Connection between self-diffusion coefficient and rotational-diffusion coefficient in gases of moderate density

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A relation between the self-diffusion coefficient D and the rotational-diffusion coefficient D_R is derived and makes it possible to calculate D_R from the known value of D. The result agrees with experiment for gases of moderate density.

The coefficients of self-diffusion and rotational diffusion are important characteristics of the thermal motion of molecules. These coefficients must be known for the description of many processes, such as interaction of radiation with matter. The self-diffusion coefficient D is measured by the methods of spin echo[1] and tracer atoms (see, e.g., Ref. 2). These methods are direct and permit D to be determined for practically any substance. The determination of D_R, however, is subject to considerable complications. Measurement of D_R by the NMR relaxation method is possible only at a definite chemical composition of the molecules. Difficulties are frequently encountered with separation of the contributions of the different relaxation mechanisms.[1] A direct theoretical calculation of D_R is impossible since there are at present no reliable data on the anisotropic part of the interaction potential. We have derived a relation that permits D_R to be calculated from the known value of the self-diffusion coefficient.

Consider a gas consisting of compact quasispherical molecules that have no dipole moment. At sufficiently high temperature $kT/\varepsilon \gg 1$ (where ε is the energy parameter of the potential) the influence of the attracting forces on the dynamics of the system is small; the principal role is played by the repelling forces. Since the dependence of the repelling part of the potential on the interparticle distance is very strong, the system considered can be described within the framework of the hard-sphere model with a suitable value of the parameter. It is necessary here to take into account the exchange of both translational energy and rotational energy in the collisions. The Liouville operator for a system of hard spheres can be represented in the form

$$\hat{\mathscr{L}}=\hat{\mathscr{L}}_0+\sum_{j>i=1}^{N}\hat{T}_{ij},$$

where $\hat{\mathscr{L}}_0$ is the Liouvillian of the free motion and $\hat{T}_{ij}$ are the operators of the binary collisions. The operators $\hat{T}_{ij}$ are defined by the relation 3

$$\hat{T}_{ij}=S_{\eta+}^{0}a^2\int d^2\mathbf{e}\,\theta(-\mathbf{v}_{ij}\mathbf{e})\,|\mathbf{v}_{ij}\mathbf{e}|\,\delta(\mathbf{r}_{ij}-a\mathbf{e})\,(\hat{b}_{ij}^{\mathbf{e}}-1),\tag{1}$$

where

$$S_{\eta+}^{0}=\lim_{\eta\to+0}\exp\{\eta\mathbf{v}_{ij}\,\partial/\partial\mathbf{r}_{ij}\},$$

$\mathbf{v}_i$ and $\mathbf{v}_j$ are the velocities of the ith and jth particles, $\mathbf{v}_{ij}=\mathbf{v}_i-\mathbf{v}_j$, a is the hard sphere diameter, and $\theta(x)$ is the Heaviside function. The action of the operator $\hat{b}_{12}^{e}$ is determined by the relation

$$\hat{b}_{12}^{\mathbf{e}}\varphi(\mathbf{P}_1,\mathbf{P}_2,\ldots;\mathbf{J}_1,\mathbf{J}_2,\ldots;\mathbf{r}_1,\ldots,\mathbf{r}_N)$$
$$=\varphi(\mathbf{P}_1^*,\mathbf{P}_2^*,\ldots;\mathbf{J}_1^*,\mathbf{J}_2^*\ldots;\mathbf{r}_1,\ldots,\mathbf{r}_N),$$

where φ is an arbitrary function, $\mathbf{P}_1$, $\mathbf{P}_2$, $\mathbf{J}_1$, $\mathbf{J}_2$ are the values and the momenta and angular momenta of the particles prior to the collision, $\mathbf{P}_1^*$, $\mathbf{P}_2^*$, $\mathbf{J}_1^*$, $\mathbf{J}_2^*$, are the corresponding values after the collision; the vector joining the colliding-particle centers was $a\mathbf{e}$. We define the adjoint operator $\hat{T}_{ij}^{+}$ by the relation $\langle A\hat{T}_{ij}B\rangle=\langle B\hat{T}_{ij}^{+}A\rangle$. Using the properties of $\hat{T}_{ij}$ (Ref. 3) we can show that

$$\hat{T}_{ij}^{+}=a^2\int d^2\mathbf{e}\,\theta(\mathbf{v}_{ij}\mathbf{e})\,|\mathbf{v}_{ij}\mathbf{e}|\,[\delta(\mathbf{r}_{ij}-a\mathbf{e})\,\hat{b}_{ij}^{\mathbf{e}}-\delta(\mathbf{r}_{ij}+a\mathbf{e})\,]S_{\eta+}^{0}.\tag{2}$$

