Maxwell effect in inert gases

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The Maxwell effect (birefringence in a flow) in inert gases is calculated. The effect which arises is due entirely to an anisotropic polarizability of a pair of particles which interact in collisions. The calculation is based on a chain of kinetic equations.

1. INTRODUCTION

The Maxwell effect can be summarized by saying that birefringence arises in the motion of viscous liquids with anisotropic molecules because of an orientating effect of velocity gradients on the anisotropic particles. For liquids this effect was recognized and studied experimentally a long time ago.[1] It has recently become possible to study the effect experimentally in molecular gases whose particles have an anisotropic polarizability.[2–4] The effect in gases is three or four orders of magnitude weaker than that in liquids.

In this paper we calculate the collision-induced Maxwell effect in inert gases. Since an individual molecule in an inert gas does not intrinsically have a polarizability anisotropy, the effect which arises is due entirely to the anisotropic polarizability of a pair of particles interacting in collisions. The calculation is based on the use of a chain of kinetic equations which include one- and two-particle distribution functions. The results show that the collision-induced Maxwell effect in the inert gases Ar and Kr, at pressures on the order of a few tens of atmospheres, is comparable in magnitude to the Maxwell effect in the molecular gases CO_2 and N_2, which has been measured experimentally.[4] We study the dependence of this effect on the nature of the potential and on the characteristic particle scattering angle in the collisions.

We compare the Maxwell effect with depolarized Rayleigh scattering of light in inert gases, which can now be reliably detected experimentally.[5–7] Both of these effects are based on a collision-induced anisotropy of the polarizability of a pair of particles. The same kinetic method is used to study the spectral structure of depolarized Rayleigh scattering of light in inert gases.

2. DIELECTRIC CONSTANT OF A GAS IN WHICH THERE IS A VELOCITY GRADIENT

The dielectric constant of a gas, ε_{ij}, can be expressed in terms of the polarizability per unit volume of the medium, α_{ij}, averaged with the help of the distribution function f_N. Restricting the discussion to the two-particle interaction approximation, we can write this averaging as

$$\varepsilon_{ij}=\frac{4\pi}{V}\iint\Big\{\sum_{k=1}^{N}\alpha_{ij}(\Gamma_k)+\sum_{k<l;k,l=1\ldots N}\Delta\alpha_{ij}(\Gamma_k,\Gamma_l,\mathbf{r}_k-\mathbf{r}_l)\Big\}$$
$$\cdot f_N(\Gamma_1\ldots\Gamma_N,\mathbf{r}_1\ldots\mathbf{r}_N)\,d\mathbf{r}_1\ldots d\mathbf{r}_N\,d\Gamma_1\ldots d\Gamma_N. \qquad (1)$$

Here we have in mind a spatial average over a volume V which physically is very small but which contains a large number $N\gg 1$ of particles. The distribution function f_N is normalized by

$$\iint f_N(\Gamma_1\ldots\Gamma_N,\mathbf{r}_1\ldots\mathbf{r}_N)\,d\Gamma_1\ldots d\Gamma_N\,d\mathbf{r}_1\ldots d\mathbf{r}_N=1\,,$$

where Γ represents a set of parameters characterizing the internal degrees of freedom of the gas molecules. For a monatomic (or inert) gas the parameter Γ includes the three components of the particle's velocity $\mathbf{v}$; for a diatomic molecule, it includes, in addition to the velocity components, the three components of the angular momentum of the molecule $\mathbf{M}$. Here $\mathbf{r}_k$ and $\mathbf{r}_l$ are the spatial coordinates of molecule k and l, respectively; $\alpha_{ji}(\Gamma_k)$ is the polarizability of the kth particle considered separately; and $\Delta\alpha_{ij}(\Gamma_k,\Gamma_l,\mathbf{r}_k-\mathbf{r}_l)$ is the collision-induced polarizability of the pair of molecules k and l, respectively.

In general, the tensor ε_{ij} consists of a scalar part $\propto\delta_{ji}$ and a traceless symmetric part; the latter part is the cause of the Maxwell effect. In (1) and all the equations below, we are thus thinking of the symmetric component of the tensors ε_{ij} and α_{ji}, respectively.

