The hard-sphere model in plasma and gas physics

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Expressions are derived for the scattering cross sections and the macroscopic properties of gases and plasmas in a hard-sphere model in which the first two terms are retained in the expansion in the small parameter of the theory. These expressions are analyzed and compared with the results of the Maxwell model and also with numerical calculations for model interaction potentials.

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1. The hard-sphere model is a common one in problems involving the scattering of atomic particles (see Refs. 1–4, for example). With simple expressions for the collision cross sections, this model furnishes analytic expressions for macroscopic properties, in particular, transport coefficients. The value of the hard-sphere model goes deeper than its simplicity: It also furnishes numerical values of macroscopic properties. Its popularity is thus not surprising.

Figure 1 shows the interaction potential for classical particles according to the hard-sphere model, along with the real interaction potential for atoms. If the particular macroscopic property of interest is determined by the repulsive region of the potential, it is reasonable to replace the real interaction potential by a model potential and adopt the hard-sphere model. The success of this approximation improves as the rate of change of the potential along the coordinate increases; i.e., for a good approximation, the following parameter must be small:

$$\xi = \left| \frac{d \ln U}{d \ln R}\Big|_{R_0} \right|^{-1} \ll 1, \qquad (1)$$

where U is the interaction potential and R is the distance between the particles. The hard-sphere model obviously corresponds to the zeroth approximation in the expansion in this small parameter.

When we replace the real potential by the hard-sphere model potential, there is some uncertainty regarding the radius of the hard sphere. This uncertainty can be eliminated by finding the next term in the expresion of the given property in the small parameter (1). Taking into account the first two terms in the expansion in parameter (1) brings us back to the real potential in the repulsive region. The expressions for the macroscopic properties turn out to be the same as in the hard-sphere model, but the effective radius of the hard sphere must be found. This modified hard-sphere model thus preserves the simplicity of the hard-sphere model and makes it possible to take into account the real, rapidly varying atomic interaction potential. It is this modified model which we will be discussing below.

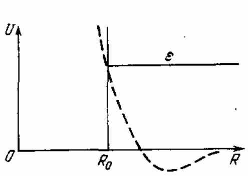

FIG. 1. Interaction potential in the hard-sphere model (solid line) and the actual interaction potential of atoms (dashed curve).

How accurate is the hard-sphere model in real situations? Table I lists values of the parameter

$$n(R_0) = -\frac{d \ln U(R)}{d \ln R}\Big|_{R_0}$$

for the interaction of two inert-gas atoms at that distance between the nuclei where the interaction potential $U(R_0)$ is 0.1 eV. We see that the conditions for the applicability of the hard-sphere model ($\xi = 1/n \ll 1$) are in fact satisfied quite well in the repulsive region.

2. In deriving expressions for the collision cross sections according to the hard-sphere model we will begin with the collision of classical particles with a steep repulsive interaction potential. The nature of the scattering of the particles in this case is illustrated in Fig. 2, from which we find the differential cross section for the scattering of the particles in the center-of-mass system to be

$$d\sigma = 2\pi\rho\, d\rho = \frac{\pi R_0^2}{2} d\cos\theta. \qquad (2)$$

Here we have used $\theta = \pi - 2\chi$ and $\rho = R_0 \sin\chi$. The differential cross section is seen to be independent of the scattering angle. Expression (2) can be used to determine integral scattering cross sections. In particular, the transport or diffusion scattering cross section is

$$\sigma^* = \int (1 - \cos\theta)\, d\sigma = \pi R_0^2. \qquad (3)$$

The scattering cross section which appears in the expression for the thermal conductivity and the viscosity of a gas is

$$\sigma^{(2)} = \int (1 - \cos^2\theta)\, d\sigma = \frac{2}{3}\pi R_0^2. \qquad (4)$$

The integral collision cross sections do not depend on

TABLE I. Values of the parameter* n.

Interacting atoms	He	Ne	Ar	Kr	Xe
He	7.6	8.1	8.8	8.2	7.6
Ne	—	7.0	8.3	9.4	8.8
Ar	—	—	7.5	9.0	7.7
Kr	—	—	—	7.2	9.1
Xe	—	—	—	—	9.6

*The parameters of the potential for the repulsive interaction of the atoms are taken from the review by Leonas.[5]

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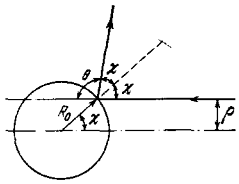

FIG. 2. Scattering of classical particles in the hard-sphere model. r_0—Radius of the hard sphere; ρ—impact parameter; θ—scattering angle.

the velocity of the colliding particles. The hard-sphere model thus has the distinguishing feature that the corresponding differential scattering cross section depends on neither the scattering angle nor the velocity of the particles, while the integral scattering cross sections do not depend on the velocity.

These properties are not restricted to the case of the scattering of particles in classical motion. Let us examine the scattering of a slow electron by an atom or molecule. The amplitude for the scattering of a slow electron is[6]

$$f(\theta) = -L, \tag{5}$$

where L is the scattering length for the scattering of the electron by an atomic particle. We then find the differential cross section for the scattering of the electron by the atom or molecule to be

$$d\sigma = 2\pi\,|f(\theta)|^2\, d\cos\theta = 2\pi L^2\, d\cos\theta. \tag{6}$$

We see that the differential cross section for the scattering of a slow electron by an atom or molecule depends on neither the scattering angle nor the velocity of the electron, and the integral cross sections are independent of this velocity. The scattering of a slow electron by an atom or molecule thus exhibits the properties of the hard-sphere model.

3. Let us examine some specific physical problems in which the hard-sphere model proves convenient. One type of problem is that involving the calculation of transport coefficients in a gas. The transport coefficients in gases and weakly ionized plasmas are expressed in terms of the cross sections for collisions of the atomic particles. We consider the case in which these cross sections are determined by a rapidly varying repulsive potential, which we approximate by[1)]

$$U(R) = Ae^{-\alpha R}. \tag{7}$$

This is the correct behavior, for example, when the interaction is determined by the overlap of electron shells of the interacting particles (an exchange interaction). Clearly, the parameters of the potential, A and α, are of the order of the corresponding atomic quantities. If we are interested in, say, the collision of particles at thermal energies, the scattering cross section is therefore determined by the characteristic distances between the particles, R_0, which are determined in turn by

$$U(R_0) \sim \varepsilon. \tag{8}$$

Since $\varepsilon \ll A$, we have $\alpha R_0 \gg 1$; in other words, the conditions for the applicability of the hard-sphere model, (1), are satisfied. Relation (8) determines the radius of the hard sphere, which may be used in the expressions for the cross sections, (3) and (4), for example.

