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On the Motion of Gaseous Ions in a Strong Electric Field. I

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This paper applies the Boltzmann method of gaseous kinetics to the problem of positive ions moving through a gas under the influence of a static, uniform electric field. The ion density is assumed to be vanishingly low, but the field is taken to be strong; that is, the energy which it imparts to the ions is not assumed negligible in comparison to thermal energy. Attention is focused upon the computation of velocity averages, and the drift velocity in particular, rather than a complete knowledge of the entire velocity distribution. It is shown in Secs. C and E that the problem so formulated is completely soluble if the mean free time between collisions of ions and molecules is a constant; this is the case for the so-called polarization force between ions and molecules which predominates over other forces at low temperature. A method for obtaining averages to any desired accuracy in the general case is developed in Sec. D. The method is applied to the hard sphere model for the high field range and mass ratio 1. An application of the resulting formula (43) to experimental material has been published earlier.

A. INTRODUCTION AND GLOSSARY

ALMOST all theoretical work which concerns itself with the drift motion of gaseous ions in an electric field deals with the case in which the drift motion is small compared to the thermal motion.[1] The velocity distribution of the ions is then almost maxwellian, and the electric field acts as a perturbation upon this distribution.

For electrons, the theory has been developed further and we know today the nature of the electronic motion when the energy picked up from the field is appreciable.[2] The saving feature for these calculations is that, even under these conditions, the velocity distribution is very nearly spherically symmetrical, because the electron loses momentum quickly, but accumulates energy in the form of random motion. This saving feature is not available in the study of ionic motion. Hershey[3] has made calculations for ions by making arbitrary assumptions about the velocity distribution function. Such a procedure throws doubt upon the results obtained.

This paper develops a procedure for extracting precise values for the most important velocity averages while by-passing the problem of the velocity distribution. It forms part of an extended study of ionic motion which is to be published elsewhere;[4] a second part is to follow which will discuss ionic diffusion. A comparison with experimental results has been published earlier.[5]

We shall assume here that the ions form a uniform stream which moves in a gas under the influence of a homogeneous static field. The ion density is assumed to be vanishingly low so that the maxwellian distribution of the gas molecules is not disturbed and collisions between ions and molecules predominate over ion-ion collisions in determining the behavior of the ions. The task is to solve the Boltzmann equation for the velocity distribution function $f(\mathbf{c})$ of those ions, or if this is impossible, to extract from the equation the values of certain averages, notably the drift velocity of the ions with the field.

The exposition will be preceded by a glossary explaining symbols. Generally, Latin capital letters will refer to the gas molecules and Latin lower case letters to the ions, Greek letters will have no special relationship; exceptions will be made for generally recognized symbols. Symbols whose meaning is obvious from the context will not be listed. We define

E = electric field.
m = ionic mass.
e = ionic charge.
$a = eE/m$ = ionic acceleration.
kT = Boltzmann's constant × absolute temperature.
z = coordinate along field direction.
x, y = coordinates at right angles to field direction.
b = impact parameter.
e_x, e_y, e_z = energies of ionic motion along x, y, z.
$e_z{}^*$ = random part of above energy.
p, q, r, s = numbers to be determined in (41).
$p^{(0)}, p^{(1)}\cdots$ = various approximations to these numbers.
M = molecular mass.
N = number density of molecules.
P = molecular polarizability.
V = potential energy of ion and molecule.
$\mathbf{c}, \mathbf{c}', \mathbf{u}, \mathbf{u}', \mathbf{v}$ = ionic velocities.
$\mathbf{C}, \mathbf{C}', \mathbf{U}, \mathbf{U}'$ = molecular velocities.
$\boldsymbol{\gamma}, \boldsymbol{\gamma}'$ = relative velocities of ion and molecule.
σ = collision cross section.
$\lambda = 1/N\sigma$ = mean free path of ion between collisions with molecules.
$\tau = 1/N\sigma\gamma$ = mean free time of ion between collisions with molecules.
τ_s = same parameter for "spiralling" collisions.
$\mathbf{w} = \mathbf{c}/(a\lambda)^{\frac{1}{2}}$ = ionic velocity rendered dimensionless.
$\beta = 1/2kT$ = temperature parameter.
ρ = distance between ion and gas molecule.
$\vartheta, \vartheta', \varphi, \varphi', \psi, \chi, \epsilon$ = angles to be defined.
$m(\mathbf{c}) = (\beta m/\pi)^{\frac{3}{2}} \exp(-\beta mc^2)$ = maxwellian velocity distribution function for ionic mass.

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[1] For a general survey, see: A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, Cambridge, 1938), Chapter IV.

[2] For a general background: see Chapman-Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, 1939), Sections 18.7–18.74. More recent papers are: J. A. Smit, Physica **3**, 543 (1937); H. W. Allen, Phys. Rev. **52**, 707 (1937).

[3] A. V. Hershey, Phys. Rev. **56**, 916 (1939).

[4] Bell System Technical Journal, 1952. In the following referred to as BSTJ.

[5] J. A. Hornbeck and G. H. Wannier, Phys. Rev. **82**, 458 (1951).

$M(\mathbf{C})=(\beta M/\pi)^{\frac{3}{2}}\exp(-\beta MC^2)$ = maxwellian velocity distribution function for molecular mass.
$h(\mathbf{c})$ = "high field" distribution function for the ions (the exact meaning of this term is to be explained in the text).
$f(\mathbf{c})$ = true velocity distribution for the ions.
$\delta(\mathbf{c})$ = vectorial δ-function in velocity space.

A special convention will be adopted to distinguish velocities before and after a collision:

$\mathbf{c}'$, $\mathbf{C}'$ = velocities before the collision.
$\mathbf{c}$, $\mathbf{C}$ = velocities after the collision.