In (1), we can carry out a partial integration over the variables Γ and $\mathbf{r}$ of $N-2$ particles. Making use of the symmetry of the function f_N with respect to the interchange of any pair of particles, we then find

$$\varepsilon_{ij}=4\pi\Big\{N\int\alpha_{ij}(\Gamma)f_1(\Gamma)\,d\Gamma+\frac{N^2}{2}\int\Delta\alpha_{ij}(\Gamma_1,\Gamma_2,\mathbf{r})$$
$$\cdot f_2(\Gamma_1,\Gamma_2,\mathbf{r})\,d\Gamma_1\,d\Gamma_2\,d\mathbf{r}\Big\}. \qquad (2)$$

The one-particle distribution function f_1 is assumed here to be spatially uniform, while the two-particle distribution function f_2 depends on only the difference between the coordinates of the interacting particles $\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$. As we will see below, this assumption is valid if the system is not too far from equilibrium.

Up to this point, the normalization of distribution functions f_1 and f_2 has involved a volume V, which we now assume is a unit volume for convenience in the calculations below. Under this assumption, everything in (2) remains the same, except that N must now be understood as the number of particles in a unit volume ($[N]=\text{cm}^{-3}$).

The first term in (2) describes the ordinary Maxwell effect for anisotropic molecules whose polarizability tensor has a symmetric component α_{ji}. This term vanishes in the case of an inert gas.

The second term in (2) describes the correction to the dielectric constant for the circumstances that the polarizabilities of two interacting particles are not additive. It is this term which describes the Maxwell effect in inert gases. We might add that this term is also responsible for the occurrence of depolarized scattering of light in inert gases, which has recently been the subject of very active research.

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3. KINETIC EQUATIONS FOR THE DISTRIBUTION FUNCTIONS OF A NONEQUILIBRIUM GAS

A kinetic equation for a one-particle distribution function f_1 for a steady nonequilibrium state of a gas with a constant velocity gradient[8–10] can be written in the form

$$mT^{-1}(v_iv_k-{}^1/_3\delta_{ik}v^2)V_{ik}=\hat{I}(\chi), \tag{3}$$

where

$$f_1=f_0(1+\chi),\quad \chi\ll1,\quad V_{ik}={}^1/_2\{\partial V_i/\partial x_k+\partial V_k/\partial x_i\},$$

where f_0 is an equilibrium Boltzmann distribution function, m is the mass of a molecule, T is the gas temperature, a repeated index means a summation, and $\mathbf{V}$ is the macroscopic velocity of the gas. It is assumed here that the deviation of f_1 from f_0 is small, so the Boltzmann collision integral $\hat{I}$ on the right side of Eq. (3) is written in linearized form.

A solution of integral equation (3) can be written formally as

$$\chi=mT^{-1}V_{ik}\hat{I}^{-1}(v_iv_k-{}^1/_3\delta_{ik}v^2). \tag{4}$$

The inverse operator $\hat{I}^{-1}$ is defined in such a way that when acting on the eigenfunctions of the Boltzmann operator $\hat{I}$ which have nonvanishing eigenvalues; it is the ordinary inverse operator, while when acting on the five hydrodynamic modes which have vanishing eigenvalues[10] it gives zero.

If ternary collisions are ignored, the equation for the two-particle distribution function f_2 is known[8] to reduce to $df_2/dt=0$, i.e., to the conservation of the function f_2 along the path traced out in phase space by the colliding particles.

Using the statistical independence of the two colliding particles before the collision, we find a general solution for the function f_2 (Ref. 8):

$$f_2(\Gamma_1,\Gamma_2,\mathbf{r})=f_1(\Gamma_{10})f_1(\Gamma_{20}). \tag{5}$$

Here Γ_{10} and Γ_{20} are the values of the velocity and angular momentum of the particles before the collision. The quantities Γ_{10} and Γ_{20} are functions of Γ_1, Γ_2, and $\mathbf{r}$. To first order in the deviation from equilibrium (i.e., in χ), the function f_2 is given by

$$f_2(\Gamma_1,\Gamma_2,\mathbf{r})=f_0(\Gamma_1)f_0(\Gamma_2)\exp[-U_{12}(\Gamma_1,\Gamma_2,\mathbf{r})/T]\{\chi(\Gamma_{10})+\chi(\Gamma_{20})\}, \tag{6}$$

where $U_{12}(\Gamma_1,\Gamma_2,\mathbf{r})$ is the potential energy of the interaction of the colliding particles.

