_2 f_2 + \frac{KT}{m} \frac{\partial f_2}{\partial \mathbf{w}_2} \right) \right] \tag{20''}$$

whence, on substituting into (1) and on designating by $\mathbf{v}$ the average velocity vector of the fluid, the following kinetic equation is obtained:

$$\frac{\partial f_1}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial f_1}{\partial \mathbf{x}_1} + \frac{1}{m} \frac{\partial f_1}{\partial \mathbf{w}_1} \cdot \left(\mathbf{X}_1 + \int \mathbf{X}_{12} n_2 \psi_{12} \, d\mathbf{x}_{12} \right)$$
$$= \tau \int n_2 \frac{\mathbf{X}_{12}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_1} \left[\frac{\partial \psi_{12}}{\partial t} + \frac{\partial \psi_{12}}{\partial \mathbf{x}_1} \cdot \left(\mathbf{w}_1 f_1 + \frac{KT}{m} \frac{\partial f_1}{\partial \mathbf{w}_1} \right) + \frac{\partial \psi_{12}}{\partial \mathbf{x}_2} \mathbf{v}_2 f_1 \right] d\mathbf{x}_2 \tag{21}$$

When the gas is dilute enough for the macroscopic quantities n and $\mathbf{v}$ not to vary very much over a distance equal to the range of the interaction force, Eq. (21) takes the following simplified form:

$$\frac{\partial f}{\partial t} + \mathbf{w} \cdot \frac{\partial f}{\partial \mathbf{x}} + \frac{\mathbf{X}}{m} \cdot \frac{\partial f}{\partial \mathbf{w}} = \tau \frac{nKT}{2m} B \left[3f + (\mathbf{w} - \mathbf{v}) \cdot \frac{\partial f}{\partial \mathbf{w}} + \frac{KT}{m} \Delta_w f \right] \tag{22}$$

where B designates the integral

$$B = -\frac{8\pi}{3KT} \int_0^\infty \frac{d\varphi}{dr} \frac{d\psi}{dr} r^2 \, dr \tag{23}$$

in which φ represents the interaction potential.

We multiply this equation by $\mathbf{dw}$, $mw_k\,\mathbf{dw}$, and $mV_kV_l\,\mathbf{dw}$, with $V_k = w_k - v_k$, to obtain the equations for the conservation of particles, for the transport of momentum, and for the transport of the components p_{kl} of the kinetic pressure tensor:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x_q}(nv_q) = 0$$

$$nm\left[\frac{\partial v_k}{\partial t} + v_q \frac{\partial v_k}{\partial x_q}\right] - nX_k + \frac{\partial p_{kq}}{\partial x_q} = 0 \tag{24}$$

$$\frac{\partial p_{kl}}{\partial t} + \frac{\partial}{\partial x_q}(v_q p_{kl}) + p_{kq}\frac{\partial v_l}{\partial x_q} + p_{lq}\frac{\partial v_k}{\partial x_q} + \tau\frac{nKT}{m}B(p_{kl} - nKT\,\delta_{kl}) = 0$$

Since the conditions are isothermal, we have neglected the thermal energy flow tensor p_{klr} in the last equation.

From the latter we have extracted the expression for the viscosity coefficient:

$$\mu = m/\tau B \tag{25}$$

2.3. The FS Hypothesis in Nonisothermal Conditions

Let us suppose the temperature to be nonuniform and designate the heat flow vector by $\mathbf{q}$. The FS hypothesis is now written

$$\hat{G}_{12}\chi_{123} = \left\{\left[f_1 f_2 + \frac{\eta}{n_1 m}\mathbf{q}_1\cdot\frac{\partial f_1}{\partial \mathbf{w}_1}\Delta_{w_2} f_2 + \frac{\eta}{n_2 m}\mathbf{q}_2\cdot\frac{\partial f_2}{\partial \mathbf{w}_2}\Delta_{w_1} f_1\right]\psi_{12} - f_{12}\right\}\tau^{-1} \tag{26}$$

and leads to the following kinetic equation:

$$\frac{\partial f}{\partial t} + \mathbf{w}\cdot\frac{\partial f}{\partial \mathbf{x}} + \frac{\mathbf{X}}{m}\cdot\frac{\partial f}{\partial \mathbf{w}} = \frac{\tau nKTB}{2m}\left[3f + (\mathbf{w} - \mathbf{v})\cdot\frac{\partial f}{\partial \mathbf{w}} + \frac{KT}{m}\Delta_w f + \frac{\eta}{nm}\mathbf{q}\cdot\frac{\partial}{\partial \mathbf{w}}\Delta_w f\right] \tag{27}$$

where η is a coefficient equal to $-1/3$ for a monatomic gas and to $-37/95 \simeq -2/5$ for a diatomic gas.