When used in this fashion the twelve components of the four vectors above satisfy the four identities

$$m\mathbf{c}'+M\mathbf{C}'=m\mathbf{c}+M\mathbf{C} \tag{1}$$

$$mc'^2+MC'^2=mc^2+MC^2. \tag{2}$$

The same convention is to apply to other vector quadruples, such as

$$\mathbf{u},\ \mathbf{U},\ \mathbf{u}',\ \mathbf{U}'.$$

For the velocities in the center-of-mass system we use

$\boldsymbol{\gamma}'=\mathbf{c}'-\mathbf{C}'$ = relative velocity before the collision.
$\boldsymbol{\gamma}=\mathbf{c}-\mathbf{C}$ = relative velocity after the collision.

In consequence of (1) and (2) the γ's obey the relation

$$\gamma'^2=\gamma^2. \tag{3}$$

χ will be the scattering angle for fixed center of mass in the c-system, that is

$$\boldsymbol{\gamma}'\cdot\boldsymbol{\gamma}=\gamma^2\cos\chi. \tag{4}$$

ϵ will be the scattering azimuth. The letter ϑ will be used for the angle between $\mathbf{c}$ and the field direction, similarly ϑ' for $\mathbf{c}'$.

The multiple integrations occurring in the theory are of the following two types. Either they are over the three components of a velocity in a cartesian velocity space; we shall denote such integrations by $d\mathbf{c}$, $d\mathbf{u}$, $d\mathbf{U}'$, etc. Or they are proper "collision" integrations which classically have the form

$$\gamma\ b\ db\ d\epsilon$$

where b is an impact parameter and ϵ an azimuth. In most cases these integrals depend on extraneous factors for their convergence, but this fact is usually disregarded for convenience; we shall follow this habit by writing the above differential in the form

$$\gamma\sigma d\mathbf{\Pi}_c.$$

The index c on $d\mathbf{\Pi}_c$ refers to the fact that it is the collision integral in the $\mathbf{c}$, $\mathbf{C}$, $\mathbf{c}'$, $\mathbf{C}'$ system of velocities. As an alternate to this notation we shall sometimes write

$$d\mathbf{\Pi}_c=\frac{1}{4\pi}\Pi(\chi)\sin\chi d\chi d\epsilon. \tag{5}$$

$\Pi(\chi)$ is the probability function of scattering; it equals unity in the isotropic case. When the differential (5) above is integrated out as it stands it will equal unity by definition, but if any other factor depending on χ enters, the resulting integral may or may not depend on γ. In any case, the cross section σ depends on γ unless we deal with the hard sphere approximation.

Furthermore

$$\mathrm{Ei}(x)=\int_x^\infty e^{-\xi}/\xi\quad d\xi\ \text{(suppression of two minus signs).}$$

$K_0(x)$, $K_1(x)$ = Modified hankel functions of order 0,1 (alteration of Macdonald function by a factor $2/\pi$.)
$P_\nu(x)$ = Legendre polynomials.
$h_\nu(c)$ = expansion coefficients defined by (11).
$\langle\ \rangle$ = the quantity in pointed brackets is to be averaged.
$I_{s,\nu}$ = a set of numbers defined by (16).

B. REDUCTION OF THE HIGH FIELD CASE: LEGENDRE DECOMPOSITION AND MOMENT FORMATION

The Boltzmann equation for the problem defined in the fourth paragraph of Part A may be found in Chapman-Cowling.[6] In our notation it reads

$$a\frac{\partial f(\mathbf{c})}{\partial c_z}=\int\int[M(\mathbf{C}')f(\mathbf{c}')-M(\mathbf{C})f(\mathbf{c})]\times[1/\tau(\gamma)]d\mathbf{\Pi}_c d\mathbf{C}. \tag{6}$$

The most important property of (6) is the fact that it is a linear equation. This fact makes possible many procedures which were barred to other investigators working on more conventional problems of kinetic theory.

Equation (6) contains two external parameters, the field strength and the gas temperature. We define the low field case as the case for which $f(\mathbf{c})$ is maxwellian to a first approximation, annulling identically the curly bracket on the right of (6). The left-hand side of (6) is then in the nature of a perturbation which proceeds in powers of the field. This case will not be discussed further as it is treated in many textbooks. A second limiting case of (6) arises when the thermal energy of the molecules is negligible in comparison with the energy the ions extract from the field. We shall call this case the high field case. In the high field case, the function $M(\mathbf{C})$ may be replaced by $\delta(\mathbf{C})$, and the gas temperature disappears from the problem. Equation (6) becomes then

$$a\frac{\partial h(\mathbf{c})}{\partial c_z}+\frac{1}{\tau(c)}h(\mathbf{c})=\int\int\delta(\mathbf{C}')h(\mathbf{c}')\frac{1}{\tau(c')}d\mathbf{\Pi}_c d\mathbf{C}. \tag{7}$$

Three out of the five integrations on the right can be carried out by the use of the δ-function. The actual manipulation is cumbersome and will be given in BSTJ.[5] It yields

$$a\frac{\partial h(\mathbf{c})}{\partial c_z}+\frac{1}{\tau(c)}h(\mathbf{c})=\frac{(M+m)^2}{4\pi Mmc}\times\int_c^{(M+m)c/|M-m|}\frac{1}{\tau(c')}\Pi(\chi)dc'\int_0^{2\pi}d\varphi' h(\mathbf{c}'). \tag{8}$$

Here the scattering angle entering into $\Pi(\chi)$ is defined by the auxiliary equation

$$\cos\chi=[(m+M)^2c^2c'^{-2}-M^2-m^2]/2mM. \tag{9}$$

The integration is over the surface of a sphere in velocity space (a plane when $M=m$) which must be known for correct substitution into $h(\mathbf{c}')$. The equation of the sphere is

$$(M-m)c'^2+2m\mathbf{c}'\cdot\mathbf{c}-(M+m)c^2=0. \tag{10}$$

The variable vector $\mathbf{c}'$ is never smaller than $\mathbf{c}$ (which

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[6] See reference 1, Chapman-Cowling, Eq. (18.71, 1).

is fixed) and equals it at the point $\mathbf{c}'=\mathbf{c}$. The center of the sphere lies on the straight line joining this point to the origin; it lies on the side of the origin from $\mathbf{c}$ when $m<M$, at infinity (making the sphere a plane) when $m=M$, and away from the origin if $m>M$. The radius of the sphere is $Mc/|M-m|$. The two variables of integration used in (8) are the azimuth φ' on the sphere measured around $\mathbf{c}'=\mathbf{c}$, and the length of the vector $\mathbf{c}'$.