The coefficients D_R and D for spherical tops are connected with the Laplace transforms of the correlation functions of the momentum and of the angular momentum by the relations

$$D=\frac{1}{3m^2}\lim_{s\to0}\langle\mathbf{P}_1(0)[s-\hat{\mathscr{L}}]^{-1}\mathbf{P}_1(0)\rangle;$$
$$D_R=\frac{1}{3I^2}\lim_{s\to0}\langle\mathbf{J}_1(0)[s-\hat{\mathscr{L}}]^{-1}\mathbf{J}_1(0)\rangle,\tag{3}$$

where I is the moment of inertia of the particle, m is its mass, $[s-\hat{\mathscr{L}}]^{-1}$ is the resolvent of the system, and $\langle\ldots\rangle$ denotes the equilibrium mean value. In the approximation of uncorrelated successive collisions, the following relations are obtained for these quantities[4]:

$$D^{-1}=\frac{m(N-1)}{k_BT}\frac{\langle\mathbf{P}_1\hat{T}_{12}\mathbf{P}_1\rangle}{\langle\mathbf{P}^2\rangle},$$
$$D_R^{-1}=\frac{I(N-1)}{k_BT}\frac{\langle\mathbf{J}_1\hat{T}_{12}\mathbf{J}_1\rangle}{\langle\mathbf{J}^2\rangle}.\tag{4}$$

Let $\mathbf{L}_1$ be the total angular momentum of particle 1:

$$\mathbf{L}_1=[\mathbf{r}_1\times\mathbf{P}_1]+\mathbf{J}_1.\tag{5}$$

In a hard-sphere system, the momentum and angular momentum change at the instant of collision, so that the increments of the momentum and of the angular momentum are connected by the simple relation

$$\mathbf{L}_1^*-\mathbf{L}_1=[\mathbf{Q}\times(\mathbf{P}_1^*-\mathbf{P}_1)],\tag{6}$$

where $\mathbf{Q}$ is the radius vector of the point of contact of the two spheres, $\mathbf{Q}=\mathbf{r}_1-\frac{1}{2}\mathbf{r}_{12}$, and $\mathbf{r}_{12}$ is the radius vector joining the centers of the molecules at the instant of the collision. From (5) and (6) we get

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$$\mathbf{J}_1^* - \mathbf{J}_1 = -{}^1/_2 [\mathbf{r}_{12}, \times (\mathbf{P}_1^* - \mathbf{P}_1)]. \tag{7}$$

We note that Eqs. (6) and (7), which are exact for a hard-sphere system, are accurate enough for real systems in which the main increments of the momentum and angular momentum take place in a region small compared with molecule sizes. Using the definitions of the operators $\hat{b}\,^e_{12}$ and $\hat{T}_{12}$, it is easy to show that relation (7) leads to the following property of the binary-collision operator:

$$\hat{T}_{12}\mathbf{J}_1 = -{}^1/_2 [\mathbf{r}_{12}, \times \hat{T}_{12}\mathbf{P}_1]. \tag{8}$$

It is also easy to show that relation (8) holds also for the adjoint operator $\hat{T}^+_{12}$. By vector multiplication of (8) from the left by $\mathbf{P}_1$ we obtain, after scalar multiplication by $\mathbf{r}_{12}$ and averaging,

$$\begin{aligned}\langle \mathbf{r}_{12}[\mathbf{P}_1, \times \hat{T}_{12}\mathbf{J}_1]\rangle &= -{}^1/_2 \langle \mathbf{r}_{12}^2 \mathbf{P}_1, \hat{T}_{12}\mathbf{P}_1\rangle \\ &\quad + {}^1/_2 \langle (\mathbf{P}_1 \mathbf{r}_{12})(\mathbf{r}_{12}, \hat{T}_{12}\mathbf{P}_1)\rangle.\end{aligned} \tag{9}$$