We solve Eq. (27) by using Grad's 13-moment method for f. The thermal conductivity coefficient λ is

$$\lambda = \frac{5K}{\tau B}\frac{1}{3 + 5\eta} = \frac{5}{3 + 5\eta}\frac{K}{m}\mu \tag{28}$$

thus

$$\lambda = (15K/4m)\mu \qquad \text{for a monoatomic gas}$$

$$\lambda = (19K/4m)\mu \qquad \text{for a diatomic gas}$$

2.4. Expression for μ and λ

We must form a hypothesis with regard to τ. The interparticle potential has an attractive zone and a repulsive zone and we take τ as representing the average duration of an interaction, which we define as the crossing time through the repulsive zone during a collision. It is during this brief and intense period of interaction that the loss of information responsible for irreversibility takes place.

Let us adopt a potential of the type shown in Fig. 1. This potential φ is the limit, when E_m tends to infinity, of

$$\begin{aligned} 0 < r < \sigma, &\qquad \varphi = -E_m[(r/\sigma) - 1] - E_i \\ r = \sigma, &\qquad \varphi = -E_i \\ r > \sigma, &\qquad \varphi = \varphi_a, \qquad d\varphi_a/dr > 0 \end{aligned}$$

Let us calculate B and τ. For a dilute gas, we take

$$\psi = e^{-\varphi/KT} \tag{29}$$

$$B = (8\pi/3K^2T^2)\int_0^\infty (d\varphi/dr)^2 e^{-\varphi/KT} r^2\, dr \tag{30}$$

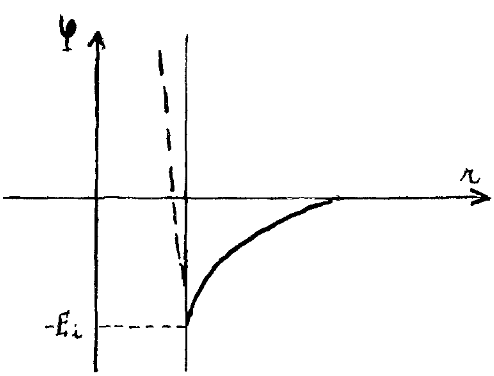

Fig. 1

Table I

Argon $\alpha = 0.343$, $\sigma = 3.405 \times 10^{-10} m$, $T_i = 60°K$				Neon $\alpha = 0.308$, $\sigma = 2.75 \times 10^{-10} m$, $T_i = 36°K$				Nitrogen $\alpha = 0.335$, $\sigma = 3.7 \times 10^{-10} m$, $T_i = 45°K$			
T	$10^5\mu_{th}$	$10^5\mu_{exp}$	$\Delta\mu/\mu$, %	T	$10^5\mu_{th}$	$10^5\mu_{exp}$	$\Delta\mu/\mu$, %	T	$10^5\mu_{th}$	$10^5\mu_{exp}$	$\Delta\mu/\mu$, %
273	2.079	2.096	0.8	273	2.925	2.973	1.6	251.5	1.55	1.563	0.8
373	2.688	2.695	0.2	293	3.08	3.111	1	283.9	1.707	1.707	0
473	3.217	3.223	0.2	373	3.65	3.646	0.1	300.4	1.781	1.781	0.1
575	3.698	3.685	0.3	473	4.273	4.248	0.6	400.2	2.202	2.191	0.5
674	4.121	4.115	0.1	558	4.748	4.708	0.8	499.7	2.566	2.559	0.3
766	4.484	4.484	0	702	5.468	5.454	0.2	572	2.805	2.797	0.15
857	4.82	4.825	0.1	775	5.802	5.802	0	763	3.369	3.374	0.15
987	5.628	5.257	0.2	867	6.199	6.23	0.5	1098	4.191	4.192	0.015
1100	5.631	5.632	0.02	959	6.574	6.626	0.8	—	—	—	—