We now choose the field direction as polar axis and expand $h(\mathbf{c})$ in spherical harmonics about that direction:

$$h(\mathbf{c})=\sum_{\nu=0}^{\infty} h_\nu(c)P_\nu(\cos\vartheta). \tag{11}$$

Figure 1 shows a spherical triangle on the unit sphere in vector space. The vectors $\mathbf{c}$, $\mathbf{c}'$, and $\mathbf{a}$, assumed drawn from the origin, show up in the figure by their piercing points. Polar angles show up as sides, azimuths as angles. With the help of Fig. 1, Eq. (11) and the decomposition theorem for spherical harmonics, we get

$$\int_0^{2\pi} h(\mathbf{c}')d\varphi'=2\pi\sum_{\nu=0}^{\infty} h_\nu(c')P_\nu(\cos\vartheta)P_\nu(\cos\psi). \tag{12}$$

Furthermore, we get for the derivative in (8)

$$\frac{\partial}{\partial c_z}\left\{\sum_{\nu=0}^{\infty} h_\nu(c)P_\nu(\cos\vartheta)\right\}=\sum_{\nu=0}^{\infty}\left[\frac{dh_\nu(c)}{dc}\frac{1}{2\nu+1}\right.$$
$$\times\{(\nu+1)P_{\nu+1}(\cos\vartheta)+\nu P_{\nu-1}(\cos\vartheta)\}$$
$$\left.+\frac{1}{c}h_\nu(c)\frac{\nu(\nu+1)}{2\nu+1}\{P_{\nu-1}(\cos\vartheta)-P_{\nu+1}(\cos\vartheta)\}\right]. \tag{13}$$

Substituting (11), (12), and (13) into (8) and annulling separately the coefficient of each Legendre polynomial in $\cos\vartheta$ we get the set of equations

$$\frac{(M+m)^2}{2Mmc}\int_c^{(M+m)c/|M-m|}\frac{h_\nu(c')}{\tau(c')}P_\nu(\cos\psi)\Pi(\chi)dc'$$
$$-\frac{h_\nu(c)}{\tau(c)}=\frac{\nu a}{2\nu-1}\left(\frac{dh_{\nu-1}(c)}{dc}-\frac{\nu-1}{c}h_{\nu-1}(c)\right)$$
$$+\frac{(\nu+1)a}{2\nu+3}\left(\frac{dh_{\nu+1}(c)}{dc}+\frac{\nu+2}{c}h_{\nu+1}(c)\right), \tag{14}$$

where

$$\nu=0,1,2,3\cdots.$$

Of the two auxiliary angles χ and ψ, appearing in the integral, χ is defined by (9); ψ is obtained from Fig. 1 and Eq. (10) as

$$\cos\psi=[(M+m)c^2-(M-m)c'^2]/2mcc'. \tag{15}$$

The second step in reducing (8) consists in applying the Mellin transformation to $h_\nu(c)$ or introducing moments. In doing this we shall assume that the angular distribution in the scattering of ions by molecules is independent of the velocity of approach (although the total cross section may not be). The assumption happens to be correct for the two cases treated in detail, the polarization force and the hard sphere model. It is not actually a necessary assumption but it has a certain convenience for writing down results.

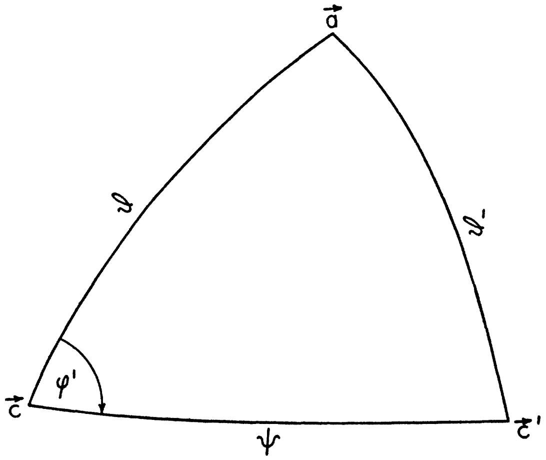

FIG. 1. Definition of the angles between $\mathbf{c}$, $\mathbf{c}'$, and $\mathbf{a}$; representation by a triangle on the unit sphere.

We multiply (14) by c^{s+2} and integrate over c from 0 to ∞. The power s must be sufficiently large to permit integration by parts on the right without integrated out part ($s\geqq-1$ is probably adequate for this). The integral over the integral term so obtained decomposes rather neatly into a product of a collision integral and a velocity average:

$$\int_0^\infty c^{s+1}dc\int_c^{(M+m)c/|M-m|}\frac{h_\nu(c')}{\tau(c')}P_\nu(\cos\psi)\Pi(\chi)dc'$$
$$=\int_1^{(M+m)/|M-m|}P_\nu(\cos\psi)\Pi(\chi)dx\int_0^\infty\frac{h_\nu(cx)}{\tau(cx)}c^{s+2}dc$$
$$=\int_1^{(M+m)/|M-m|}\frac{dx}{x^{s+3}}P_\nu(\cos\psi)\Pi(\chi)\int_0^\infty\frac{h_\nu(c)}{\tau(c)}c^{s+2}dc.$$