If the macroscopic properties of the gas in which we are interested are determined by the repulsive part of an atomic interaction potential,[2)] we can therefore use the hard-sphere model to calculate the scattering cross sections. Since we have a small parameter to work with, we would naturally like to write the next term in the expansion for the scattering cross section in (3) and (4), thereby obtaining a more definite expression for the radius of the hard sphere. Let us determine r_0, the radius of the hard sphere in the zeroth approximation, from

$$U(r_0) = \varepsilon.$$

In calculating the corresponding integral cross section (the diffusion cross section, for example), we obviously find

$$\sigma^* = \pi\left(r_0 + \frac{a}{\alpha}\right)^2 \equiv \pi R_0^2, \tag{9a}$$

in the next approximation. Here a is a numerical coefficient of the order of unity, and $(\alpha r_0)^{-1}$ is the small parameter of the expansion. According to (7) we thus have

$$U(R_0) = U(r_0)\, e^{-a} = \varepsilon e^{-a}. \tag{9b}$$

Expression (9) is thus convenient for determining the integral cross section (in this case, the diffusion cross section). In the Appendix we calculate the cross sections $\sigma^*(\varepsilon)$ and $\sigma^{(2)}(\varepsilon)$ for a rapidly varying potential and average them over a Maxwell distribution.

The form in which the cross section is represented does not depend on the shape of the potential in this case, as long as the potential varies rapidly. To demonstrate this point, we approximate the potential by $U(R) = BR^{-n}$ instead of (7). A rapidly varying potential corresponds to the condition $n \gg 1$; i.e., the small parameter of the theory in this case is $1/n$. We can then replace (9a) by

$$\sigma^* = \pi r_0^2\left(1 + \frac{a}{n}\right)^2 = \pi R_0^2,$$

so that

$$U(R_0) = U(r_0)\left(1 + \frac{a}{n}\right)^{-n} = \varepsilon e^{-a}.$$

We have thus ended up with expression (9b) again.

Table II gives expressions for certain kinetic trans-

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1) This approximation, we might note, holds for an arbitrary potential which varies monotonically over some distance interval. Specifically, we have

$$U(R) = U(R_0)\exp[-\alpha(R - R_0)],$$

where $\alpha = -d\ln U/dR|_{R_0}$, and this approximation holds for $\Delta R = |R - R_0| < |d^2\ln U/dR^2|_{R_0}|^{-1/2}$. The potential $U(R) = BR^{-n}$, for example, can be approximated by (7) in the interval $|R - R_0| < R_0/\sqrt{n}$. We see that in this distance interval the condition $|\ln(U(R)/U(R_0))| < \sqrt{n}$ holds; i.e., if the potential varies rapidly, there may be an important change in the potential itself in this interval.

2) Actually, the applicability condition here is $\varepsilon \ll D$, where D is the depth of the well in the interaction potential.

TABLE II. Expressions for the kinetic transport coefficients in the hard-sphere model.

Coefficient	Expression from Refs. 1–4, 7	Expression for the hard-sphere model[1-4,7]	Expression for the cross section in the modified hard-sphere model[8-10]
1. Diffusion coefficient of particles in a gas*	$D=\frac{3\sqrt{\pi T}}{8N\bar{\sigma}^{*}\sqrt{2\mu}}$, $\bar{\sigma}^{*}=\int_0^\infty e^{-x}x^2\sigma^{*}(x)\,dx$, $x=\frac{\mu v^2}{2T}$, $\sigma^{*}=\int(1-\cos\theta)\,d\sigma$	$D=\frac{3\sqrt{\pi T}}{8N\sigma_1\sqrt{2\mu}}$, $\sigma_1=\pi R_0^2$	$\sigma_1=\pi r_1^2$, where $U(r_1)=2{,}2T$
2. Thermal conductivity of a gas*	$\varkappa=\frac{25\sqrt{\pi T}}{32\sqrt{M}\,\overline{\sigma^{(2)}}}$, $\overline{\sigma^{(2)}}=\int_0^\infty e^{-x}x^2\sigma^{(2)}(x)\,dx$, $x=\frac{Mv^2}{4}$, $\sigma^{(2)}=\int(1-\cos^2\theta)\,d\sigma$	$\varkappa=\frac{25\sqrt{\pi T}}{32\sqrt{M}\,\sigma_2}$, $\sigma_2=\frac{2}{3}\pi R_0^2$	$\sigma_2=\frac{2}{3}\pi r_2^2$, where $U(r_2)=0{,}83T$
3. Viscosity*	$\eta=\frac{5\sqrt{\pi TM}}{24\,\overline{\sigma^{(2)}}}$	$\eta=\frac{5\sqrt{\pi TM}}{24\sigma_2}$	
4. Drift velocity of an electron in a gas in a static electric field**	$w=\frac{eE}{3mN}\left\langle\frac{1}{v^2}\frac{d}{dv}\left(\frac{v^2}{\sigma_e^{*}}\right)\right\rangle$	$w=\frac{2eE}{3mN}\left\langle\frac{1}{v}\right\rangle\frac{1}{\sigma_e^{*}}$, $\sigma_e^{*}=4\pi L^2$, L is the scattering length for the scattering of an electron by a gas particle	$\sigma_e^{*}=\sigma_e(v_0)$, $v_0=\frac{3}{2\langle\frac{1}{v}\rangle}$, $v_0^M=\frac{3}{4}\sqrt{\frac{2\pi T_e}{m}}$***)
5. Transverse-diffusion coefficient of electrons in a gas in a static electric field**	$D_\perp=\frac{1}{3N}\left\langle\frac{v}{\sigma_e^{*}}\right\rangle$	$D_\perp=\frac{\langle v\rangle}{3N\sigma_e^{*}}$	$\sigma_e^{*}=\sigma_e(v_0)$, $v_0=\frac{\langle v^2\rangle}{\langle v\rangle}$, $v_0^M=\frac{3}{4}\sqrt{\frac{2\pi T_e}{m}}$***)
6. Energy lost by an electron per unit time due to elastic scattering by gas particles**	$\left(\frac{d\varepsilon}{dt}\right)_{el}=\frac{m^2}{M}N\langle v^3\sigma_e^{*}\rangle$	$\left(\frac{d\varepsilon}{dt}\right)_{el}=\frac{m^2}{M}N\langle\sigma_e^{*}v^3\rangle$	$\sigma_e^{*}=\sigma_e(v_0)$, $v_0=\frac{\langle v^4\rangle}{\langle v^3\rangle}$, $v_0^M=\frac{15}{16}\sqrt{\frac{2\pi T_e}{m}}$***)

*Here T is the gas temperature, N is the number density of the gas particles, M is the mass of the gas particle, μ is the reduced mass of the colliding particle and the gas particle, and v is the relative collision velocity.