whence

$$B = \frac{8\pi}{3}\sigma\left\{\frac{KT}{E_m}e^{-(E_m-E_i)/KT}\left[e^{E_m/KT}\left(\frac{E_m{}^2}{K^2T^2}-\frac{2E_m}{KT}+2\right)-2\right]\right\}$$

$$+\cdots+\frac{8\pi}{3K^2T^2}\int_\sigma^\infty\left(\frac{d\varphi_a}{dr}\right)^2 e^{-\varphi_a/KT}r^2\,dr$$

$$E_m\to\infty,\qquad B\to(8\pi/3)\sigma(E_m/KT)e^{E_i/KT} \tag{31}$$

The time spent in the repulsive zone by a particle of mass $m/2$, velocity g at infinity, and impact parameter p is given by

$$\tau_c(p,g) = 2\int_{r_m}^{\sigma}\left\{g^2\left(1-\frac{p^2}{r^2}\right)-\frac{4}{m}\left[-E_i+E_m\left(1-\frac{r}{\sigma}\right)\right]\right\}^{-1/2}dr \tag{32}$$

But since the potential is very repulsive, r_m is close to σ and p^2/r^2 can be replaced by p^2/σ^2 with the other terms unchanged. Thus it follows that

$$\tau_c(p,g) = \frac{m\sigma}{E_m}\left[g^2\left(1-\frac{p^2}{\sigma^2}\right)+\frac{4E_i}{m}\right]^{1/2}$$

whence, on taking the average over p and g and on introducing a scaling coefficient α, we obtain

$$\tau = \int_0^\sigma\int_0^\infty \tau_c(p,g)\left(\frac{m}{4\pi KT}\right)^{3/2}\left[\exp\left(-\frac{mg^2}{4KT}\right)\right]4\pi g^2\frac{2p\,dp}{\sigma^2}\,dg \tag{33}$$

E_m disappears from the product τB and it follows that

$$\mu = \frac{m}{\tau B} = \frac{9(\pi mKT)^{1/2}}{64\pi\alpha\sigma^2[G_{3/2}(T_i/T)-\sqrt{\pi}(T_i/T)^{3/2}]e^{T_i/T}} \tag{34}$$

$$T_i = E_i/K \tag{35}$$

$$G_{3/2}(x) = 2\int_0^\infty(\lambda^2+x)^{3/2}\exp(-\lambda^2)\,d\lambda$$

$$= 1+\frac{3}{2}x+\frac{19}{16}x^2+\frac{5}{32}x^3\cdots$$

$$-\frac{3}{8}[0.857582+\log x]x^2\left[1+\frac{x}{6}+\frac{x^2}{16}\cdots\right] \tag{36}$$

Table I shows a comparison with experiment with μ in MKSA units.[8]

3. THE NEW HYPOTHESIS

The weak point of the old hypotheses was the need to calculate τ phenomenologically. The new one allows us to deduce τ from the interparticle potential. Under isothermal conditions, it is written as

$$
\begin{aligned}
f_{123} = {} & f_1 f_2 f_3 \psi_{123} + (f_{12} - f_1 f_2 \psi_{12}) f_3 \psi_{13} \psi_{23} \\
& + (f_{23} - f_2 f_3 \psi_{23}) f_1 \psi_{12} \psi_{13} + (f_{13} - f_1 f_3 \psi_{13}) f_2 \psi_{12} \psi_{23} \\
& + \cdots + \alpha_0 \left[\frac{(\mathbf{w}_1 - \mathbf{w}_3) \cdot \mathbf{X}_{13} + (\mathbf{w}_2 - \mathbf{w}_3) \cdot \mathbf{X}_{23}}{(KT/m)^{1/2} X_m} \right] (f_{12} - f_1 f_2 \psi_{12}) \frac{f_3}{n_3 \sigma^3} \\
& + \cdots + \alpha_0 \left[\frac{(\mathbf{w}_1 - \mathbf{w}_2) \cdot \mathbf{X}_{12} + (\mathbf{w}_1 - \mathbf{w}_3) \cdot \mathbf{X}_{13}}{(KT/m)^{1/2} X_m} \right] (f_{23} - f_2 f_3 \psi_{23}) \frac{f_1}{n_1 \sigma^3} \\
& + \cdots + \alpha_0 \left[\frac{(\mathbf{w}_2 - \mathbf{w}_3) \cdot \mathbf{X}_{23} + (\mathbf{w}_1 - \mathbf{w}_2) \cdot \mathbf{X}_{12}}{(KT/m)^{1/2} X_m} \right] (f_{13} - f_1 f_3 \psi_{13}) \frac{f_2}{n_2 \sigma^3} \qquad (37)
\end{aligned}
$$

The arguments in favor of the hypothesis are as follows:
In equilibrium we have

$$f_{ij} = f_i f_j \psi_{ij} \tag{38}$$

$$f_{123} = f_1 f_2 f_3 \psi_{123} \tag{39}$$

On substituting the first of these equations into (37), we obtain the second.