Here x is defined as c'/c and ψ and χ are functions of x only as is seen from (9) and (15). Thus, the last line is a product of two independent integrals. We write for the first factor $I_{s,\nu}$; it is a collision integral not involving the velocity distribution. This can be made explicit by using χ as integration variable. We get from (9)

$$x=c'/c=(M+m)/(M^2+m^2+2Mm\cos\chi)^{\frac{1}{2}},$$

and from (15)

$$\cos\psi=(m+M\cos\chi)/(M^2+m^2+2Mm\cos\chi)^{\frac{1}{2}},$$

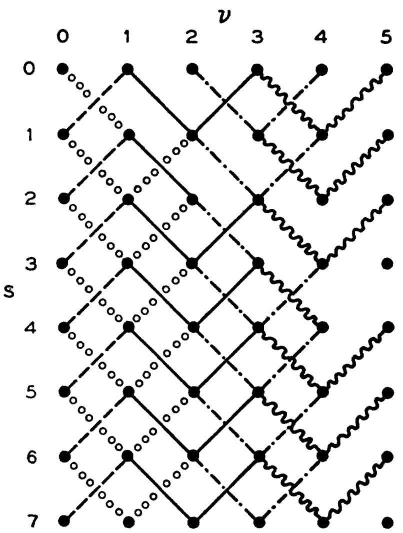

FIG. 2. Interconnection between the averages $\langle c^s P_\nu(\cos\vartheta)\rangle$ through the equation system (17); case of constant mean free time.

so that $I_{s,\nu}$ becomes

$$I_{s,\nu}=\left\langle\left\{\frac{(M^2+m^2+2Mm\cos\chi)^{\frac{1}{2}}}{M+m}\right\}^s \times P_\nu\left\{\frac{m+M\cos\chi}{(M^2+m^2+2Mm\cos\chi)^{\frac{1}{2}}}\right\}\right\rangle. \quad (16)$$

With the help of these numbers $I_{s,\nu}$, the integrated equation (14) takes the form,

$$(2\nu+1)(1-I_{s,\nu})\left\langle\frac{c^s P_\nu(\cos\vartheta)}{a\tau(c)}\right\rangle =\nu(\nu+s+1)\langle c^{s-1}P_{\nu-1}(\cos\vartheta)\rangle +(\nu+1)(s-\nu)\langle c^{s-1}P_{\nu+1}(\cos\vartheta)\rangle. \quad (17)$$

C. VELOCITY AVERAGES FOR CONSTANT MEAN FREE TIME; THE POLARIZATION FORCE

For the case $\tau(c)=\text{const}$, Eqs. (17) permit computation by recurrence of the averages of all products of integer powers of the velocity components. This is shown in Fig. 2. Each average $\langle c^s P_\nu(\cos\vartheta)\rangle$ is marked in this figure as a dot in an s–ν-plane if s is integer. Equations (17) connecting these averages are shown as lines with different equations leading to the same dot shown in different outline. These equations generally have the shape of a V; there are two notable exceptions to this rule, however, which make the recurrence method possible: the equations $\nu=0$ have no left leg and the equations $s=\nu$ have no right leg. Starting out with the average $s=0$, $\nu=0$, which equals unity by definition, one can thus proceed systematically, as shown in Fig. 3, to get other averages. The averages reached are the ones for which s and ν are non-negative integers of equal parity with the restriction $s\geqq\nu$. One verifies easily that this set is equivalent to the set of all products of integer powers of the velocity components.

We shall now explicitly follow for a certain distance the path outlined in Fig. 3. It so happens that the most important averages are the first three obtained in this manner:

$$s=1,\quad \nu=1,\qquad \langle c_z\rangle=\frac{M+m}{M}\,\frac{a\tau}{\langle 1-\cos\chi\rangle} \quad (18)$$

$$s=2,\quad \nu=0,\qquad \langle c^2\rangle=\frac{(M+m)^3}{M^2 m}\,\frac{(a\tau)^2}{\langle 1-\cos\chi\rangle^2} \quad (19)$$

$$s=2,\quad \nu=2,\qquad \langle c^2P_2(\cos\vartheta)\rangle =\frac{4(M+m)^3(a\tau)^2}{M^2\langle 3M\sin^2\chi+4m(1-\cos\chi)\rangle}$$

or more conveniently with the help of (19)

$$\langle c_z^2\rangle=\frac{(M+m)^3\langle M^2\sin^2\chi+4m(1-\cos\chi)\rangle(a\tau)^2}{M^2m\langle 1-\cos\chi\rangle^2\langle 3M\sin^2\chi+4m(1-\cos\chi)\rangle} \quad (20)$$

$$s=3,\quad \nu=1,\ \cdots\ \text{etc.}$$

The three equations (18)–(20) give the drift velocity, the total energy, and the energy partition of the travelling ion. Formula (18) can actually be derived from a low field theory. Equation (18) thus states that, for problems involving a constant mean free time, the high field and low field mobilities are numerically identical. One would suspect that the intermediate field value would have to fall in line too. This is indeed the case and led to the discovery of the theorem in Sec. E.

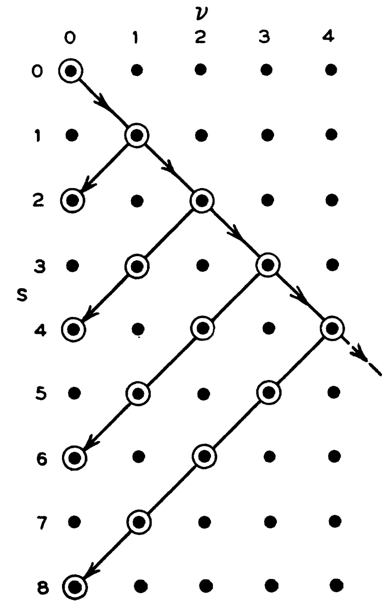

FIG. 3. Order to be followed in calculating by recursion the averages $\langle c^s P_\nu(\cos\vartheta)\rangle$; case of constant mean free time.