4. MAXWELL EFFECT FOR ANISOTROPIC AND ISOTROPIC MOLECULES

For anisotropic molecules, the Maxwell effect is described by the first term in (2). We substitute into that expression the function f_1 from (3), (4) and the polarizability of a molecule, α_{ij}, in the form

$$\alpha_{ij}=-{}^1/_2(\alpha_\parallel-\alpha_\perp)\{M_iM_j/M^2-{}^1/_3\delta_{ij}\}, \tag{7}$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the polarizabilities along and perpendicular to the axis of the molecule. As a result, we find an expression for the dielectric constant:

$$\varepsilon_{ij}=-2\mu V_{ij}, \tag{8}$$

where

$$\mu=4\pi\frac{Nm}{T}\frac{\alpha_\parallel-\alpha_\perp}{2}\int\left\{\frac{M_iM_j}{M^2}-\frac{1}{3}\delta_{ij}\right\}\cdot f_0\hat{I}^{-1}\left\{v_iv_j-\frac{1}{3}v^2\delta_{ij}\right\}d\Gamma$$

is Maxwell's constant, which is expressed in seconds.

In the determination of the constant μ, the sign was chosen in such a way that the coefficient μ is always positive (the negative definiteness of the operator $\hat{I}^{-1}$ is taken into account). The expression found for Maxwell's constant μ is the same as that given in the literature (the coefficient β from Ref. 2). We will use it below to make a comparison with the new birefringence effect in inert gases. An order-of-magnitude estimate of the constant μ yields the following expression, as can be seen from (8):

$$\mu\sim\frac{\alpha_\parallel-\alpha_\perp}{\bar{v}\sigma_{vv}}\frac{\sigma_{Mv}}{\sigma_{MM}}=(\alpha_\parallel-\alpha_\perp)\frac{T}{\eta}\frac{\sigma_{Mv}}{\sigma_{MM}}, \tag{9}$$

where $\bar{v}=(T/m)^{1/2}$, η is the shear viscosity coefficient, and σ_{vv}, σ_{MM} and σ_{Mv} are the cross sections for collisions involving a change in velocity, for collisions involving a change in angular momentum, and for inelastic collisions which couple rotational and translational degrees of freedom.

In the case of an inert gas, the Maxwell effect is determined by the second term in (2), since the quantity $\alpha_\parallel-\alpha_\perp$ is zero. The induced anisotropic polarizability of a pair of interacting praticles can be expressed in terms of the distance between these particles, $\mathbf{r}$:

$$\Delta\alpha_{ij}(\mathbf{r})=\Delta\alpha(r)\{r_ir_j/r^2-{}^1/_3\delta_{ij}\}. \tag{10}$$

We recall that $\Delta\alpha(r)$ is the nonadditive part of the polarizability of a pair of particles separated by a small distance. Using the explicit expressions for f_1, f_2, and $\Delta\alpha_{ij}$ [expressions (4), (6), and (10), respectively], along with (2), we can write an expression for ε_{ij} in terms of V_{ij}:

$$\varepsilon_{ij}=2\pi N^2\int\Delta\alpha(r)\{r_ir_j/r^2-{}^1/_3\delta_{ij}\}f_0(v_1)f_0(v_2)\cdot\exp[-U_{12}(r)/T]\{\chi(\mathbf{v}_{10})+\chi(\mathbf{v}_{20})\}d\mathbf{v}_1d\mathbf{v}_2d\mathbf{r},$$

where

$$\chi(\mathbf{v}_0)=V_{ik}mT^{-1}\hat{I}^{-1}(v_{i0}v_{k0}-{}^1/_3\delta_{ik}v_0^2). \tag{11}$$

The operator $\hat{I}^{-1}$ in (11) acts on the variable v_0. Since this is a scalar operator, the result of its application to the tensor $v_{i0}v_{k0}-\frac{1}{3}\delta_{ik}v_0^2$ is the same tensor, with a constant factor $-\nu^{-1}(v_0)$ which depends on the modulus of v_0^2. This factor reflects the dependence of the rate of (gas-kinetic) collisions ν on the energy of the colliding particles. Below we assume that this dependence is weak in comparison with a Maxwell distribution.