**Here e is the electron charge, E is the electric field, m is the electron mass, N is the number density of the gas particles, v is the electron velocity, σ_e^{*} is the diffusion cross section for the scattering of an electron by an atomic particle, M is the mass of the gas particle, and the angle brackets denote an average over the electron velocity.

***Here v_0^M is the value of the velocity in the argument of the cross section for a Maxwellian distribution of electrons with a temperature T_e.

port coefficients according to the hard-sphere model. The modified hard-sphere model referred to in this table corresponds to retention of the next term in the expansion. The argument in the collision cross section is determined by both the dependence of the scattering cross section on the energy or velocity of the collision and the shape of the particle energy distribution. For atoms and molecules, this would be a Maxwellian distribution, while for the scattering of slow electrons by atoms it would depend on the particular way in which the electrons reach equilibrium. Table II shows some specific values of the argument in the cross section for a Maxwellian electron distribution.

Equations (9) describe the collision cross section for heavy atomic particles. It follows from these equations that, with an accuracy corresponding to the first two terms in the expansion in the small parameter, the particle scattering cross section in the modified hard-sphere model, for a rapidly varying interaction potential, is

$$\sigma(\varepsilon)=\sigma(\varepsilon_0)\left(1+\frac{2}{\alpha R_0}\ln\frac{\varepsilon_0}{\varepsilon}\right). \tag{10}$$

This cross section was used in taking the average over the Maxwellian distribution of the particles in Table II (see Appendix I). For the scattering of slow electrons by atoms or molecules, the diffusion cross section is (see Ref. 7, for example)

$$\sigma^{*}=4\pi\left(L^2+\frac{4\pi}{5}\beta vL+\frac{\pi^2\beta^2v^2}{6}\right), \tag{11}$$

where L is the scattering length for scattering by the atom or molecule, v is the electron velocity, β is the polarizability of the atom or molecule, and we are using atomic units, with $\hbar=m_e=e^2=1$. The expansion of the cross section for low electron energies is thus $\sigma(v)=\sigma_0+Av$, where σ_0 is the cross section for scattering at a zero collision velocity, and $A=d\sigma/dv|_{v=0}$. This form of the cross section was used in taking the averages in Table II.

The convenience of the modified hard-sphere model can be seen in Table II. Taking into account the following term in the expansion in the small parameter of the theory does not change the expressions for the macroscopic properties according to the hard-sphere model, but it does refine the radius of the hard sphere, when this parameter is determined by the collision of heavy atomic particles, or it tells us the particular collision velocities for which we should take the cross sections in the expressions for the parameters determined by the collisions of slow electrons with atoms.

Figure 3 compares the thermal conductivities calculated for helium from the asymptotic expression in Table II, on the one hand, with experimental values, on the other. In the case under consideration here, the thermal energies of the helium atoms are considerably larger than the depth of the well in the potential for the interaction of two atoms. The thermal conductivity is thus determined by the repulsive part of the potential.

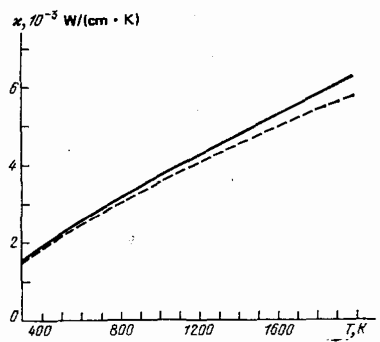

FIG. 3. Thermal conductivity of helium. Dashed curve—experimental[11,12]; solid curve—calculated from the formula in Table II. The use of the interaction potential in the form in (7), with the parameters A = 196 eV and α = 4.21 Å from Ref. 5, leads to the following analytic expression for the thermal conductivity in this case: $\varkappa=7.37\sqrt{T}/(14.82-\ln T)^2$, where the helium temperature T is in kelvins, and the thermal conductivity is in units of 10^{-3} W/(cm K).

TABLE III.

m/M	$\ll 1$	0.1	0.2	0.5	0.8	1.0	1.5	2.0	3.0	4.0	$\gg 1$
A	$0.897\left(\frac{m}{M}\right)^{1/4}$	0.490	0.572	0.701	0.777	0.811	0.864	0.893	0.925	0.943	1.000
c	$1.120\sqrt{\frac{m}{M}}$	3.75	2.79	1.84	1.47	1.34	1.17	1.09	1.02	0.977	0.867

Since the interaction potential is described by a simple expression, we can derive a simple analytic expression for the thermal conductivity.

4. Table III shows another example of this type, in this case for the transport coefficients of ions in a static electric field E in an atomic gas. These coefficients are determined by the cross section for the elastic collisions of ions with the gas particles. In this case the average ion energy is of order $\bar{\varepsilon} \sim eE\lambda$ [$\bar{\varepsilon}$ is the energy acquired by the ion in the field between successive collisions, $\lambda \sim (N\sigma)^{-1}$ is the mean free path, and σ is the collision cross section]. The ion drift velocity is given in order of magnitude by $w \sim \sqrt{eE\lambda/m}$, where m is the ion mass, and the ion diffusion coefficient in the gas is $D \sim \sqrt{eE/m\lambda}$. In these estimates we are assuming that the ion mass is comparable to that of the gas particles. Clearly, the proportionality factors in these expressions depend on the ratio of the ion mass m to the mass of the gas atom, M. We write the ion drift velocity as

$$w = A\sqrt{\frac{eE}{\mu N\sigma^*(cw)}}, \quad w \gg \sqrt{\frac{T}{M}}, \tag{12}$$

where μ is the reduced mass of the ion and the gas atom, σ^* is the diffusion cross section for the collision of these particles, and A and c are numerical parameters which depend on the ratio of m and M and which are listed in Table III.[3)] In this case, we might note, the diffusion cross section for the scattering of the ion by the atom is

$$\sigma^* = \pi R_1^2, \quad U(R_1) = 0.81c^2\frac{\mu w^2}{2}. \tag{13}$$

Equations (12) and (13) thus describe an unambiguous relationship between the interaction potential of the ion and the atom, on the one hand, and the ion drift velocity, on the other, in strong fields.