A convenient interpretation of (19) may be had by combining (18) and (19) in the following way

$$\langle mc^2\rangle = m\langle c_z\rangle^2 + M\langle c_z\rangle^2. \tag{21}$$

The left side is the total energy of the ion, the first term on the right is the energy visible in the drift motion; it follows therefore that the second term is the "invisible" or random part of the mean energy. Formula (21) thus states that

random energy/visible energy
= molecular mass/ion mass. (22)

Formula (20) is best interpreted by writing out the partition of the energy between the three translational degrees of freedom. This can be done in two ways; either the total or the random energy may be partitioned. In the first case we get

$$e_x : e_y : e_z = \langle M \sin^2\chi\rangle : \langle M \sin^2\chi\rangle : \langle 4m(1-\cos\chi) + M \sin^2\chi\rangle. \tag{23}$$

In the second case

$$e_x : e_y : e_z{}^* = (M+m)\langle \sin^2\chi\rangle : (M+m)\langle \sin^2\chi\rangle : \langle 2m(1-\cos\chi)^2 + M \sin^2\chi\rangle. \tag{24}$$

For small ion mass (electrons) both formulas give equipartition for any law of scattering. But generally this is not so. For instance we get from (23) for isotropic scattering

$$e_x : e_y : e_z = M : M : (M+6m) \tag{25}$$

and from (24)

$$e_x : e_y : e_z{}^* = (M+m) : (M+m) : (M+4m). \tag{26}$$

This gives for equal masses the ratios

$$e_x : e_y : e_z = 1:1:7$$
$$e_x : e_y : e_z{}^* = 1:1:5/2.$$

For heavy ions the unbalance is even greater, most of the ion's energy being in its drift as can be seen already from (22). No limiting finite partition of the total energy exists therefore; the partition formula (26) becomes

$$e_x : e_y : e_z{}^* = 1:1:4.$$

The theory developed in this section applies exactly to the polarization force between ions and atoms. This force is occasionally preponderant at room temperature; if it is not then it may predominate over others at low temperature, because it has a cross section varying inversely as the velocity. The interaction potential equals

$$V = \tfrac{1}{2}(e^2P/\rho^4). \tag{27}$$

Classical theory is usually applicable to the scattering problem, because angular momentum quantum numbers run as high as 30 or 50 in normal situations.[7] The solution of this scattering problem gives rise to two kinds of orbits: orbits like hyperbolas for large angular momentum and spirals for small angular momentum.[8] The critical impact parameter b separating the two kinds of orbits is given by

$$b^4 = 4e^2P(M+m)/Mm\gamma^2. \tag{28}$$

This leads to a mean free time τ_s between spiralling collisions which is given by

$$\tau_s = (1/2\pi eN)\{Mm/P(M+m)\}^{\frac{1}{2}}. \tag{29}$$

This is indeed a constant mean free time, because the formula does not contain the velocity of encounter γ.

There is no mean free time definable for "hyperbolic" collisions, because small angle deflections are infinitely probable. However, the actual expressions entering into (18), (19), and other formulas are always of the form,

$$(1/\tau^n)\langle\varphi(\chi)\rangle^n,$$

and become equal to 0/0 if very weak encounters are taken into account. There are standard ways of making these expressions definite.[9] We find in Hassé

$$(1/\tau)\langle 1-\cos\chi\rangle \sim (1/\tau_s)\times 1.1052, \tag{30}$$

and we computed in this laboratory

$$(1/\tau)\langle \sin^2\chi\rangle \sim (1/\tau_s)\times 0.772. \tag{31}$$

With the help of the identifications above, formula (18) for the drift velocity becomes

$$\langle c_z\rangle = \frac{0.9048}{2\pi}\left(\frac{1}{M}+\frac{1}{m}\right)^{\frac{1}{2}}\frac{E}{MP^{\frac{1}{2}}}. \tag{32}$$

The formula for the total energy needs no discussion for a special model; it does not involve the angular distribution when written in the form (21) or (22).

For the partition of the energy we get from (23)

$$e_x : e_y : e_z = M : M : (M+5.73m) \tag{33}$$

and from (24)

$$e_x : e_y : e_z{}^* = (M+m) : (M+m) : (M+3.72m). \tag{34}$$

There is an obvious similarity of (33) with (25), or (34) with (26). The reason for this is that the polarization force scatters very nearly isotropically, that is (31) is about $\frac{2}{3}$ of (30). Tracing this feature back we observe that the contribution of the spiralling orbits to (30) and (31) predominates; in these orbits the two particles very nearly "forget" the direction whence they came.[8]

D. GENERAL METHOD FOR DETERMINING VELOCITY AVERAGES; APPLICATION TO THE HARD SPHERE MODEL AND $m=M$

The results obtained in Sec. C are in the nature of a lucky accident. Generally we can expect neither a dove-

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[7] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **144A**, 554 (1931). Theodore Holstein, private communication.

[8] P. Langevin, Ann. de Chim. Phys. **5**, 245 (1905).

[9] H. R. Hassé, Phil. Mag. **1**, 1939 (1926).

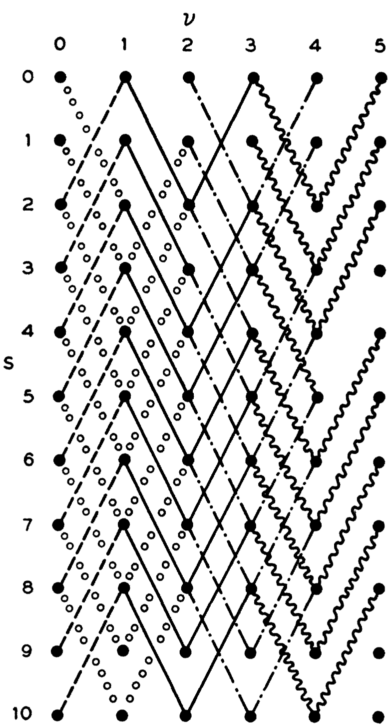

FIG. 4. Interconnection between the averages $\langle c^s P_\nu(\cos\vartheta)\rangle$ through the equation system (17); case of constant mean free path.

tailing of equations as it occurs in Fig. 2, nor that the computable averages contain the physically important quantities. As an example of a more normal situation we see in Fig. 4 the analog of Fig. 2 for the case of a constant mean free path. Only two averages are seen to be directly computable, namely $\langle c^2 \cos\vartheta\rangle$ and $\langle c^4\rangle$. Neither one of them has any physical importance.