We transform to the center-of-mass coordinate system of the colliding particles, and we separate the radial and angular parts in expressions (11):

$$\varepsilon_{ij}=-V_{ij}\frac{m}{T}\frac{N^2}{\nu}2\pi\int_0^\infty v^2\,dv\int_0^\infty r^2\,dr\,f_0(v)\Delta\alpha(r)\cdot\exp\left[-\frac{U_{12}(r)}{T}\right]\int dO_{\mathbf{v}}\int dO_{\mathbf{r}}\left\{\frac{r_ir_j}{r^2}-\frac{1}{3}\delta_{ij}\right\}\cdot\left\{v_{0i}v_{0j}-\frac{1}{3}\delta_{ij}v_0{}^2\right\}\frac{1}{2},$$

$$\int f_0(V_{\text{c.m.}})d\mathbf{V}_{\text{c.m.}}=1\,. \tag{12}$$

As usual, we have integrated over the center-of-mass variables, and we have noted that the reduced mass is $m/2$. Here $\mathbf{v} = \mathbf{v}_2 - \mathbf{v}_1$ is the relative velocity of the colliding particles, $f_0(v)$ is a Boltzmann distribution in relative velocities, and $\mathbf{V}_{\text{c.m.}}$ is the velocity of the center of mass of the colliding particles. In the integration of expression (12) over dO_r it is convenient to use a spherical coordinate system whose z axis is directed along the vector $\mathbf{v}$, while the direction of the vector $\mathbf{r}$ is specified by two angles: the polar angle ψ and the azimuthal angle φ. The direction of the vector $\mathbf{v}$ is specified with respect to a fixed coordinate system. In this coordinate system, we can carry out the integration over dO_{v} and $d\varphi$ completely, without resorting to any model regarding the potential U_{12}. The final expression is

$$\begin{aligned}\varepsilon_{ij} = &-V_{ij} m T^{-1} N^2 \nu^{-1} \cdot 2\pi \int_0^\infty v^2\, dv \int_0^\infty r^2\, dr\, 4\pi f_0(v) \\ &\cdot \Delta\alpha(r) \exp[-U_{12}(r)/T]\,[v^2 + 4U_{12}(r)/m] \\ &\cdot \int_0^\pi \sin\psi\, d\psi \{{}^1/_4 \sin^2\psi \sin^2\theta + {}^1/_5 \sin(\psi-\beta)\sin(\psi+\beta)\}.\end{aligned} \tag{13}$$

Here θ is the angle between the vectors $\mathbf{v}$ and $\mathbf{v}_0$, and β is that between $\mathbf{v}$ and $\mathbf{r}_0$ (ψ is the angle between $\mathbf{r}$ and $\mathbf{v}$). The angles θ and β are functions of ψ, r and v; they characterize the position of the vector $\mathbf{v}_0$ with respect to the vectors $\mathbf{v}$ and $\mathbf{r}$, respectively. It is not difficult to verify that the relation $\beta = \psi + \theta$ holds for a repulsion of the particles, and the relation $\beta = \psi - \theta$ holds for an attraction. Expression (13) is a microscopic expression for Maxwell's constant for isotropic molecules, μ_{is}. An obvious consequence of expression (13) is that there is no Maxwell effect for collisions which do not involve a change in velocity ($\theta = 0$, $\psi = \beta$), i.e., for rectilinear paths. It follows that the effect under discussion here is dominated by collisions with a large change in velocity, which occur at small distances r.

We estimate μ_{is} from (13):

$$\mu_{\text{is}} \sim \frac{\overline{\Delta\alpha}}{\bar{v}\sigma_{vv}} \bar{\theta} N d^3 \sim \overline{\Delta\alpha} \frac{T}{\eta} \bar{\theta} N d^3, \tag{14}$$

where d is the effective interaction radius of the particles, and $\bar{\theta} \sim U/T$ is the characteristic scattering angle of the particles in the collision. The ratio of Maxwell's constants for isotropic and anisotropic molecules is given by the simple expression

$$\frac{\mu_{\text{is}}}{\mu} \sim N d^3 \frac{\overline{\Delta\alpha}\bar{\theta}}{\alpha_\parallel - \alpha_\perp} \frac{\sigma_{MM}}{\sigma_{Mv}}. \tag{15}$$

We will be discussing expressions (14) and (15) below.