5. The hard-sphere model is of interest not only for problems involving the collisions of atoms with a rapidly varying repulsive potential but also for problems in which the results are determined by the interaction itself. As one such problem we consider the equation of state in a gas with a high temperature and a low density, which is written as follows if we retain the first term of the expansion in the small density (see Ref. 15, for example):

$$P = NT(1 + NB); \tag{14}$$

[3)]These quantities were calculated from the data of Skullerud,[13] who calculated the unknown characteristics by the Monte-Carlo method for the ion-atom interaction potential $U \sim R^{-n}$. The results of these calculations were analyzed in the modified hard-sphere model in Ref. 14.

TABLE IV. Collision cross sections in the hard-sphere model and exact values of the cross sections for classical particles interacting by the potential $U(R) = BR^{-n}$. The elastic cross section is $\sigma = C(B/\varepsilon)^{2/n}$, where ε is the energy in the center-of-mass system. This table gives the values of the coefficient C and also the ratio of the cross section in the hard-sphere model, σ_{ac}, to the exact cross section σ_T. The exact cross sections are taken from Refs. 3, 4, and 16–18; the model cross sections are calculated from expressions (A1.12) and (A1.16).

n	Exact cross section		Cross section in the hard-sphere model		Ratio of cross sections	
	σ_T^*	$\sigma_T^{(2)}$	σ_{ac}^*	$\sigma_{ac}^{(2)}$	σ_{ac}^*/σ_T^*	$\sigma_{ac}^{(2)}/\sigma_T^{(2)}$
4	3.75	3.87	3.33	4.37	0.888	1.127
6	3.49	3.24	3.27	3.42	0.936	1.056
8	3.39	2.95	3.23	3.02	0.953	1.025
10	3.32	2.76	3.22	2.81	0.969	1.016
12	3.29	2.65	3.20	2.68	0.974	1.010
14	3.26	2.56	3.19	2.58	0.972	1.008

here P is the gas pressure, T is the gas temperature, N is the density of atoms in the gas, and B is the second virial coefficient, given by

$$B(T) = \frac{1}{2}\int\left\{1 - \exp\left[-\frac{U(R)}{T}\right]\right\} d\mathbf{R}, \tag{15}$$

where U is the interaction potential of the two atoms and R is the distance between them. In this particular case the thermal energy of the atoms is much larger than the depth of the well of their interaction potential. The value of the virial coefficient is thus determined by the repulsive part of the interaction potential, and according to Eq. (15) it is

$$B(T) = \frac{2\pi R_0^3}{3}, \quad U(R_0) = cT, \tag{16}$$

where the dimensionless coefficient c is of the order of unity. This coefficient is calculated in Appendix 2 and found to be $c = 1.78$.

6. Clearly, the hard-sphere model can be used in its range of applicability, where the interaction potential of classical particles varies rapidly with the distance between the particles, or where the cross section for scattering of electrons by atoms or molecules depends only slightly on the collision velocity. In practice, we would like to know the accuracy of the model. The accuracy can be determined by comparing the exact collision cross section with that calculated from Eqs. (A1.12) and (A1.16), which correspond to the hard-sphere model. This comparison is made in Table IV. It is even more informative to compare the physical characteristics calculated from the hard-sphere model with the exact solutions, where the latter are available. Here we will compare the transport coefficients for the hard-sphere model and the Maxwell model. According to the Maxwell model, the collision cross section varies with the reciprocal of the collision velocity, $\sigma \sim 1/v$. From this dependence we can generate some simple analytic expressions for the transport coefficients.

The Maxwell model is advantageous in problems involving the motion of electrons in a gas, as can be seen from Table II. Under the assumption that $\nu = Nv\sigma^*(v)$ does not depend on the velocity, we can immediately find the drift velocity, the transverse diffusion coefficient, and the energy lost by the electron per unit time due to elastic collisions:

$$w=\frac{eE}{m\nu},\quad D_{\perp}=\frac{\langle v^2\rangle}{2\nu}=\frac{2\bar{\varepsilon}}{3m\nu},\quad \left(\frac{d\varepsilon}{dt}\right)_{el}=\frac{m^2}{M}\nu\langle v^2\rangle=2\frac{m}{M}\bar{\varepsilon}\nu, \quad (17)$$

where $\bar{\varepsilon}$ is the average electron energy, and these expressions do not involve the electron energy distribution.

The Maxwell model is convenient in the case of collisions of heavy particles because analytic expressions can be derived for the integral relations from the particle collision integral. It is thus possible to generate analytic expressions for the transport coefficients of the particles in a gas. In Appendix III we illustrate the procedure by calculating the ion drift velocity in a gas, which turns out to be

$$w=\frac{eE}{\mu\nu}, \quad (18)$$

where μ is the reduced mass of the gas and $\nu=Nv\sigma^*(v)$ is the rate at which ions collide with gas atoms [cf. Eq. (15)]. This expression holds for an arbitrary electric field, and we do not need to know the ion velocity distribution in order to determine the drift velocity.

Using this expression for the case of a weak field, and also using the Einstein relation

$$\frac{w}{E}=\frac{eD}{T}, \quad (19)$$

we find the ion diffusion coefficient in the gas to be

$$D=\frac{T}{\mu\nu}. \quad (20)$$

This result also holds in the limit in which the ion charge approaches zero; i.e., expression (20) gives the diffusion coefficient of atoms or molecules in a gas.

Table V summarizes the expressions for the transport coefficients according to the Maxwell model. The corresponding expressions from the hard-sphere model are given in Table II. Table V compares transport coefficients found from the hard-sphere model with the exact values in the case in which the Maxwell model holds. We see that although the applicability conditions of the hard-sphere model are not satisfied in this case, this model still predicts results which are quite acceptable in practice.

TABLE V. Expressions for the transport coefficients according to the Maxwell model.

Coefficient	Expression for the Maxwell model	Ratio of the result calculated for the hard-sphere model to that from the Maxwell model
1. Diffusion coefficient of particles in a gas	$D=\frac{T}{\mu\nu}$, $\nu=Nv\sigma^*(v)$	1.18
2. Thermal conductivity of a gas	$\varkappa=\frac{5T}{Mk^{(2)}}$, $k^{(2)}=\bar{v}\sigma^{(2)}(v)$	0.935
3. Viscosity of a gas	$\eta=\frac{4T}{3k^{(2)}}$	0.935
4. Electron drift velocity*	$w=\frac{eE}{m\nu}$	1.00
5. Transverse-diffusion coefficient of electrons*	$D_{\perp}=\frac{2\bar{\varepsilon}}{3m\nu}$	1.00
6. Electron energy loss per unit time*	$\left(\frac{d\varepsilon}{dt}\right)_{el}=2\frac{m}{M}\bar{\varepsilon}\nu$	0.906

*The electron is moving in a gas in a static electric field; $\bar{\varepsilon}$ is the average electron energy, and M is the mass of the gas particle.