A method will be described in this section which permits computation of averages under very general conditions, allowing in principle even the inclusion of temperature effects. A test application of the method to a case in which the distribution function was known by other means (Monte Carlo method) will be described in BSTJ. In this article the numerical work will be restricted to a case obeying the following assumptions: (a) that we deal with the high field case, (b) that the mass of the ions and molecules are equal, and (c) that the ions and molecules interact with each other like hard spheres. This specialization has in view the experimental work of Hornbeck[5] on He^+, Ne^+, and A^+ travelling in the parent gases.

The way of computing averages from a diagram such as Fig. 4 is closely tied up with certain special features of the equation system (14). At first sight (and this first sight lasted in the author's case for many months) it seems that it is a recursion system permitting substitution of an arbitrary function $h_0(c)$; the "zeroth" equation then gives a derived $h_1(c)$, the first equation $h_2(c)$, etc. However, a closer examination shows a quite different situation. Suppose we have obtained somehow functions $h_0, h_1, \cdots h_n$ and we are trying to use the nth equation to determine h_{n+1}. This equation is of the form

$$dh_{n+1}/dc + [(n+2)/c]h_{n+1}(c) = \text{known material.} \tag{35}$$

We solve for h_{n+1} by multiplying with c^{n+2} and integrating. This gives

$$c^{n+2}h_{n+1}(c) = \int^c (\text{known material})\, dc. \tag{36}$$

The left-hand side is such that it must vanish both at $c=0$ and $c=\infty$. It follows that the right hand integral, when taken between the limits 0 and ∞, must equal zero. The recursion system is therefore of such a structure that, at each stage, it imposes a condition upon the h_ν's already determined if the new $h_{n+1}(c)$ is to exist at all.

The integrability conditions whose essential feature was indicated in (36) were already written out earlier. They are the ones among the set (17), for which $s=\nu$; it was remarked at the time that these equations have no "right leg". Thus they connect averages which could be computed by other means if $h_0(c)$ were known. We shall refer to these relations as "singular relations".

The method which can be based on this feature is fairly straightforward. An initial trial function $h_0(c)$ is improved step by step through the adjustment of free parameters using the singular relations. It will be shown in BSTJ that each singular relation is always reducible to a relation between averages involving $h_0(c)$ only by the use of a fairly obvious process of elimination. In our case the elimination procedure may be read off from Fig. 4. Using the dimensionless variable

$$w = \frac{c}{(a\lambda)^{\frac{1}{2}}} \tag{37}$$

we shall write down the first few of these relations. We obtain from the singular relation $s=\nu=1$

$$\langle w^4\rangle = 10, \tag{38}$$

from the singular relation $s=\nu=2$

$$3\langle w^7\rangle = 112\langle w^3\rangle, \tag{39}$$

and from the singular relation $s=\nu=3$

$$(295/56)\langle w^6\rangle = 27\langle w^2\rangle + (17/330)\langle w^{10}\rangle. \tag{40}$$

With the help of Eqs. (38), (39), and (40) and the normalization condition a succession of improved functions $h_0(w)$ can be constructed which will lead to successive approximations to any average desired. This procedure resembles somewhat the Ritz method of quantum mechanics. Just as in that method a good choice of trial functions greatly improves the approximation. In the choice of the trial functions below use has been made of the fact that the true function $h_0(w)$

has a logarithmic singularity at $w=0$ and that it vanishes at infinity as

$$w^k \exp[-\tfrac{1}{2}w^2]$$

the power k being unknown. No proof will be given here of these facts, which are useful rather than essential for the success of the method. A thorough discussion of this point will be found in BSTJ.

On the basis of this information we write down the following trial function for $h_0(w)$:

$$h_0 = p\,\mathrm{Ei}(\tfrac{1}{2}w^2) + qK_0(\tfrac{1}{2}w^2) + r\exp(-\tfrac{1}{2}w^2) + sw^2K_1(\tfrac{1}{2}w^2). \quad (41)$$

The best zero-order function is $K_0(\frac{1}{2}w^2)$. We find in zero order, from normalization only

$$q^{(0)} = \frac{\pi}{2\Gamma^2(\frac{3}{4})} = 1.04605 \quad p^{(0)} = r^{(0)} = s^{(0)} = 0;$$

in first order, using (38)

$$p^{(1)} = -0.46543 \qquad r^{(1)} = s^{(1)} = 0$$
$$q^{(1)} = 1.45285;$$

in second order, using (38) and (39)

$$p^{(2)} = -0.80856$$
$$q^{(2)} = 1.88127 \qquad s^{(2)} = 0$$
$$r^{(2)} = -0.09804;$$

in third order, using (38), (39), and (40)

$$p^{(3)} = -1.15071$$
$$q^{(3)} = 2.37034$$
$$r^{(3)} = -0.29016$$
$$s^{(3)} = 0.02062.$$

No convergence feature is visible or expected from these coefficients. Numerical convergence is observable, though, on the actual function (41) or on the averages derived from it. Through the intermediary of $\langle w^3\rangle$ we find for the drift velocity

$$\langle w_z\rangle^{(0)} = 1.04605 \quad (42a)$$

$$\langle w_z\rangle^{(1)} = 1.14256 \quad (42b)$$

$$\langle w_z\rangle^{(2)} = 1.14616 \quad (42c)$$

$$\langle w_z\rangle^{(3)} = 1.14661 \quad (42d)$$

which gives a limiting value

$$\langle w_z\rangle = 1.1467. \quad (43)$$

For the total energy we find

$$\langle w^2\rangle^{(0)} = 2.1884 \quad (44a)$$

$$\langle w^2\rangle^{(1)} = 2.3395 \quad (44b)$$

$$\langle w^2\rangle^{(2)} = 2.3511 \quad (44c)$$

$$\langle w^2\rangle^{(3)} = 2.3531 \quad (44d)$$

giving

$$\langle w^2\rangle = 2.353. \quad (45)$$

No zero-order value exists for $\langle w_z^2\rangle$; the other orders give

$$\langle w_z^2\rangle^{(1)} = 1.8006 \quad (46a)$$

$$\langle w_z^2\rangle^{(2)} = 1.7696 \quad (46b)$$

$$\langle w_z^2\rangle^{(3)} = 1.7685 \quad (46c)$$

giving

$$\langle w_z^2\rangle = 1.768. \quad (47)$$

Interpretation of (43), (45), and (47) proceeds the same way as of (18), (19), and (20). From (43) and (45) we get

$$\langle w^2\rangle = 1.790\langle w_z\rangle^2. \quad (48)$$

According to (21) this factor is equal to 2 for all mean free time models. The energy partition equals

$$e_x : e_y : e_z = 1:1:6.04 \quad (49)$$

or

$$e_x : e_y : e_z^* = 1:1:1.54. \quad (50)$$

In the last formula, the change from the mean free time formula (26) is most strongly noticed.