5. COLLISION-INDUCED SPECTRUM OF DEPOLARIZED RAYLEIGH SCATTERING OF LIGHT

The Maxwell effect in a gas of isotropic molecules is based on the appearance of the anisotropic polarizability of a pair of interacting molecules in the course of a collision. The same collision-induced polarizability underlies the appearance of a depolarized Rayleigh scattering in a gas of spherically symmetric molecules; the latter effect can now be reliably detected experimentally.[5-7,11-13]

We can write an expression for the correlation function of the dielectric constant of an inert gas with a collision-induced anisotropic polarizability $\Delta\alpha_{ij}(\mathbf{r})$ [see expression (10)]:

$$\begin{aligned}\langle \delta\varepsilon_{ij}(\mathbf{R}, t)\, \delta\varepsilon_{kl}(0,0) \rangle = &(2\pi N^2)^2 \int \Delta\alpha_{ij}(\mathbf{r})\, \Delta\alpha_{kl}(\mathbf{r}') \\ &\cdot \langle \delta f_2(t, \mathbf{R}, \mathbf{v}_1, \mathbf{v}_2, \mathbf{r})\, \delta f_2(0, 0, \mathbf{v}_1', \mathbf{v}_2', \mathbf{r}') \rangle d^4\mathbf{v}\, d\mathbf{r}\, d\mathbf{r}'.\end{aligned} \tag{16}$$

We recall that f_2 is a two-particle distribution function which, like f_1, has been normalized to unit volume; $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the coordinate of the center of mass of the system; and $\mathbf{r}$ is the distance between the colliding particles. The equation of motion of the correlation function $\langle \delta f_2(0) \delta f_2(t) \rangle$ like that for the function f_2, reduces to the conservation of this function along the path traced out by the system of two particles. The initial condition is

$$\begin{aligned}&\langle \delta f_2(0, \mathbf{R}, \mathbf{v}_1, \mathbf{v}_2, \mathbf{r})\, \delta f_2(0, 0, \mathbf{v}_1', \mathbf{v}_2', \mathbf{r}') \rangle \\ &= \frac{1}{N^2} \delta(\mathbf{R}) f_0(\mathbf{v}_1) f_0(\mathbf{v}_2) \exp\left[-\frac{U(r)}{T}\right] \{\delta(\mathbf{v}_1 - \mathbf{v}_1') \\ &\cdot \delta(\mathbf{v}_2 - \mathbf{v}_2')\, \delta(\mathbf{r} - \mathbf{r}') + \delta(\mathbf{v}_1 - \mathbf{v}_2')\, \delta(\mathbf{v}_2 - \mathbf{v}_1')\, \delta(\mathbf{r} + \mathbf{r}')\}.\end{aligned} \tag{17}$$

Using the equation of motion of the correlation function, using initial condition (17), and transforming to the center-of-mass system of the colliding particles, we find

$$\begin{aligned}\langle \delta\varepsilon_{ij}(\mathbf{R}, t)\, \delta\varepsilon_{kl}(0,0) \rangle = &(4\pi)^2 (N^2/2) \int \Delta\alpha_{ij}(\mathbf{r})\, \Delta\alpha_{kl}(\mathbf{r}_0) \\ &\cdot f_0(\mathbf{V}_{\text{c.m.}}) f_0(v)\, \delta(\mathbf{R} - \mathbf{V}_{\text{c.m.}} t) \exp[-U(r)/T]\, d\mathbf{V}_{\text{c.m.}}\, d\mathbf{v}\, d\mathbf{r}.\end{aligned} \tag{18}$$

Here $\mathbf{r}_0$ is the distance between the colliding particles at time $t = 0$, under the condition that this distance is $\mathbf{r}$ at time t. The distance $\mathbf{r}_0$ is thus a function of the quantities $\mathbf{r}$ and t: $\mathbf{r}_0 = \mathbf{r}_0(\mathbf{r}, t)$.

