Drift velocity of C_{60}^+ in gases follows rarefied gas dynamics

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The drift velocities of C_{60}^+ in He, Ne, Ar, and Kr were found to be estimated with high accuracy using the drag coefficient of a solid body in free molecule flow. That is, massive C_{60}^+ behaves in gases as if it were a large classical body.

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Although C_{60} molecules are extremely massive, they still show a quantum-mechanical effect, i.e., de Broglie wave interference [1]. Herein, we report another extreme property of this fullerene: The fullerene moving in gases behaves as if it were a large classical body in free molecule flow [2]. Mobilities of fullerene ions C_n^+ ($n=30$–60) were measured for helium pressure at 2–5 Torr and drifting voltages between 2 and 10 V/cm [3]. In the case of C_{60}^+, the standard mobility K_0 is 4.3 $cm^2\,V^{-1}\,s^{-1}$. The drift velocity v_d is given by $v_d = N_0 K_0(E/N)$, where N_0 ($=2.687\times10^{19}$ cm^{-3}) is the number density at standard temperature and pressure, N is the number density of helium at an arbitrary state, and E is the electric field. The range of the measurement is $E/N = 1$–10 Td, where 1 Td $=10^{-17}$ V cm^2. The linear equation $v_d = N_0 K_0(E/N)$ holds at most up to $E/N=10$ Td.

First we used Monte Carlo simulation methods to calculate the drift velocities of C_{60}^+ for given values of E/N. (The helium density N was chosen to be equal to the density at a pressure of 1 Torr and a temperature of 300 K.) The helium atom and C_{60}^+ were assumed to be rigid spheres. The diameter d_{He} of the helium atom was set so as to be equal to the viscosity diameter, 2.193×10^{-8} cm [4]. The diameter of the skeleton of C_{60} is about 7.1×10^{-8} cm. The effective diameter d_{ion} of C_{60}^+ was chosen to be 1.47 times the diameter of the skeleton. The value 1.47 was determined in such a way that the calculated drift velocities agreed with the measured data [3] at small E/N.

In the Monte Carlo simulation, the motion of C_{60}^+ in a uniform electric field and the collision of C_{60}^+ with a helium atom were calculated separately for each time step Δt. Decoupling the motion and collision is allowed for such a small Δt that the collision probability of C_{60}^+ is much less than unity [5]. The calculation of the motion is elementary. The collision probability P_c of C_{60}^+ is given by [6]

$$P_c = N\pi d^2 \bar{g}\Delta t, \tag{1}$$

where d is $(d_{He}+d_{ion})/2$ and $\bar{g}$ is the relative speed between C_{60}^+ and the helium atom averaged over the velocity distribution of the helium atom. For the Maxwellian (equilibrium) velocity distribution, the speed $\bar{g}$ is given by

$$\bar{g} = v_{mp}\left[\left(S+\frac{1}{2S}\right)\mathrm{erf}\,S+\frac{1}{\sqrt{\pi}}e^{-S^2}\right], \tag{2}$$

where S is the speed ratio defined as $S=V/v_{mp}$, V is the speed of C_{60}^+, and v_{mp} ($=\sqrt{2kT/m_{He}}$) is the most probable speed of the helium atom at temperature T. Here k is the Boltzmann constant and m_{He} is the mass of the helium atom. For $T=300$ K, we have $v_{mp}=1120$ m/s. The helium gas is assumed to be in equilibrium. From the rarefied gas dynamics point of view, let us first examine the validity of this assumption for a typical state of helium gas at 1 Torr and a common temperature of 300 K for helium and C_{60}^+. The mean free path λ_{ion} of C_{60}^+ becomes 1.84×10^{-4} cm [7]. Since $d_{ion}=1.04\times10^{-7}$ cm, the Knudsen number λ_{ion}/d_{ion} becomes 1760 for a flow around C_{60}^+. This is much larger than unity; the background gas is almost undisturbed by C_{60}^+ and in equilibrium if it was initially in equilibrium.