E. THE PROBLEM OF INTERMEDIATE FIELDS; A CONVOLUTION THEOREM

It was pointed out in Sec. B that the solution of the general problem (6) of ionic motion contains two external parameters, the gas temperature and the electric field. Since that time, all efforts were dealing with the "high field" Eq. (8), in which the gas temperature is taken to be zero and the electric field often scales out, as in (37).

Whenever the mean free time condition of Sec. C is satisfied, the problem of intermediate fields is taken care of by the following convolution theorem:

Given the general Eq. (6) for constant mean free time,

$$a\tau\frac{\partial f(\mathbf{c})}{\partial c_z} + f(\mathbf{c}) = \int\!\!\int M(\mathbf{C}')f(\mathbf{c}')d\mathbf{\Pi}_c d\mathbf{C}, \quad (51)$$

and the "high field" equation derived from it,

$$a\tau\frac{\partial h(\mathbf{c})}{\partial c_z} + h(\mathbf{c}) = \int\!\!\int \delta(\mathbf{C}')h(\mathbf{c}')d\mathbf{\Pi}_c d\mathbf{C}, \quad (52)$$

and the maxwellian equation derived from (51) by dropping the field term

$$m(\mathbf{c}) = \int\!\!\int M(\mathbf{C}')m(\mathbf{c}')d\mathbf{\Pi}_c d\mathbf{C}, \quad (53)$$

then the solution $f(\mathbf{c})$ of (51) is the convolution of the solution $h(\mathbf{c})$ of (52) and the solution $m(\mathbf{c})$ of (53):

$$f(\mathbf{c}) = \int h(\mathbf{u})m(\mathbf{c}-\mathbf{u})d\mathbf{u}. \quad (54)$$

We carry through the proof by constructing explicitly the equation satisfied by the convolution. We replace the running variables $\mathbf{c}$, $\mathbf{c}'$, $\mathbf{C}$, $\mathbf{C}'$ in (52) by $\mathbf{u}$, $\mathbf{u}'$, $\mathbf{U}$, $\mathbf{U}'$ and multiply in $m(\mathbf{c}-\mathbf{u})$. We get

$$a\tau\frac{\partial h(\mathbf{u})}{\partial u_z}m(\mathbf{c}-\mathbf{u})+h(\mathbf{u})m(\mathbf{c}-\mathbf{u}) =\int\int\delta(\mathbf{u}')h(\mathbf{u}')m(\mathbf{c}-\mathbf{u})d\mathbf{\Pi}_u d\mathbf{U}.$$

We now *define* $f(\mathbf{c})$ by the relation (54), and integrate the above equation over $\mathbf{u}$. The second member on the left comes out to be $f(\mathbf{c})$. For the first member, we carry out an integration by parts:

$$\int\frac{\partial h(\mathbf{u})}{\partial u_z}m(\mathbf{c}-\mathbf{u})d\mathbf{u}=-\int h(\mathbf{u})\frac{\partial m(\mathbf{c}-\mathbf{u})}{\partial u_z}d\mathbf{u} =+\int h(\mathbf{u})\frac{\partial(m(\mathbf{c}-\mathbf{u}))}{\partial c_z}d\mathbf{u} =\frac{\partial}{\partial c_z}\int h(\mathbf{u})m(\mathbf{c}-\mathbf{u})d\mathbf{u}=\frac{\partial f(\mathbf{c})}{\partial c_z}.$$

For the right-hand member we observe that we have the eightfold integration

$$d\mathbf{\Pi}_u d\mathbf{U}d\mathbf{u}.$$

This is an integration over the collision angles and all final velocity components. By a general principle of kinetic theory[10] we can replace in this integration the final velocity components by the initial ones and write

$$d\mathbf{\Pi}_u d\mathbf{U}d\mathbf{u}=d\mathbf{\Pi}_u d\mathbf{U}'d\mathbf{u}'.$$

This puts us in a position to eliminate the δ-function by integration. We find

$$a\tau\frac{\partial f(\mathbf{c})}{\partial c_z}+f(\mathbf{c})=\int h(\mathbf{u}')m(\mathbf{c}-\mathbf{u})d\mathbf{\Pi}_u d\mathbf{u}' \tag{55}$$

with the side condition that $\mathbf{u}$, $\mathbf{U}$, $\mathbf{u}'$, $\mathbf{U}'$ form a quadruple of vectors in the sense discussed in Sec. A, for which in addition

$$\mathbf{U}'=0. \tag{56}$$

Equations (51) and (55) agree, provided we can prove the identity

$$\int m(\mathbf{c}-\mathbf{u})d\mathbf{\Pi}_u=\int\int M(\mathbf{C}')m(\mathbf{c}'-\mathbf{u}')d\mathbf{\Pi}_c d\mathbf{C}. \tag{57}$$

Equation (57) expresses an identity connecting elementary functions of known arguments. In this sense (57) itself can be considered an elementary relation. The actual proof of it is very complicated and will be given in BSTJ. Thus the theorem (54) may be considered proved.