TABLE VI.

n	4	6	8	10	12	14	∞
a_n	1.59	1.71	1.76	1.83	1.85	2.05	2.25
b_n	0.975	0.907	0.864	0.851	0.838	0.835	0.826

This analysis demonstrates the attractiveness of the hard-sphere model in which two terms are retained in the expansion in the small parameter in the expressions for the collision cross sections and for the macroscopic properties of gases. This procedure does not alter the expressions for the corresponding macroscopic properties which are predicted by the traditional hard-charge approaches zero; i.e., expression (20) gives the ments for which the cross sections are to be taken, or it refines the radius of the hard sphere. The expansion of the macroscopic properties in the small parameter of the hard-sphere model thus leads to a good description of the actual situation, without complicating the general expressions.

7. In practice, how reliable is the hard-sphere model for calculations of transport coefficients? The asymptotic approach in the hard-sphere model runs into two difficulties. First, the expressions for the cross sections may converge only slowly to their limits, for which the small parameter of the theory vanishes. Second, the real interaction potential of atomic particles has an attractive region, while the model assumes that the interaction is repulsive over the entire range of distances between the particles. The well in the interaction potential makes its presence felt even if it is shallow in comparison with the thermal energy of the colliding particles.

To determine how the average cross sections converge toward their asymptotic limits, we write the corresponding expressions in the same form[4)] as in Table II:

$$\Omega^{(1,1)}=\pi R_1^2,\qquad U(R_1)=a_nT, \quad (21)$$

$$\Omega^{(2,2)}=\frac{2}{3}\pi R_2^2,\quad U(R_2)=b_nT. \quad (22)$$

Table VI shows the coefficients a_n and b_n found from the exact expressions for the Ω integrals in the case of a repulsive interaction potential $U(R)=BR^{-n}$. We see from this table that for the average cross section $\Omega^{(1,1)}$ the coefficient a_n converges slowly toward its asymptotic limit as $n\to\infty$. In practice, therefore, it is more convenient to choose the value of a_n for a large but realistic value of n. The value of a_n found in this manner is not the same as its asymptotic value.

Can we, for the average cross section $\Omega^{(1,1)}$, take the potential well into account roughly when the scat-

4) Writing the cross section in this form is convenient because the interaction region responsible for the given process automatically reduces to a single point. Accordingly, as we go on to incorporate other factors we will try to keep the expressions in this form.

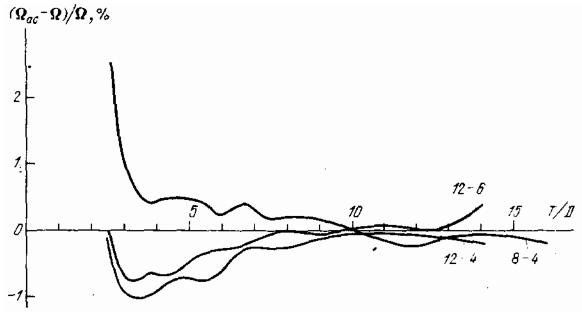

FIG. 4. Comparison of the average cross section $\Omega^{(1,1)}$ (Ω_{ac}) calculated from (24) for the corresponding interaction potential with tabulated values of Ω for this interaction potential.

tering is determined by the repulsive region? In this case the potential in the scattering region is conveniently approximated by $U(R) = BR^{-n} - C(R)$, where $n \gg 1$, and where the function $C(R)$ varies slowly over the distance R and may be treated as a constant. The second term, which causes a "shift" of the potential, takes into account the actual behavior in the repulsive region. Incorporating this part of the potential, we convert (21) to

$$\Omega^{(1,1)} = \pi R_1^2, \quad U(R_1) = aT - F. \tag{23}$$

Clearly, the parameter F is of the order of the well depth, D. For the real potential, the following empirical relation between the average cross section and the potential may be proposed:

$$\Omega_{\rm ac}^{(1,1)} = \pi R_1^2, \quad U(R_1) = 1.9(T - 2.5D). \tag{24}$$

Figures 4 and 5 show the results calculated from these expressions for the 12-6, 12-4, and 8-4 model potentials, given by

$$\left.\begin{aligned} U_{12-6} &= D(x^{-12} - 2x^{-6}), \\ U_{12-4} &= \frac{D}{2}(x^{-12} - 3x^{-4}), \\ U_{8-4} &= D(x^{-8} - 2x^{-4}), \end{aligned}\right\} \tag{25}$$

where $x = R/R_m$, R is the distance between the particles, and R_m is the distance between the particles at the potential minimum $[U'(R_m) = 0]$. Figure 4 compares the values of $\Omega^{(1,1)}$ calculated from (24) with the exact values for these potentials.[3] Figure 5 compares the values found for the potentials with their exact values. The interaction potentials U_{ac} were constructed from (24), in which we used the tabulated values of the Ω integrals[3] for the corresponding interaction potentials. We may conclude from these comparisons that expression (24) generates accurate values of the average cross section and of the corresponding diffusion coefficient from known interaction potentials. We see from Fig. 4 that the accuracy of this procedure is no worse than 1% if $T > 3D$; this condition corresponds to the repulsive region of the interaction. The inverse procedure—reconstructing the particle interaction potential from the measured diffusion coefficients—is far less accurate. Furthermore, this inverse procedure requires knowledge of another parameter: the depth of the potential well. The reconstruction of the interaction potential from the measured transport coefficients is less convenient than a reconstruction from the differential scattering cross section. The latter procedure is the procedure currently used to find the interaction potentials of atomic particles.

Summarizing this analysis, we conclude that the modified hard-sphere model, which takes into account the actual nature of the interaction between the colliding particles, is convenient for calculating the transport coefficients and other characteristics of the interactions and collisions of particles. This model rests on the assumption that the scattering of the particles is determined by the repulsive part of the interaction potential. This approach also leads to simple relations between the interaction potential and the average cross sections which appear in the expressions for the kinetic transport coefficients. Even more important are the simple expressions for the differential scattering cross section, which are required for determining the properties of nonequilibrium gases and plasmas and for finding the parameters of the processes which occur in them.