When particle 3 is very far from the other two, we have

$$
\begin{aligned}
f_{13} = f_1 f_3, \qquad f_{23} = f_2 f_3, \qquad \psi_{13} = \psi_{23} = 1, \\
\mathbf{X}_{13} = \mathbf{X}_{23} = 0, \qquad \psi_{123} = \psi_{12}
\end{aligned} \tag{40}
$$

as well as

$$f_{123} = f_{12} f_3 \tag{41}$$

In fact, the substitution of Eqs. (40) into (37) leads to (41). Examination of relation (37) shows that the first four terms express velocity as products of terms of the type $(f_{12} - f_1 f_2 \psi_{12}) f_3 / n_3$ by terms of the type $(\mathbf{w}_1 - \mathbf{w}_3) \cdot \mathbf{X}_{13}$. Factors of the first type are products of divergences of the type $(f_{12} - f_1 f_2 \psi_{12})$ between the double distribution function f_{12} and a form analogous to that of the equilibrium $f_1 f_2 \psi_{12}$, by the quotients of the type f_3/n_3 which, in a homogeneous medium, represent the distribution of the velocities. Factors of the second type are scalar products of the interaction force by the relative velocity vector—i.e., the power involved in the interaction force in its movement around the center of mass. It seems reasonable to choose this quantity to express the velocity correlations. X_m is an average value of the interaction force and α_0 is a constant of the coupling.

Let us substitute expression (37) into Eq. (2). It follows that

$$[f_{12} - f_1 f_2 \psi_{12}] \frac{\alpha_0}{(mKT)^{1/2}\sigma^3 X_m} \int [X_{13}^2 + X_{23}^2]\, \mathbf{dx}_3$$

$$= -\left[\frac{\partial f_{12}}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial f_{12}}{\partial \mathbf{x}_1} + \mathbf{w}_2 \cdot \frac{\partial f_{12}}{\partial \mathbf{x}_2} + \frac{\mathbf{X}_1 + \mathbf{X}_{12}}{m} \cdot \frac{\partial f_{12}}{\partial \mathbf{w}_1} + \frac{\mathbf{X}_2 + \mathbf{X}_{21}}{m} \cdot \frac{\partial f_{12}}{\partial \mathbf{w}_2}\right]$$

$$- \int \left[\frac{\mathbf{X}_{13}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_1} + \frac{\mathbf{X}_{23}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_2}\right] [f_1 f_2 f_3 (\psi_{123} - 3\psi_{12}\psi_{23}\psi_{13})$$

$$+ \cdots + f_{12} f_3 \psi_{13}\psi_{23} + f_{23} f_1 \psi_{12}\psi_{13} + f_{13} f_2 \psi_{12}\psi_{23}]\, \mathbf{dx}_3\, \mathbf{dw}_3$$

$$- \frac{\alpha_0}{(mKT)^{1/2}\sigma^3 X_m} \int [(\mathbf{w}_1 - \mathbf{w}_3)\cdot \mathbf{X}_{13} + (\mathbf{w}_2 - \mathbf{w}_3)\cdot \mathbf{X}_{23}]$$

$$\times \left[\mathbf{X}_{13} \cdot \frac{\partial}{\partial \mathbf{w}_1} + \mathbf{X}_{23} \cdot \frac{\partial}{\partial \mathbf{w}_2}\right] [f_{12} - f_1 f_2 \psi_{12}] \frac{f_3}{n_3}\, \mathbf{dx}_3\, \mathbf{dw}_3 \cdots$$

$$- \frac{\alpha_0}{(mKT)^{1/2}\sigma^3 X_m} \int \left[\mathbf{X}_{13} \cdot \frac{\partial}{\partial \mathbf{w}_1} + \mathbf{X}_{23} \cdot \frac{\partial}{\partial \mathbf{w}_2}\right]$$