With the help of the convolution theorem, all velocity averages known for the high field case by the method of Sec. C become now known for the intermediate and low field range as well. The calculation proceeds as follows. Suppose we wish to compute the velocity average,

$$\langle c_x^m c_y^n c_z^p\rangle=\int c_x^m c_y^n c_z^p f(\mathbf{c})d\mathbf{c}, \tag{58}$$

for m, n, p integer. We apply the convolution theorem (54) to $f(\mathbf{c})$, decompose the three factors into

$$c_x^m=[u_x+(c_x-u_x)]^m,\quad c_y=[u_y+(c_y-u_y)]^n,\quad c_z^p=[u_z+(c_z-u_z)]^p,$$

and expand each of them by the binomial theorem. We find

$$\langle c_x^m c_y^n c_z^p\rangle=\sum_{\mu=0}^{m}\sum_{\nu=0}^{n}\sum_{\pi=0}^{p}\binom{\mu}{m}\binom{\nu}{n}\binom{\pi}{p} \times\int h(\mathbf{u})u_x^{\mu}u_y^{\nu}u_z^{\pi}d\mathbf{u}\int m(\mathbf{v})v_x^{m-\mu}v_y^{n-\nu}v_z^{p-\pi}d\mathbf{v}. \tag{59}$$

The second integral is a thermal average, the first a high field average computable by the method of Sec. C. Thus the average (59) is a finite sum of products of computable averages and is itself computable.

From (18) and (59) we get for the drift velocity $\langle c_z\rangle$

$$\langle c_z\rangle=\frac{M+m}{M}\frac{a\tau}{\langle 1-\cos\chi\rangle}. \tag{60}$$

This means that Eq. (18) holds independently of the temperature as was stated then. For the total energy we get, from (19) and (59),

$$\langle mc^2\rangle=3kT+\frac{(M+m)^3}{M^2}\frac{(a\tau)^2}{\langle 1-\cos\chi\rangle^2} \tag{61}$$

and for its z component

$$\langle mc_z^2\rangle=kT +\frac{(M+m)^3\langle M\sin^2\chi+4m(1-\cos\chi)\rangle(a\tau)^2}{M^2\langle 1-\cos\chi\rangle^2\langle 3M\sin^2\chi+4m(1-\cos\chi)\rangle} \tag{62}$$

and the x component

$$\langle mc_x^2\rangle=kT +\frac{(M+m)^3\langle\sin^2\chi\rangle(a\tau)^2}{M^2\langle 1-\cos\chi\rangle^2\langle 3M\sin^2\chi+4m(1-\cos\chi)\rangle}. \tag{63}$$

Little has to be added for interpretation. In all energy formulas the thermal and the high field contributions add. The former has the gas value and obeys equi-

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[10] Reference 6, Sec. 3.52.

partition, the latter has the value it would have if the gas temperature were zero. Its properties were examined in Sec. C.

The foregoing development completely solves the problem of intermediate fields if the assumption of a constant mean free time can be made. There remains the question what to do in other cases, particularly for the model treated in Sec. D. It is true that, in principle, the general problem could be solved by the method developed there. For the gas temperature complicates only the central term in (14), while the method of solution was based on the structure (35) of the higher outside term which remains unaffected. However, the further course of the calculation in Sec. D makes the method less desirable. We would be able to produce a number for the drift velocity for a given numerical ratio of the electric field and the temperature, but we would not gain direct information about the functional relationship. This relationship would only reveal itself indirectly after extended numerical computations. It is to be hoped that a more satisfactory way of proceeding can be found.

In conclusion, I wish to thank Miss C. L. Froelich and the computation staff of the Bell Telephone Laboratories for carrying out the computation mentioned in Sec. D.

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Coherent Scattering Processes Arising from Quantum Correlations

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Quantum statistical forces in ideal symmetric and antisymmetric fluids establish an ordered arrangement of their fluid molecules in space. The coherent scattering properties of these fluids resulting from this spatial order are studied in this paper.

I. INTRODUCTION

IN an earlier paper[1] we studied the incoherent slow neutron scattering by ideal monatomic symmetric, or Bose-Einstein (B.E.), and antisymmetric, or Fermi-Dirac (F.D.), fluids. These were presumed to represent possible asymptotic models of liquid He^4 and He^3, respectively. We should like to complete here the theory of the scattering properties of these fluids by an investigation of their coherent scattering, especially for slow neutrons, resulting from the respective spatial correlations of their atoms. These spatial correlations are caused by the quantum statistical attractive and repulsive forces in the phase space of these systems of ideal dimensionless atoms.

In the wave kinematic approximation the coherent scattering of short wave electromagnetic radiation by atoms is similar to the coherent scattering of slow neutrons with comparable de Broglie wavelengths. The possible, though small, neutron-electron interaction of nonmagnetic origin together with their electromagnetic coupling will be neglected here. Then the linear momentum exchange, with vanishingly small energy exchange, between these fluids and the incident slow neutrons, which is the coherent scattering process, is determined primarily by the specific slow nuclear scattering amplitudes of the fluid atoms. These quantities are, in turn, the specific amplitude structure factors of the nuclei for slow neutrons. These are supposed to be known, at present, only empirically, in contrast to the atomic structure factors for radiation which can be evaluated with sufficient precision from first principles. The additional difference between the two types of radiative and neutron scattering processes consists in the diversity of the nuclear scattering amplitudes for different neutron-nucleus spin configurations. This difference vanishes for nuclei of zero spin angular momentum, for instance, as in the case of He^4.

Our problem is to investigate the statistical or correlation coherent scattering structure factors of ideal symmetric and antisymmetric fluids. The study of the physical characteristics will then bring out a series of remarkable analogies exhibited by B.E. fluids and normal fluids both near and away from their respective critical regions.

The structure factors will be defined in the next section, while their evaluation and discussion will be reserved for the subsequent sections.

II. THE COHERENT SCATTERING OF SLOW NEUTRONS BY IDEAL SYMMETRIC AND ANTISYMMETRIC FLUIDS (ASYMPTOTIC LIQUID He^4 AND He^3 MODELS)

The possible practical interest of these fluids may be associated with He^4 and He^3 atoms with zero or half-unit of spin angular momenta. This justifies the limitation of the study of the scattering to these two spin cases. One of the main differences in the correlation of symmetric and antisymmetric fluids arises from the

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[1] Goldstein, Sweeney, and Goldstein, Phys. Rev. **77**, 319 (1950).