Using the definition of $\hat{T}^+_{12}$ and Eq. (8) we can show that the left-hand side of (9) is equal to $2\langle \mathbf{J}_1 \hat{T}_{12} \mathbf{J}_1\rangle$. We transform the right hand side of (9) likewise with account taken of the properties of the operator $\hat{T}_{12}$. As a result we get

$$\begin{aligned}-2\langle (\mathbf{J}_1, \hat{T}_{12}\mathbf{J}_1)\rangle &= -{}^1/_2 a^2 \langle (\mathbf{P}_1, \hat{T}_{12}\mathbf{P}_1)\rangle \\ &\quad + {}^1/_2 \langle (\mathbf{P}_1 \mathbf{r}_{12})(\mathbf{r}_{12}, \hat{T}_{12}\mathbf{P}_1)\rangle.\end{aligned} \tag{10}$$

The product $(\mathbf{r}_{12} \cdot \hat{T}_{12}\mathbf{P}_1)$ is proportional to the longitudinal component of the momentum at the collision (to the component parallel to the vector $\mathbf{r}_{12}$). This quantity is not affected by participation of the rotational degrees of freedom in the collision. Therefore the value of $\langle (\mathbf{P}_1 \cdot \mathbf{r}_{12})(\mathbf{r}_{12} \cdot \hat{T}_{12}\mathbf{P}_1)\rangle$ is equal to the value of the same quantity for a system in which the rotational degrees of freedom do not participate in the collisions ("smooth" spheres). For this system $\hat{T}_{12}\mathbf{J}_1 = 0$ and

$$\langle (\mathbf{P}_1 \hat{T}_{12} \mathbf{P}_1)\rangle = 3k_B T D_E/(N-1),$$

where D_E is the Enskog value of the self-diffusion coefficient:

$$D_E = \frac{3}{8}\left(\frac{k_B T}{\pi m}\right)^{1/2} \frac{1}{n a^2 g(a)}. \tag{11}$$

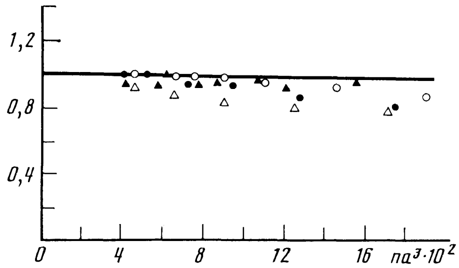

FIG. 1. Dependence of the values of $(D/D_E)^{-1} - (4/a^2)(D_R/D_E)^{-1}$ on the reduced density na^3 (○—CF_4, $a = 4.6$ Å; ●—CF_3Br, $a = 5.1$ Å; △—SF_6, $a = 5.2$ Å; ▲—CF_3Cl, $a = 4.8$ Å).

Here n is the particle-number density and $g(a)$ is the contact value of the pair-correlation function [4]. It follows then from (10) that $\langle (\mathbf{P}_1 \cdot \mathbf{r}_{12})(\mathbf{r}_{12} \cdot \hat{T}_{12}\mathbf{P}_1)\rangle$ can be expressed in terms of D_E. Using Eq. (4) and simple algebra, we obtain a simple relation between D_R and D:

$$D^{-1} - \frac{4}{a^2} D_R^{-1} = D_E^{-1}. \tag{12}$$

The diameter a of the hard sphere is obtained from the limiting value of Dn at zero density. This value was determined by extrapolating the experimental $Dn(n)$ plot. Figure 1 shows the dependence of $(D/D_E)^{-1} - (4/a^2)(D_R/D_E)^{-1}$ on the reduced density, obtained from experimental data for modrately dense gases ($na^3 < 0.2$).[5-8] According to (12) this quantity should be equal to unity. It follows from the figure that the relation established describes well the experimental results.

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