

O₂⁻ Ion Mobility in Compressed He and Ne Gas¹

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We report measurements of the drift mobility of O₂⁻ ions in dense He and Ne gas (in the temperature range 45 < T < 330 K spanning a range of gas densities from dilute gas up to liquid values. Measurements have been carried out by means of the pulsed photoinjection technique. Ions are produced by resonant electron attachment to O₂ impurities. In the low-density region the experimental results show a strong temperature dependence, in disagreement with the prediction of classical kinetic theory even though realistic interaction potentials are considered. On the other side of the density range, the ionic mobility in Ne seems to be explainable in terms of a hydrodynamic model including electrostriction effects.

KEY WORDS: electrostriction; hydrodynamic drag; kinetic theory; ion drift mobility.

1. INTRODUCTION

The motion of ions in gases or liquids under the influence of an electric field can give important information on the scattering processes between the charged particle and the atoms of the host medium and on its microscopic structure. In very low-density gases (at room temperature and at number densities less than $\approx 10^{17}$ cm⁻³) ion drift mobilities have been used to determine the scattering cross section for momentum transfer within the Boltzmann formalism of kinetic theory [1]. In liquids, ion motion has been explained in terms of hydrodynamics [2]. There is,

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however, a lack of information in the intermediate-density region, which is important to study the transition from the kinetic to the hydrodynamic regime. Moreover, understanding the ionic conduction can explain the prebreakdown and breakdown phenomena in dielectric fluids. We have therefore carried out drift mobility measurements of O_2^- ions in He and Ne gas in a wide temperature and density range.

2. EXPERIMENTS

We used the same pulsed photoinjection technique developed for drift mobility measurements of excess electrons in dense nonpolar gases. Details can be found in the literature [3], and a schematic drawing of the apparatus is shown in Fig. 1. O_2^- ions are produced by electron attachment to O_2 molecules present as impurities in the gas. An impurity content of some tens of parts per million is sufficient to produce ions in a detectable amount. In contrast to the usual way of producing positive ions in the parent gas by means of X-ray ionization [4], this ion production technique allows to use a negative ionic species as a common probe in different gases. The ions move under the influence of an electric field in the drift space between two electrodes. The drift time is determined by analyzing the induced current [5]. The experimental cell can withstand pressures up to 14 MPa and can be thermoregulated within 0.01 K in the range $25 < T < 330$ K. The drawback of this technique is that at low density the amount of ions produced by electron attachment may be insufficient to produce a detectable signal if the gas is too pure (impurity content below 50 ppm).

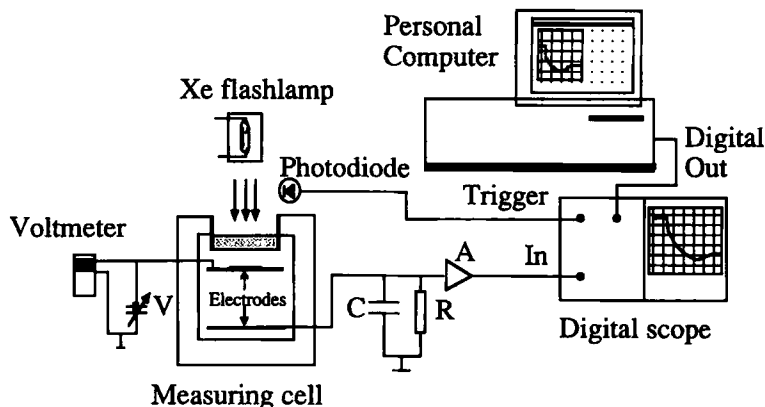


Fig. 1. Schematic diagram of the experimental apparatus.

3. RESULTS AND DISCUSSION

3.1. Low-Density Results

In Fig. 2, we show some typical results for the drift mobility μ of O₂⁻ in He [6] (open symbols) and Ne [7] (filled symbols) at room temperature for some gas densities N as a function of the reduced electric field E/N (1 mTd = 10⁻²⁰ V · cm²). The lowest density attained in our measurement $N \approx 2.9 \times 10^{19}$ cm⁻³ is very close to the ideal gas density at standard temperature and pressure, $N_i = 2.69 \times 10^{19}$ cm⁻³, and corresponds to an average interatomic distance $\bar{d} \approx 33$ Å. The ion mean free path ℓ can be estimated from the mobility using the Drude result $\ell = \sqrt{(3k_B T M)}(\mu/e)$, where M is the reduced mass, with the result that $\ell \approx 65$ Å for $T = 300$ K. These numbers have to be compared to the atom and ion radii, which are of the order of $r \approx 4$ Å, yielding a maximum mean free path to atomic dimension ratio $\ell/r \approx 16$.

It is known that the recommended value of ℓ/r for the applicability of kinetic theory is larger than the previously quoted value. However, this value $\ell/r \approx 16$ is not so small as to rule out kinetic theory definitely. Therefore, owing to these observations and as a consequence of the lack of a theory for this intermediate density range, we used kinetic theory as a starting point to interpret our experimental results.