$$\times [(\mathbf{w}_1 - \mathbf{w}_2)\cdot \mathbf{X}_{12} + (\mathbf{w}_1 - \mathbf{w}_3)\cdot \mathbf{X}_{13}][f_{23} - f_2 f_3 \psi_{23}] \frac{f_1}{n_1}\, \mathbf{dx}_3\, \mathbf{dw}_3 \cdots$$

$$- \frac{\alpha_0}{(mKT)^{1/2}\sigma^3 X_m} \int \left[\mathbf{X}_{13} \cdot \frac{\partial}{\partial \mathbf{w}_1} + \mathbf{X}_{23} \cdot \frac{\partial}{\partial \mathbf{w}_2}\right]$$

$$\times [(\mathbf{w}_2 - \mathbf{w}_3)\cdot \mathbf{X}_{23} + (\mathbf{w}_1 - \mathbf{w}_2)\cdot \mathbf{X}_{12}][f_{13} - f_1 f_3 \psi_{13}] \frac{f_2}{n_2}\, \mathbf{dx}_3\, \mathbf{dw}_3 \quad (42)$$

This expression is written as

$$f_{12} - f_1 f_2 \psi_{12} = \tau_2 \hat{A}(f_{12}, f_{23}, f_{13}, f_1, f_2, f_3) \quad (43)$$

where $\hat{A}$ designates an operator defined by the right-hand side of Eq. (42) and τ_2 is a quantity analogous to a time:

$$\frac{1}{\tau_2} = \frac{2\alpha_0}{(mKT)^{1/2}\sigma^3 X_m} \int X_{13}^2\, \mathbf{dx}_{13} \quad (44)$$

Let us solve Eq. (43) by iteration:

$$f_{12}^{(p+1)} - f_1 f_2 \psi_{12} = \tau_2 \hat{A}(f_{ij}^{(p)} \cdots)$$

The first iteration gives

$$f_{12} = f_1 f_2 \psi_{12} + \tau_2 \hat{A}(f_1 f_2 \psi_{12} \cdots)$$

Thus

$$f_{12} = f_1 f_2 \psi_{12} - \tau_2 \left[\frac{\partial}{\partial t} + \mathbf{w}_1 \cdot \frac{\partial}{\partial \mathbf{x}_1} + \mathbf{w}_2 \cdot \frac{\partial}{\partial \mathbf{x}_2} + \cdots + \frac{\mathbf{X}_1 + \mathbf{X}_{12}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_1} + \frac{\mathbf{X}_2 + \mathbf{X}_{21}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_2} \right] f_1 f_2 \psi_{12} + \cdots - \tau_2 \int \left[\frac{\mathbf{X}_{13}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_1} + \frac{\mathbf{X}_{23}}{m} \cdot \frac{\partial}{\partial \mathbf{w}_2} \right] f_1 f_2 f_3 \psi_{123} \, \mathbf{dx}_3 \, \mathbf{dw}_3$$

This relation is identical to that obtained from the old hypotheses but the collisional time τ_2 is now determined by the expression (44). The kinetic equation is written

$$\frac{\partial f}{\partial t} + \mathbf{w} \cdot \frac{\partial f}{\partial \mathbf{x}} + \frac{\mathbf{X}}{m} \cdot \frac{\partial f}{\partial \mathbf{w}} = \frac{1}{\tau_1} \left[3f + (\mathbf{w} - \mathbf{v}) \cdot \frac{\partial f}{\partial \mathbf{w}} + \frac{KT}{m} \Delta_w f \right] \tag{45}$$

with

$$\frac{1}{\tau_1} = -\frac{4\pi}{3} \frac{n}{m} \tau_2 \int_0^\infty \frac{d\varphi_{12}}{dx_{12}} \frac{d\psi_{12}}{dx_{12}} x_{12}^2 \, dx_{12} \tag{46}$$

$$= -\frac{2\pi n}{3\alpha_0} \left(\frac{KT}{m} \right)^{1/2} X_m \sigma^3 \frac{\int_0^\infty (d\varphi_{12}/dx_{12})(d\psi_{12}/dx_{12}) x_{12}^2 \, dx_{12}}{\int_0^\infty (d\varphi_{13}/dx_{13})^2 \, dx_{13}} \tag{47}$$

$$= -\frac{n\sigma^3}{2\alpha_0} \left(\frac{KT}{m} \right)^{1/2} X_m \frac{\int_0^\infty (d\varphi_{12}/dx_{12})(d\psi_{12}/dx_{12}) x_{12}^2 \, dx_{12}}{\int_0^\infty (d\varphi_{13}/dx_{13})^2 x_{13}^2 \, dx_{13}}$$