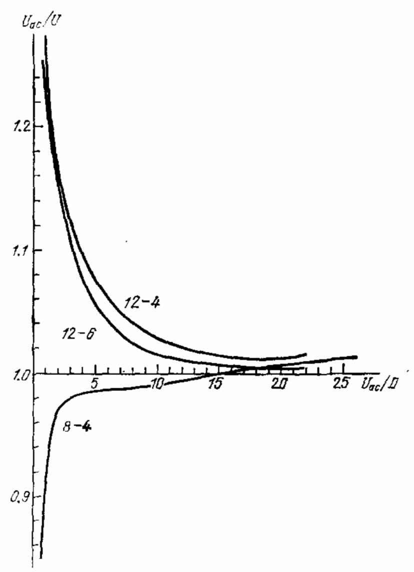

FIG. 5. Comparison of the interaction potential U_{ac} constructed from (24) using the tabulated values of $\Omega^{(1,1)}$ for the given interaction U, on the one hand, with this interaction potential, on the other.

APPENDIX 1. CALCULATION OF THE DIFFUSION CROSS SECTION FOR A RAPIDLY VARYING POTENTIAL

The diffusion scattering cross section is

$$\sigma^* = \int (1 - \cos\theta) \cdot 2\pi\rho d\rho, \tag{A1.1}$$

where ρ is the impact parameter of the collision, and θ is the scattering angle, determined by[19]

$$\theta = \pi - 2\int_{r_0}^{\infty} \left[1 - \frac{\rho^2}{R^2} - \frac{U(R)}{\varepsilon}\right]^{-1/2} \frac{\rho\, dR}{R^2}; \tag{A1.2}$$

Here R is the distance between the particles, ε is the collision energy in the center-of-mass system, $U(R)$ is the interaction potential, and r_0 is the distance of closest approach, which satisfies

$$1-\frac{\rho^2}{r_0^2}-\frac{U(r_0)}{\varepsilon}=0. \tag{A1.3}$$

We expand the cross section (A1.1) in the small parameter $1/n$, where $n=-\mathrm{d}\ln U(R)/\mathrm{d}\ln R$. In the zeroth approximation we assume $U(R)=0$ for $r>r_0$ and $U(R)=\infty$ for $r\leq r_0$. We then find

$$\theta=\pi-2\arcsin\frac{\rho}{r_0}-2\Delta\theta, \tag{A1.4}$$

$$\Delta\theta=\int_{r_0}^{\infty}\left\{\left[1-\frac{\rho^2}{R^2}-\frac{U(R)}{\varepsilon}\right]^{-1/2}-\left(1-\frac{\rho^2}{R^2}\right)^{-1/2}\right\}\frac{\rho\,\mathrm{d}R}{R^2}. \tag{A1.5}$$

Expressions (A1.4) and (A1.5) are exact. This is a convenient representation for the scattering angle, since we have $\Delta\theta=1/n$ in our case. To avoid divergences in the evaluation of integral (A1.5), we use

$$\frac{\mathrm{d}}{\mathrm{d}\rho}\int_{r_0}^{\infty}\left[\left(1-\frac{\rho^2}{R^2}\right)^{1/2}-\left(1-\frac{\rho^2}{R^2}-\frac{U(R)}{\varepsilon}\right)^{1/2}\right]\mathrm{d}R$$
$$=-\frac{\mathrm{d}r_0}{\mathrm{d}\rho}\left(1-\frac{\rho^2}{r_0^2}\right)^{1/2}-\int_{r_0}^{\infty}\left\{\left(1-\frac{\rho^2}{R^2}\right)^{-1/2}-\left[1-\frac{\rho^2}{R^2}-\frac{U(R)}{\varepsilon}\right]^{-1/2}\right\}\frac{\rho\,\mathrm{d}R}{R^2},$$

finding

$$\Delta\theta=\frac{\mathrm{d}r_0}{\mathrm{d}\rho}\sqrt{1-\frac{\rho^2}{r_0^2}}+\frac{\mathrm{d}}{\mathrm{d}\rho}\int_{r_0}^{\infty}\left[\sqrt{1-\frac{\rho^2}{R^2}}-\sqrt{1-\frac{\rho^2}{R^2}-\frac{U(R)}{\varepsilon}}\right]\mathrm{d}R. \tag{A1.6}$$

Since the last integral converges near $R\approx r_0$ ($R-r_0\sim 1/n$), we find, with an accuracy to $1/n$,

$$\int_{r_0}^{\infty}\left[\sqrt{1-\frac{\rho^2}{R^2}}-\sqrt{1-\frac{\rho^2}{R^2}-\frac{U(R)}{\varepsilon}}\right]\mathrm{d}R$$
$$\approx\sqrt{1-\frac{\rho^2}{r_0^2}}\int_{r_0}^{\infty}\left[1-\sqrt{1-\left(\frac{r_0}{R}\right)^n}\right]\mathrm{d}R$$
$$=\sqrt{r_0^2-\rho^2}\int_0^1\frac{(1-\sqrt{1-x})\,\mathrm{d}x}{nx^{1+(1/n)}}=\frac{2}{n}(1-\ln 2)\sqrt{r_0^2-\rho^2},$$

where

$$x=\left(1-\frac{\rho^2}{r_0^2}\right)^{-1}\frac{U(R)}{\varepsilon}=\frac{r_0^n}{R^n}.$$

Hence

$$\Delta\theta=\sqrt{1-\frac{\rho^2}{r_0^2}}\frac{\mathrm{d}r_0}{\mathrm{d}\rho}+\frac{2(1-\ln 2)}{n}\frac{\mathrm{d}}{\mathrm{d}\rho}\left(\sqrt{r_0^2-\rho^2}\right). \tag{A1.7}$$

Expressions (A1.3), (A1.4), and (A1.7) can be used to derive an expression for the scattering angle in the case of a rapidly varying repulsive potential. Introducing $u=U(R_0)/\varepsilon$, we find from these expressions

$$\theta=2\arcsin\sqrt{u}-2\left[\frac{2-(n-2)\ln 2}{n}\right]\frac{\sqrt{u(1-u)}}{1+[(n-2)/2]}$$
$$\approx 2\arcsin\sqrt{u}-2\ln 2\frac{\sqrt{u(1-u)}}{1+(n/2)u}, \tag{A1.8}$$

where $n=-\mathrm{d}\ln u/\mathrm{d}\ln r_0$. This expression is important in its own right, since it allows us to find the dependence of the scattering angle on the impact parameter ρ, which is in turn related to the distance of closest approach, r_0, by expression (A1.3):

$$1-\frac{\rho^2}{r_0^2}=u. \tag{A1.9}$$

Figure 6 compares exact values of the scattering angle from Ref. 20 for the interaction potential $U(R)=AR^{-12}$