Whether C_{60}^+ with velocity $\mathbf{V}$ collides or not in Δt with a helium atom is determined using the probability P_c. If it occurs, a collision partner (helium atom) of C_{60}^+ is necessary to determine the postcollisional velocity of C_{60}^+. In the

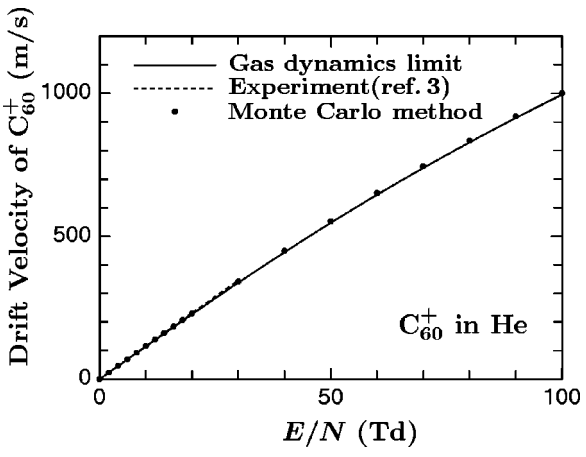

FIG. 1. Drift velocity of C_{60}^+ in He as a function of reduced electric field E/N. The dashed line represents the experimental data obtained for $E/N<10$ Td, the circles represent the result of the Monte Carlo calculation, and the solid line represents the gas dynamics limit.

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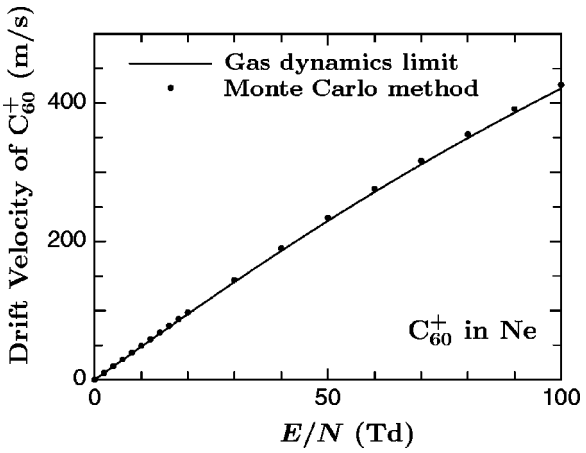

FIG. 2. Drift velocity of C_{60}^+ in Ne as a function of reduced electric field E/N.

Monte Carlo calculation of ion drift velocities, the velocity $\mathbf{v}$ of a helium atom is randomly sampled from the Maxwellian distribution; the Cartesian components of $\mathbf{v}$ are given by [5]

$$v_1 = A\cos\varphi,\ v_2 = A\sin\varphi,\ v_3 = A'\sin\varphi', \tag{3}$$

where $A = v_{\mathrm{mp}}(-\ln U)^{1/2}$, $A' = v_{\mathrm{mp}}(-\ln U)^{1/2}$, $\varphi = 2\pi U$, and $\varphi' = 2\pi U$. Here four U's are mutually independent random numbers uniformly distributed between 0 and 1. Hereafter, we use the same symbol U for all independent random numbers. The sampled velocity is accepted with the probability proportional to the relative speed $|\mathbf{v}-\mathbf{V}|$ between C_{60}^+ and the helium atom. If the velocity $\mathbf{v}$ is rejected, velocity sampling is continued until an acceptable velocity is found. The postcollisional velocity $\mathbf{V}'$ of C_{60}^+ is given by [7]

$$\mathbf{V}' = \mathbf{V} + \frac{m_{\mathrm{He}}}{m_{\mathrm{He}} + m_{\mathrm{ion}}}[(1-\cos\chi)\mathbf{g} + (\sin\chi)\mathbf{h}], \tag{4}$$

where m_{ion} is the mass of C_{60}^+, the Cartesian components of $\mathbf{h}$ are

$$h_1 = \sqrt{g_2^2 + g_3^2}\cos\varepsilon,$$

$$h_2 = -\frac{g_1 g_2\cos\varepsilon + g g_3 \sin\varepsilon}{\sqrt{g_2^2 + g_3^2}}, \tag{5}$$

$$h_3 = -\frac{g_1 g_3\cos\varepsilon - g g_2 \sin\varepsilon}{\sqrt{g_2^2 + g_3^2}},$$