4. VISCOSITY COEFFICIENT OF A DILUTE GAS

Equation (45) leads to the following expression for the viscosity coefficient:

$$\mu = \tfrac{1}{2} nKT \tau_1 \tag{48}$$

For a dilute gas

$$\psi_{12} = e^{-\varphi_{12}/KT} \tag{49}$$

and

$$\frac{1}{\tau_1} = \frac{n\sigma^3}{2\alpha_0 (mKT)^{1/2}} X_m \frac{\int_0^\infty (d\varphi_{12}/dx_{12})^2 e^{-\varphi_{12}/KT} x_{12}^2 \, dx_{12}}{\int_0^\infty (d\varphi_{12}/dx_{12})^2 x_{12}^2 \, dx_{12}} \tag{50}$$

For the interparticle potentials, measurements of the effective cross sections[9] give the form shown in Fig. 2. Let us approximate the repulsive part by a straight line having a very steep slope E_m/σ starting from σ

$$x_{12} < \sigma, \qquad \varphi = -KT_i - E_m[(x_{12}/\sigma) - 1] \tag{51}$$

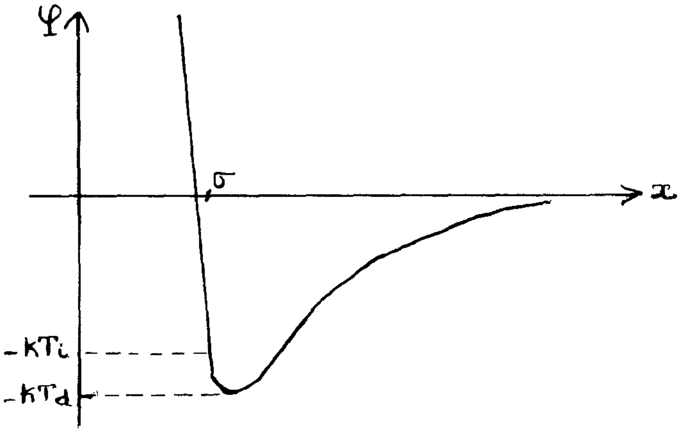

Fig. 2

The integrals of (50) can be limited to the domain $0 < x_{12} < \sigma$, for which the functions involved are very large. Similarly, we consider $X_m = E_m/\sigma$, whence

$$1/\tau_1 = (3n\sigma^2/2\alpha_0)(KT/m)^{1/2}e^{T_i/T}, \qquad E_m \to \infty \tag{52}$$

and

$$\mu = (\alpha_0/3\sigma^2)(mKT)^{1/2}e^{-T_i/T} \tag{53}$$

Tables IIA–IIC compare theoretical and experimental results.[8]

Table IIA. Neon[a]

T, °K	$10^5\mu_{\text{th}}$, DP	$10^5\mu_{\text{exp}}$, DP	$\Delta\mu/\mu$, %
273	2.909	2.973	2
293	3.069	3.111	1.3
373	3.652	3.646	0.2
473	4.287	4.248	0.9
523	4.574	4.532	0.9
558	4.766	4.708	1.2
702	5.492	5.454	0.7
775	5.827	5.802	0.4
867	6.225	6.23	0.07
959	6.6	6.626	0.4
1100	7.138	7.21	1

[a] $\sigma = 2.315 \times 10^{-10}$ m, $\alpha_0 = 0.5437$, $T_i = 72.9$°K.

Table IIB. Nitrogen[a]

T, °K	$10^5\mu_{\text{th}}$, DP	$10^5\mu_{\text{exp}}$, DP	$\Delta\mu/\mu$, %
251.5	1.543	1.563	1.3
283.9	1.703	1.707	0.2
300.4	1.781	1.781	0.01
400.2	2.205	2.101	0.6
499.7	2.571	2.559	0.4
572	2.81	2.797	0.4
763	3.369	3.374	0.1
1098	4.18	4.192	0.2

[a] $\sigma = 3.275 \times 10^{-10}$ m, $\alpha_0 = 0.5474$, $T_i = 84.8$°K.