The Fourier component is space ($\mathbf{R}$) and time (t) of expression (18) for $i = k$, $j = l$ determines the spectrum of the depolarized scattering of light, $\Phi(\omega, q)$:

$$\begin{aligned}\Phi(\omega, q) \approx \Phi(\omega, 0) \propto (N^2/2)\, \text{Re} \int_0^\infty e^{i\omega t} \int \Delta\alpha_{ij}(\mathbf{r}) \\ \cdot \Delta\alpha_{ij}(\mathbf{r}_0) f_0(v) \exp[-U(r)/T]\, d\mathbf{v}\, d\mathbf{r}\, dt.\end{aligned} \tag{19}$$

Here we have taken account of the circumstance that the spatial size of the correlation function (18) is on the order of the interaction radius of the particles and much smaller than the wavelength of the scattered light, $\lambda = 2\pi/q$; i.e., we can set $\mathbf{q} = 0$. It can be seen from (19) that the spectrum of the scattered light is determined by the temporal correlation function of the polarizability induced during the collision, $\Delta\alpha_{ij}$. Since this correlation time is on the order of the particle collision time τ_{coll}, the width of the depolarized spectrum, $\Delta\omega$, is given by $\Delta\omega \sim 1/\tau_{\text{coll}}$ in order of magnitude.

The intensity of the depolarized scattering integrated over the spectrum can be found from (19), where we must set $t = 0$ and $\mathbf{r}_0 = \mathbf{r}$. The expression found in this way for the integrated intensity of the depolarized scattering, I_{dep}, is the same as the expression given in the literature.[11] We will use it below for some numerical estimates of $\overline{\Delta\alpha}$ for inert gases.

6. DISCUSSION

To make a comparison with experiments in inert gases, it is convenient to use the ratio of the intensity of the depolarized scattering, I_{dep}, to that of the polarized scattering, I_{pol}:

$$I_{\text{dep}}/I_{\text{pol}}\approx{}^1/_{30}(\overline{\Delta\alpha}/\alpha_0)^2Nd^3. \tag{20}$$

The quantity $\overline{\Delta\alpha}$ here is the polarizability averaged over the spatial interaction volume of the particles, and d^3 is the effective interaction volume. Using experimental results on depolarized Rayleigh scattering of light in inert gases,[11-13] we can calculate the following quantity from (20):

$$(\overline{\Delta\alpha}/\alpha_0)^2d^3\approx\begin{cases}2.5\cdot10^{-23}\ \text{cm}^3\ \text{for Kr}\\ 1.25\cdot10^{-23}\ \text{cm}^3\ \text{for Ar}\ .\end{cases}$$

The Maxwell effect in inert gases [see (13) and (14)] is proportional to the quantity $\overline{\Delta\alpha d^3\theta}$. The light-scattering effect which we are discussing here does not depend explicitly on the angle (θ) through which the particles are scattered in the collision; it occurs at angles $\theta\approx0$, i.e., for rectilinear particle paths. For a rectilinear path, the collision-induced Maxwell effect is zero. Furthermore, the component $\propto(\overline{\Delta\alpha})^2$ of the light scattering is thus insensitive to the sign of $\Delta\alpha(r)$; this sign changes as we go from a region of molecular repulsion into a region of attraction. In contrast, the Maxwell effect, $\propto\overline{\Delta\alpha}$ is sensitive to the sign of $\Delta\alpha(r)$.

Consequently, although the Maxwell effect and the appearance of a depolarized scattering isotropic gases are based on the same phenomenon—the appearance of a collision-induced anisotropic polarizability of the medium—the Maxwell effect is more sensitive to the nature of the interaction potential. It can be seen from (14) that the Maxwell effect increases in strength as the characteristic scattering angle $\overline{\theta}\sim U/T$ increases. An effort to observe the effect which we have been discussing here should thus be made in gases for which the depth of the van der Waals potential is comparable to T. In particular, for Ar, Kr, and Xe at room temperature we would have

$$(U/T)_{\text{Ar}}=0.5\quad(U/T)_{\text{Kr}}=0.7,\quad(U/T)_{\text{Xe}}\approx1.$$

To calculate Maxwell's constant μ_{is} in inert gases from (14), we need to know more than simply the quantity $(\overline{\Delta\alpha}/\alpha_0)^2d^3$, obtained from an experiment on depolarized scattering. We also need to know the effective particle interaction volume d^3. Assuming that the interaction radius is limited on one side to a value equal to twice the hard-sphere radius ($2r_{\text{Ar}}=4\cdot10^{-8}$ cm; Refs. 2–4) and on the other side by the radius at the minimum of van der Waals molecules, r_{vdW} ($r_{\text{vdW}}=12\cdot10^{-8}$ cm for Ar; Ref. 14), we find the range of d^3:

$$700\cdot10^{-23}\ \text{cm}^3>d_{\text{Ar}}{}^3>25\cdot10^{-23}\ \text{cm}^3. \tag{21}$$

This range imposes a corresponding range on μ_{is}. The results of the calculations of μ_{is} are summarized in Table I, which also shows experimental values[2-4] of μ for anisotropic molecules.