$\mathbf{g}$ $(=\mathbf{v}-\mathbf{V})$ is the relative velocity before collision, χ is the deflection angle of the relative velocity, and ε is the azimuthal angle specifying a collision plane. Since C_{60}^+ and the helium atom are assumed to be rigid spheres, scattering is isotropic, i.e., $\cos\chi = 1-2U$. Since the collision plane has no preferred direction, we have $\varepsilon = 2\pi U$.

The number of simulated ions, N_i, was chosen to be 20 000. The drift velocity v_d is obtained from

$$v_d = \frac{d\langle z\rangle}{dt}, \tag{6}$$

where

$$\langle z\rangle = \frac{1}{N_i}\sum_{i=1}^{N_i} z_i. \tag{7}$$

Here, the electric field is in the z direction, z_i is the position of the ith ion, and $\langle z\rangle$ denotes the position of the center of mass of a system of ions. Initially, we set $z_i = 0$ for all ions and the velocities of ions are sampled from the Maxwellian distribution with temperature 300 K. After the initial transient, the drift velocity v_d becomes independent of time t. The drift velocities obtained using this Monte Carlo method are plotted in Fig. 1, in comparison with the experimental values (dashed line). The two agree well at small E/N, as they should. Note that the probability error of a single drift velocity obtained by the Monte Carlo method is negligibly small for the present calculation. That is, we obtained the values of v_d ten times using the independent sets of the initial velocities of ions, and we determined the probability error of a single datum of v_d. For example, the probability errors of the drift velocity of C_{60}^+ in argon gas (mentioned later) were $\pm 0.0014\,\%$ at 50 Td and $\pm 0.000\,67\,\%$ at 100 Td.

Next we used a rarefied gas dynamics method to calculate the drift velocity of C_{60}^+. Ion C_{60}^+ is extremely massive, so we cannot deny that it may be subject to rarefied gas dynamics. Now let us regard C_{60}^+ as a classical body flying with a constant velocity v_d in the direction of the electric field in helium gas. Since the Knudsen number of 1760 is very large, the flow around C_{60}^+ is in the free molecule regime. Different from the Monte Carlo simulation, the velocity of C_{60}^+ is assumed to show no fluctuation. The drift velocity v_d for this gas dynamics limit can be obtained from the balance between the accelerating force eE and the gas dynamic drag given by $C_D N m_{\mathrm{He}} v_d^2 \pi d^2/2$, where e is the elementary charge and C_D is the drag coefficient for the free molecule flow. The drag coefficient $C_D(S)$ is given by [2]

$$C_D(S) = \frac{e^{-S^2}}{\sqrt{\pi}S^3}(1+2S^2) + \frac{4S^4+4S^2-1}{2S^4}\mathrm{erf}\,S, \tag{8}$$

where $S = v_d/v_{\mathrm{mp}}$. [Since the elastic collision between the rigid spheres was assumed, C_D for specular reflection should be used. The factor $\exp(-S^2/2)$ in Eq. (8–6) of Ref. [2] should be corrected as $\exp(-S^2)$.] The force balance can be expressed as

$$\frac{E}{N} = \frac{\pi d^2 m_{\mathrm{He}}}{2e} v_d^2 C_D\left(\frac{v_d}{v_{\mathrm{mp}}}\right). \tag{9}$$

Although this relation between v_d and E/N is nonlinear, we can easily obtain E/N for a given v_d. The solid line in Fig. 1 shows Eq. (9). This gas dynamics limit shows a good agreement with the Monte Carlo data. The momentum of C_{60}^+ is much larger than that of a helium atom, so that individual collisions of C_{60}^+ with a helium atom have only a