Table IIC. Argon[a]

T, °K	$10^5\mu_{\text{th}}$, DP	$10^5\mu_{\text{exp}}$, DP	$\Delta\mu/\mu$, %
273	2.069	2.096	1.3
373	2.692	2.695	0.001
473	3.226	3.223	0.001
500	3.358	3.34	0.6
573	3.706	3.685	0.6
674	4.126	4.115	0.2
766	4.485	4.484	0.0002
857	4.817	4.825	0.002
987	5.257	5.257	0
1100	5.613	5.632	0.3

[a] $\sigma = 3.115 \times 10^{-10}$ m, $\alpha_0 = 0.5688$, $T_i = 109.4$°K.

5. VISCOSITY COEFFICIENT OF A MODERATELY DENSE GAS

The following considerations are for a gas at pressures lower than 150 atm. A possible formula for $\psi_{12}(x_{12})$ is

$$\varphi_{12}(x_{12}) = \exp\left\{ -\frac{\psi_{12}}{KT} + \frac{2\pi n}{\sigma}\int_0^\infty [e^{-\varphi_{13}/KT} - 1] \times \left[\int_{|x_{12}-x_{13}|}^{|x_{12}+x_{13}|} (e^{-\varphi_{23}/KT} - 1)x_{23}\, dx_{23}\right] x_{13}\, dx_{13}\right\} \tag{54}$$

The integral in the numerator of formula (47) is written

$$\int_0^\infty \frac{d\varphi_{12}}{dx_{12}}\frac{d\psi_{12}}{dx_{12}}x_{12}^2\,dx_{12} = -\frac{E_m}{\sigma}\int_0^\sigma \frac{d\psi_{12}}{dx_{12}}x_{12}^2\,dx_{12}$$

$$= -\frac{E_m}{\sigma}\left[\psi_{12}(\sigma) - \psi_{12}(0) - \int_0^\sigma 2\psi_{12}x_{12}\,dx_{12}\right]$$

$$= -\frac{E_m}{\sigma}\psi_{12}(\sigma), \qquad E_m \to \infty$$

Let us set

$$x_{12} \geqslant \sigma, \qquad \varphi = -KT_i h(x), \qquad x = x_{12}/\sigma \tag{55}$$

It follows that, to first order in T_i/T,

$$\psi_{12}(\sigma) = \exp\left[\frac{T_i}{T} + \frac{5}{12}\pi n\sigma^3\left(1 - \beta_1\frac{T_i}{T}\right)\right] \tag{56}$$

$$\beta_1 = (24/5)\int_1^2 (2x^2 - x^3)h(x)\,dx \tag{57}$$

On the other hand, in formula (37) let us replace $\alpha_0/n\sigma^3$ by an expansion of the form $(\alpha_0/n\sigma^3) + \alpha_1 + \alpha_2 n\sigma^3$, or take it that τ_2 is reduced by the triple collisions by a factor $1 - \beta_2\pi n\sigma^3$. The two hypotheses are equivalent with

$$\pi\beta_2 = \alpha_1/\alpha_0 \tag{58}$$

Comparison with experiment shows that β_2 is independent of the nature of the gas,

$$\beta_2 = 0.5093 \tag{59}$$

We arrive at the following formula:

$$\mu_p = \frac{\alpha_0}{3\sigma^2}\frac{(mKT)^{1/2}}{1 - \beta_2\pi n\sigma^3}\exp -\left[\frac{T_i}{T} + \frac{5}{12}\pi n\sigma^3\left(1 - \beta_1\frac{T_i}{T}\right)\right] \tag{60}$$

Comparison with experiment is made by using the potential

$$\begin{aligned} x = x_{12}/\sigma, \qquad & 1 < x < c, \qquad && \varphi = -KT_i \\ & c < x, && \varphi = -KT[a(x/c)^{-12} + (1 - a)(x/c)^{-6}] \end{aligned} \tag{61}$$

where c and a designate the parameters to be optimized. Tables IIIA–IIIC compare theoretical and experimental results for μ_p and Table IV for the second virial coefficient.[10]

Table IIIA. Neon[a]