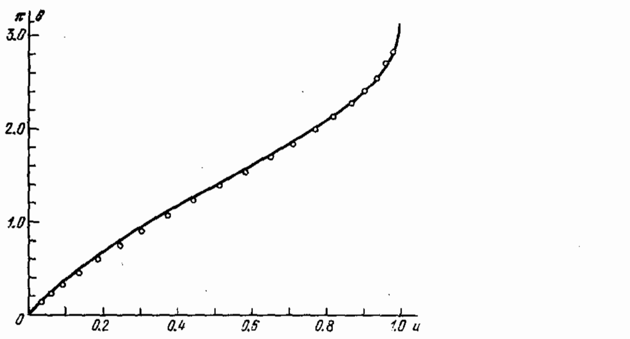

FIG. 6. The scattering angle θ in the center-of-mass system for the interaction potential $U=AR^{-12}$. The quantity plotted along the abscissa is $u=U(r_0)/E$, where r_0 is the distance of closest approach of the particles, and E is the kinetic energy of the particles in the center-of-mass system. Curve—Results calculated from the modified hard-sphere model, from Eq. (A1.8); circles—exact results.[20]

with values calculated from expression (A1.8). The discrepancy does not exceed 3% in the region of collision parameters where the scattering is significant.

In calculating the diffusion scattering cross section we note that this cross section is dominated by values $u\sim 1$, for which expression (A1.8) becomes

$$\theta=2\arcsin\sqrt{u}-\frac{4\ln 2}{n}\sqrt{\frac{1-u}{u}}. \tag{A1.10}$$

Assuming the second term to be small, we find, with an accuracy to terms $\sim 1/n$,

$$\sigma^*=\int_0^{\infty}(1-\cos\theta)\,\pi\,\mathrm{d}\rho^2=\pi\int 2u\,[(1-u)\,\mathrm{d}r_0^2-r_0^2\,\mathrm{d}u]$$
$$+\pi\int\frac{4\ln 2}{n}\sqrt{\frac{1-u}{u}}\cdot 2\sqrt{u(1-u)}\;r_0^2\,\mathrm{d}u.$$

Working from (A1.9), we have used the relation $\mathrm{d}\rho^2=(1-u)\mathrm{d}r_0^2-r_0^2\mathrm{d}u$, and we have made use of the circumstance that the first term is a fraction $\sim 1/n$ of the second. Evaluating the integral over $\mathrm{d}u$ in the first term by parts, we find[5)]

$$-\int_1^0 2\pi r_0^2u\,\mathrm{d}u=\pi R_0^2u^2\Big|_0^1-\int \pi u^2\cdot 2r_0\,\mathrm{d}r_0$$
$$=\pi R_0^2+\int_0^1 2\pi u r_0^2\frac{\mathrm{d}u}{n}=\pi R_0^2\left(1+\frac{1}{n}\right),$$

where $u(R_0)=1$, i.e., $U(R_0)=\varepsilon$. Repeating these calculations for the other integrals, and restricting the discussion to terms $\sim 1/n$, we finally find

$$\sigma^*=\pi R_0^2\left(1+\frac{3-4\ln 2}{n}\right). \tag{A1.11}$$

We write the diffusion cross section in the form $\sigma^*=\pi R_1^2$, i.e.,

$$R_1=R_0+\frac{1.5-2\ln 2}{n}.$$

We find

$$u(R_1)=\left(\frac{R_0}{R_1}\right)^n\approx\exp\left(-\frac{3}{2}+2\ln 2\right)=4e^{-3/2}=0.89.$$

The diffusion scattering cross section is therefore[6]

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5) We note that the value $\rho=0$ corresponds to $u=1$, while $\rho=\infty$ corresponds to $u=0$.

$$\sigma^* = \pi R_1^2, \text{ where } \frac{U(R_1)}{\varepsilon} = 0.89. \quad \textbf{(A1.12)}$$

Let us take the average of the cross section over a Maxwellian particle distribution. We find the average cross section, which appears in the expression for the diffusion coefficient:

$$\overline{\sigma^*(T)} = \frac{1}{2}\int_0^\infty \sigma^*(\varepsilon)\, e^{-x} x^2\, dx, \quad \textbf{(A1.13)}$$

where $x = \varepsilon/T$ and T is the gas temperature. From (A1.12) we find $\sigma^*(\varepsilon) \sim \varepsilon^{-2/n}$, so that

$$\sigma^*(\varepsilon) = \sigma^*(\varepsilon_0)\left(\frac{\varepsilon}{\varepsilon_0}\right)^{2/n} = \sigma^*(\varepsilon_0)\left[1 - \frac{2}{n}\ln\frac{\varepsilon}{\varepsilon_0}\right]. \quad \textbf{(A1.14)}$$

This expression holds at $\varepsilon \sim \varepsilon_0$, where the second term is smaller than the first. Substituting (A1.14) into (A1.13), we find the average cross section to be

$$\overline{\sigma^*(\varepsilon)} = \sigma^*(\varepsilon_0)\left(1 + \frac{2}{n}\ln\frac{\varepsilon_0}{T} - \frac{1}{n}\int_0^\infty x^2 \ln x e^{-x}\, dx\right).$$

We choose ε_0 such that the first and third terms cancel out. We find $\varepsilon_0 = T\exp[\psi(3)]$, where $\psi(3) = -C + (3/2)$ is the derivative of the gamma function, and $C = 0.577$ is the Euler constant. We thus have

$$\overline{\sigma^*(\varepsilon)} = \sigma^*\left[T\exp\left(-C + \frac{3}{2}\right)\right]$$

and using (A1.12) we find the average diffusion cross section to be

$$\overline{\sigma^*} = \pi r_1^2, \quad \frac{U(r_1)}{T} = 4e^{-C} = 2.25. \quad \textbf{(A1.15)}$$

This method can also be used to derive expressions for other cross sections for large-angle scattering if the interaction potential varies rapidly over space. In particular, for the cross section in the expressions for the thermal conductivity and the viscosity we have[7]

$$\sigma^{(2)} = \int (1 - \cos^2\theta)\, d\sigma = \frac{2}{3}\pi R_2^2, \quad \frac{U(R_2)}{T} = 0.23. \quad \textbf{(A1.16)}$$

The average cross section is

$$\overline{\sigma^{(2)}} = \frac{2}{3}\pi r_2^2, \quad \frac{U(r_2)}{T} = 0.83. \quad \textbf{(A1.17)}$$