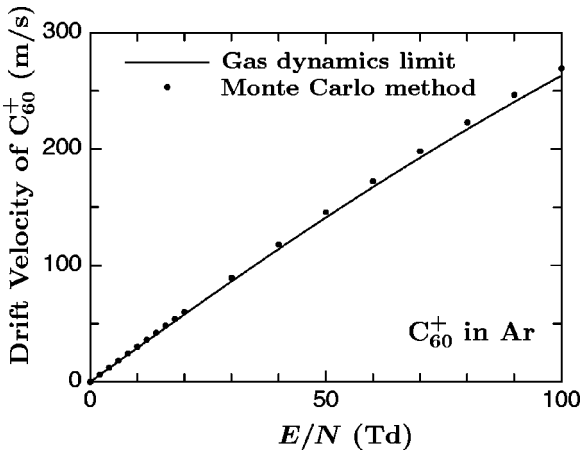

FIG. 3. Drift velocity of C_{60}^+ in Ar as a function of reduced electric field E/N.

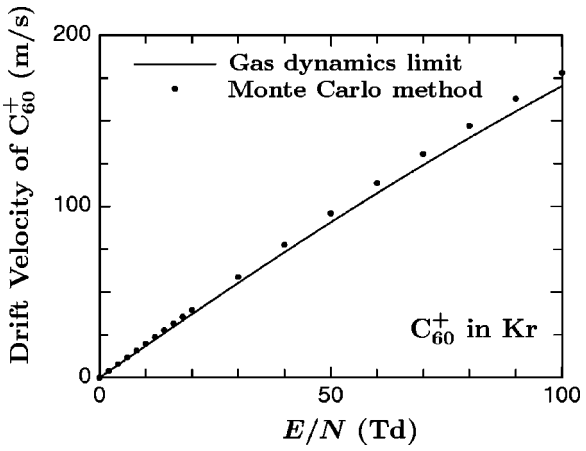

FIG. 4. Drift velocity of C_{60}^+ in Kr as a function of reduced electric field E/N.

small influence on the change in velocity of C_{60}^+, and hence the assumption that C_{60}^+ is flying with the constant velocity v_d may be valid.

To examine the applicability of Eq. (9), we calculated the drift velocities of C_{60}^+ in Ne, Ar, and Kr using the Monte Carlo method and we compared the results with Eq. (9). Equation (9) depends on d_{He} and m_{He}. These should be replaced by the corresponding values for Ne, Ar, and Kr. The viscosity diameters are 2.602×10^{-8} cm, 3.659×10^{-8} cm, and 4.199×10^{-8} cm for Ne, Ar, and Kr, respectively [4]. We see from Figs. 2–4 that as the atom becomes heavier, Eq. (9) shows a larger deviation from the Monte Carlo data. As the mass of the atom increases, the change in momentum of C_{60}^+ in collision increases, and hence the velocity component V_z of C_{60}^+ shows a larger fluctuation around the drift velocity v_d. That is, the approximation of the gas dynamics method that C_{60}^+ is flying with the constant velocity v_d begins to be inaccurate with increasing the mass of the atom. To go further, let us consider the case in which the drift velocity is equal for different gases, which is realized, say, at $E/N=16$ Td for He and $E/N=100$ Td for Kr. In this case, the standard deviations of the velocity V_z normalized by the drift velocity v_d are 0.32 for He and 0.41 for Kr. This is the reason why the data of the gas dynamics limit for heavy gases show a larger deviation from the Monte Carlo data. The magnitude of E/N also affects the fluctuations of the velocity V_z of C_{60}^+. In the case of Kr, the relative errors of the gas dynamics limit with respect to the Monte Carlo data were 6.2 % at 10 Td and 4.3 % at 100 Td. For larger E/N, the momentum of C_{60}^+ in the direction of the electric field is larger, and hence the velocity V_z shows a smaller fluctuation in collision, thus resulting in a smaller relative error in the data of the gas dynamics limit.

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