It can be seen from Table I that at pressures of the inert gases Ar and Kr on the order of 70–80 atm the collision-induced Maxwell effect in these gases is, even at the lower limit of the estimate, comparable to the Maxwell effect in the molecular gases CO_2 and N_2, which was found experimentally in Refs. 2–4. We recall that in an inert gas the Maxwell effect is proportional to the pressure, while in an ordinary molecular gas it is independent of the pressure.[2-4]

The gases listed in Table I have been selected in such a way that the polarizabilities of the pairs Ar, N_2 and Kr, CO_2 are approximately the same, to facilitate a comparison of μ and μ_{is}.

We conclude with some numerical estimates of the basic parameters of an experiment to observe birefringence in inert gases. As a starting point we adopt the experimental apparatus of van Houten and Beenakker,[2] which uses a cylindrical Couette cell with cylinders of radii $R_1=19.98$ mm and $R_2=25.55$ mm. The inner cylinder rotates at an angular velocity $\Omega=20\ \text{s}^{-1}$. An upper limit is imposed on the gas pressure by the condition that the flow must remain stable. For Couette flow, this condition reduces to the following restriction on the Reynolds number[15] $\text{Re}=h\Omega R_2/\nu$:

$$\text{Re}\leqslant\text{Re}_{\text{cr}}=41.3(R_2/h)^{1/2}, \tag{22}$$

where $h=R_2-R_1$, $\nu=\eta/\rho$ is the kinematic viscosity of the gas, and ρ is the density of the gas.

Under flow-stability condition (22), we have a limitation on the magnitude of the birefringence effect in an inert gas:

$$|\varepsilon_{ij}|=2|\mu_{\text{is}}V_{ij}|\sim\mu_{\text{is}}\Omega(R_2/h)\leqslant41.3\mu_{\text{is}}\nu(R_2/h)^{1/2}h^{-2}. \tag{23}$$

Substituting in the values of μ_{is} from Table I and the values of the parameters R_2, h, and Ω from Ref. 2, we find the estimate $|\varepsilon_{ij}|\leqslant2\cdot10^{-16}$. The equality here corresponds to the following maximum gas pressures: $P_{\text{Ar}}\approx0.5$ atm and $P_{\text{Kr}}\approx0.25$ atm. The value found for the magnitude of the birefringence, ε_{ij}, for inert gases is about two orders of magnitude smaller than the values of ε_{ij} which have been measured for anisotropic gases (Table I). In this particular apparatus, the pressure of the inert gas cannot be raised to the values (on the order of 70–80 atm) at which the magnitude of the effect would become comparable to that in anisotropic gases, because the stability condition (22) would be violated. As can be seen from (23), however, reducing the gap size h from 5 mm to 1 mm reduces ε_{ij} by a factor of about 60, i.e., brings it close to values which have been measured experimentally.[4] In order to observe the birefringence effect in in-

TABLE I. Values of μ for various gases ($\varepsilon_{ij}=-2\mu V_{ij}$).

Gas	α_0, 10^{-24} cm^3 [2]	$\alpha_\parallel-\alpha_\perp$, 10^{-24} cm^3 [2]	$\overline{\Delta\alpha}/\alpha_0$	d^3, 10^{-22} cm^3	$\bar{v}\sigma_{vv}$, 10^{-10} cm^3/s [2–4]	σ_{vv}/σ_{MM} [2–4]	μ, 10^{-16} s $P=1$ atm	 $P=10$ atm
Ar	1.64	–	0.22	2.5	1.8	–	0.03	0.3
	1.64	–	$4.2\cdot10^{-2}$	70	1.8	–	0.15	1.5
Kr	2.48	–	0.22	2.5	1.6	–	0.06	0.6
	2.48	–	$3.5\cdot10^{-2}$	210	1.6	–	0.5	5
CO_2	2.59	2	–	–	2.1	0.06	4.65	4.65
N_2	1.74	0.69	–	–	1.1	0.06	2.2	2.2

ert gases, it will thus be necessary either to raise the accuracy of the measurements of ε_{ij} by about two orders of magnitude under the conditions of van Houten and Beenakker's experiments[4] or to reduce the gap between the cylinders, h, by a factor of several units.

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