APPENDIX 2. CALCULATION OF THE SECOND VIRIAL COEFFICIENT

We wish to determine the value of the second virial coefficient, (16),

$$B(T) = \int_0^\infty 2\pi R^2\, dR\, (1 - e^{-U/T}), \quad \textbf{(A2.1)}$$

for an interaction potential $U(R)$ which varies rapidly with the distance R between the atoms. In the hard-sphere model this integral is equal to half the volume bounded by the sphere $(2\pi/3)R_0^3$, where $U(R_0) \sim T$. We must determine this volume more accurately, i.e., take into account the first two terms in the expansion in the small parameter for this integral. For this purpose we approximate the potential in the region with $U(R) \sim T$ as $U(R) = AR^{-n}$; for a rapidly varying potential, we would have $n \gg 1$. Evaluating the integral (A2.1) we find

$$B = \frac{2\pi}{3}\left(\frac{C}{T}\right)^{3/n}\Gamma\left(1 + \frac{3}{n}\right).$$

We see that $B = (2\pi/3)/R_0^3$, where

$$\frac{U(R_0)}{T} = \lim_{n\to\infty}\left[\Gamma\left(1 + \frac{3}{n}\right)\right]^{-n/3} = e^{-\psi(1)} = e^C = 1.78; \quad \textbf{(A2.2)}$$

where $\psi(1)$ is the logarithmic derivative of the gamma function. Expression (A2.2) can be used to determine the volume, which also appears in the expression for the second virial coefficient in the case of a rapidly varying repulsive interaction potential.

APPENDIX 3. ION DRIFT VELOCITY IN A GAS

To derive an expression for the ion drift velocity in a gas in a static electric field for the Maxwell model, we begin from the Boltzmann equation,

$$\frac{e\mathbf{E}}{m}\frac{\partial f}{\partial \mathbf{v}_1} = J_c, \quad \textbf{(A3.1)}$$

where $f(\mathbf{v}_1)$ is the velocity distribution function of the ions, m is the mass of the ion, and J_c is the collision integral, given by

$$J_c = \int [f(\mathbf{v}_1)\varphi(v_2) - f(\mathbf{v}_1')\varphi(v_2')]\, Nv\, d\sigma\, d\mathbf{v}_2; \quad \textbf{(A3.2)}$$

Here $\mathbf{v}_1$ and $\mathbf{v}_2$ are the velocities of the ion and the gas particle before the collision, $\mathbf{v}_1'$ and $\mathbf{v}_2'$ are the same, but after the collision, $v = |\mathbf{v}_1 - \mathbf{v}_2|$ is the relative collision velocity, $\varphi(v_2)$ is the Maxwellian velocity distribution function for the gas particles, N is the number density of gas particles, and the distribution functions are normalized.

Multiplying the Boltzmann equation by the ion momentum $m\mathbf{v}_1$, and integrating over the ion velocity, we find

$$e\mathbf{E} = \int m\mathbf{v}_1 J_c\, d\mathbf{v}_1. \quad \textbf{(A3.3)}$$

The left side of this expression is the force exerted on the ion by the electric field, while the right side is the frictional force in the gas which results from the collisions of the ion with gas particles and which balances the force exerted by the field. Our problem is to evaluate the right side of this expression.

In the right side of (A3.3) we make use of the reversibility of the laws of mechanics with respect to time in elastic collisions of particles, and in the second term we make the interchange $\mathbf{v}_{1,2} \rightleftarrows \mathbf{v}_{1,2}'$. We find

$$\int m\mathbf{v}_1 J_c\, d\mathbf{v}_1 = \int m(\mathbf{v}_1 - \mathbf{v}_1') f(\mathbf{v}_1)\varphi(v_2)\, Nv\, d\sigma\, d\mathbf{v}_1\, d\mathbf{v}_2. \quad \textbf{(A3.4)}$$

We integrate over the scattering angle, singling out the part which depends on this angle. We evaluate the integral $\int m(\mathbf{v}_1 - \mathbf{v}_1')$, and we use

$$\mathbf{v}_1 = \mathbf{v}_{cm} + \frac{M}{m+M}\mathbf{v}, \quad \mathbf{v}_1' = \mathbf{v}_{cm} + \frac{M}{m+M}\mathbf{v}',$$

where M is the mass of the gas particle, $\mathbf{v}_{c.m.}$ is the velocity of the center of mass of the colliding particles, and $\mathbf{v}$ and $\mathbf{v}'$ are the relative velocity of the ion and the gas particle respectively before and after the collision. After these steps we find

$$\int m(\mathbf{v}_1 - \mathbf{v}_1')\, d\sigma = \int \mu(\mathbf{v} - \mathbf{v}')\, d\sigma,$$

where $\mu = mM/(m+M)$ is the reduced mass of the colliding particles. We can also write $\mathbf{v}' = \mathbf{v}\cos\theta + \mathbf{k}v\sin\theta$, where θ is the scattering angle, and $\mathbf{k}$ is the unit vector perpendicular to $\mathbf{v}$. Since all directions perpendicular to the relative velocity are equiprobable, we find, after an integration over the scattering angle,

$$\int m(\mathbf{v}_1-\mathbf{v}_1')\,d\sigma=\mu\mathbf{v}\int(1-\cos\theta)\,d\sigma=\mu\mathbf{v}\sigma^*,$$

where $\sigma^*(v)$ is the diffusion cross section for scattering of the ion by the gas particle.

Using this result in (A3.4) we find

$$\int m\mathbf{v}_1 J_c\,d\mathbf{v}_1=\mu\int \mathbf{v}f(\mathbf{v}_1)\,\varphi(v_2)\,Nv\sigma^*\,d\mathbf{v}_1d\mathbf{v}_2.$$

We now make use of the conditions of the Maxwell model, according to which the quantity $v\sigma^*(v)$ does not depend on the relative velocity of the particles. We introduce the rate at which the ion collides with gas particles,

$$\nu=Nv\sigma^*(v)$$

and we bring it outside the integral sign. Using $\mathbf{v}=\mathbf{v}_1-\mathbf{v}_2$, we find

$$\int m\mathbf{v}_1 J_c\,d\mathbf{v}_1=\mu\nu(\langle\mathbf{v}_1\rangle-\langle\mathbf{v}_2\rangle),$$

where the angle brackets indicate that averages are taken over the distributions of the ions and of the gas particles. Introducing the ion drift velocity $\mathbf{w}=\langle\mathbf{v}_1\rangle$, and noting that the average velocity of the gas particles is zero, $\langle\mathbf{v}_2\rangle=0$, we find, using (A3.3),

$$e\mathbf{E}=\mu\nu\mathbf{w},$$

from which we find the ion drift velocity to be

$$\mathbf{w}=\frac{e\mathbf{E}}{\mu\nu}. \qquad \text{(A3.5)}$$

This simple expression holds only for the Maxwell model, which allowed us to break up the integrand into factors which depend exclusively on the scattering angle and exclusively on the particle velocities.

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Translated by Dave Parsons