T, °K	P, atm	$10^{-26}n$, m^{-3}	$10^5\mu_p$(th), MKSA	$10^5\mu_p$(exp), MKSA	$\Delta\mu/\mu$, %
223.15	55.94	17.874	2.568	2.643	2.8
223.15	140.7	42.909	2.708	2.724	0.57
248.15	49.57	14.293	2.772	2.827	1.92
248.15	143.15	39.328	2.91	2.894	0.55
298.15	59.75	14.293	3.181	3.201	0.6
298.15	156.3	35.748	3.298	3.267	0.95
373.15	55.79	7.131	3.689	3.702	0.34
373.15	154.83	28.616	3.802	3.747	1.47

[a] $\sigma = 2.315 \times 10^{-10}$ m, $c = 1.172$, $a = 0.8249$, $\beta_1 = 3.0565$, $T_i = 72.9$°K.

Table IIIB. Nitrogen[a]

T, °K	P, atm	$10^{-26}n$, m^{-3}	$10^5\mu_p$(th), MKSA	$10^5\mu_p$(exp), MKSA	$\Delta\mu/\mu$, %
223.15	29.99	10.298	1.486	1.485	0.1
223.15	85.93	30.915	1.715	1.714	0.08
223.15	143.8	51.511	2.018	2.054	1.7
248.15	33.93	10.298	1.62	1.607	0.8
248.15	83.4	25.755	1.786	1.766	1.1
248.15	152.5	46.372	2.068	2.072	0.16
298.15	6.77	1.696	1.785	1.781	0.26
298.15	41.67	10.302	1.865	1.839	1.4
298.15	62.58	15.455	1.917	1.887	1.6
373.15	26.35	5.138	2.143	2.133	0.5
373.15	80.52	15.455	2.224	2.213	1.4
373.15	137.76	25.755	2.359	2.331	1.2

[a] $\sigma = 3.275 \times 10^{-10}$ m, $c = 1.012$, $a = -3.52665$, $\beta_1 = 2.9624$, $T_i = 84.8$°K.

Table IIIC. Argon[a]

T, °K	P, atm	$10^{-26}n$, m^{-3}	$10^5\mu_p$(th), MKSA	$10^5\mu_p$(exp), MKSA	$\Delta\mu/\mu$, %
223.15	30.90	10.84	1.844	1.85	0.31
223.15	91.01	36.122	2.225	2.219	0.3
223.15	152.13	65.022	2.837	2.879	1.4
248.15	34.93	10.84	2.029	2.027	0.14
248.15	87.35	28.9	2.292	2.276	0.72
248.15	156.24	54.182	2.767	2.77	0.1
298.15	28.84	7.221	2.325	2.316	0.41
298.15	84.36	21.679	2.525	2.494	1.23
298.15	138.94	36.122	2.758	2.73	1.01
373.15	36.61	7.221	2.782	2.775	0.28
373.15	91.55	18.06	2.93	2.9	1.02
373.15	166.6	32.518	3.154	3.124	0.96

[a] $\sigma = 3.115 \times 10^{-10}$ m, $c = 1.2705$, $a = -0.2822$, $\beta_1 = 3.062$, $T_i = 109.4$°K.

Table IV

Argon			Neon			Nitrogen		
T, °K	$10^6 A_1$(th), m^3	$10^6 A_1$(exp), m^3	T, °K	$10^6 A_1$(th), m^3	$10^6 A_1$(exp), m^3	T, °K	$10^6 A_1$(th), m^3	$10^6 A_1$(exp), m^3
200	−47.29	−47.6	60	−24.9	−24.8	200	−32.5	−35.2
300	−15.7	−15.6	120.8	0	0	300	−4.23	−4.2
411.3	0	0	200	6.99	7.6	326	0	0
500	7.19	7.3	300	10.12	11.3	400	8.82	9
600	12.61	12.5	400	11.59	12.8	500	16.34	16.9
673	15.51	15.74	600	12.99	13.8	600	21.24	21.3

6. CONCLUSION

The closure hypothesis we have presented allows us to obtain a kinetic equation in which the collision term is of Fokker–Planck type with coefficients that are expressed as a function of the moments. The expressions for the transport coefficients are simple and are in good agreement with experiment.[11]

Let us add that the expression for the viscosity coefficient of a dilute gas in $T^{1/2}e^{-T_i/T}$ was proposed in 1919 by Reinganum based on phenomenological reasoning.

ACKNOWLEDGMENT

We would like to thank M. Laigle for the numerical calculations and his many suggestions.

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