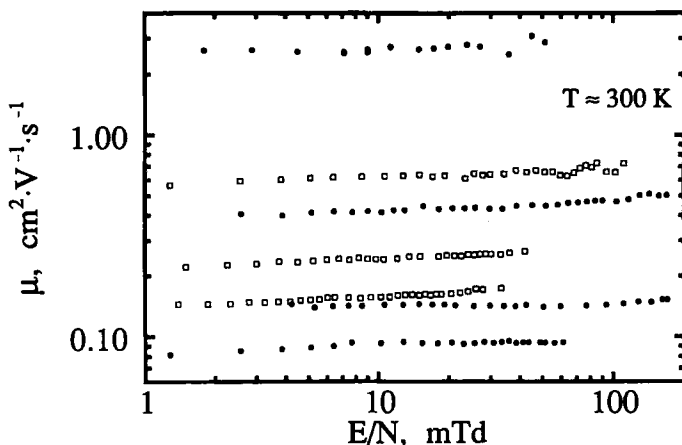


Fig. 2. Electric field dependence of the mobility of O₂⁻ ions in Neon gas (filled symbols) and in He gas (open symbols) for several densities at $T = 300$ K. The gas densities are, from the top; $(0.29, 2.01, 6.09, 10.1) \times 10^{20}$ cm⁻³ for Ne and $(2.23, 6.33, 10.24) \times 10^{20}$ cm⁻³ for He.

If a hard-sphere cross section is assumed $Q \approx 50 \text{ \AA}^2$ [6, 7], for our experimental E/N values the condition $eE/NQ \ll k_B T$ is fulfilled, i.e., ions are in thermal equilibrium with the atoms of the host gas. Therefore, μ should be field independent. By contrast the experimental data show a small, linear dependence on E .

To allow comparison between different data sets with the same T but different densities, the μ data are extrapolated to zero field. In Fig. 3 we show a typical result for the density-normalized mobility $\mu_0 N$ as a function of N at $T=96 \text{ K}$ for He (open symbols) and for Ne (filled symbols). For both gases and at all T , $\mu_0 N$ shows a positive linear dependence on N . This experimental behavior is in agreement with the only existing previous measurements in He at 77 K [9]. Once more, the results are in contrast with the kinetic theory, which predicts $\mu_0 N$ independent of N at constant T . Even the Enskog theory, which accounts for the finite molecule size and which should therefore be more appropriate for higher densities, is in disagreement with our results because it predicts a small decrease in $\mu_0 N$ with N [8].

For all measurements along isotherms, the density dependence of $\mu_0 N$ is strictly linear, even at the lowest densities reached. Since the density range investigated varies from isotherm to isotherm, we extrapolate the data for $N \rightarrow 0$, thus yielding $(\mu_0 N)_0$, to compare different isotherms data and, therefore, to study the temperature dependence of the mobility. In Fig. 4, we report the O_2^- zero-field zero-density mobility $(\mu_0 N)_0$ as a function of T for

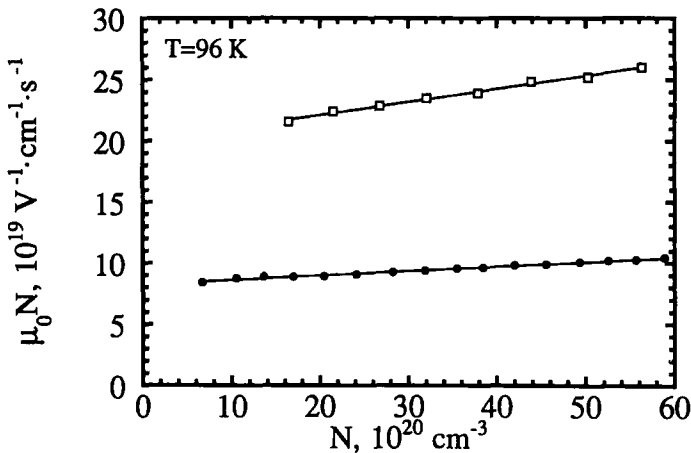


Fig. 3. Density dependence of the density-normalized zero-field mobility $\mu_0 N$ of Ne (filled symbols) and He (open symbols) at $T=96 \text{ K}$. The solid line has no theoretical meaning.

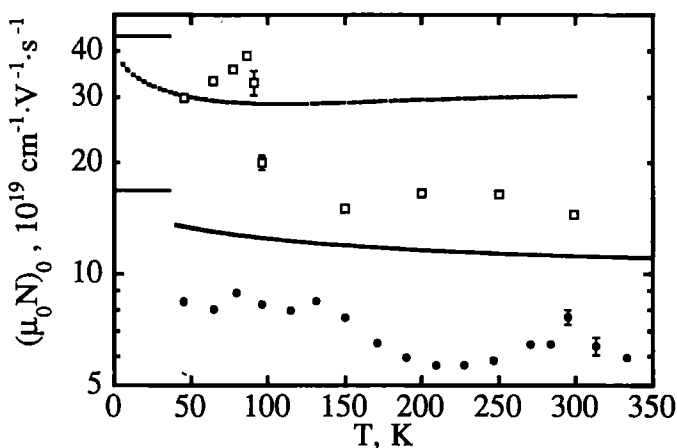


Fig. 4. Zero-field zero-density density-normalized mobility $(\mu_0 N)_0$ as a function of temperature for He (open symbols) and Ne (filled symbols). The lower and upper horizontal bars at the left are the polarization limit values for Ne and He, respectively. The dashed line and the solid line are the predictions of kinetic theory for a realistic atom-ion interaction potential for He and Ne, respectively.

He (open symbols) and Ne (filled symbols). In both gases the O₂⁻ mobility shows a very strong and complicated temperature dependence. $(\mu_0 N)_0$ lies well below the so-called polarization limit of kinetic theory [1], (shown in Fig. 4 as solid dashes), $(\mu_0 N)_P = 4.81 \times 10^{-4} / (\alpha M)^{1/2}$, where α is the atomic polarizability. The polarization limit is the low-temperature limit when scattering is determined only by the polarization potential due to the interaction of the ionic charge and the dipole moment induced by it on the atom. For He $(\mu_0 N)_P \approx 43.7 \times 10^{19} (\text{V} \cdot \text{cm} \cdot \text{s})^{-1}$ and for Ne $(\mu_0 N)_P \approx 16.9 \times 10^{19} (\text{V} \cdot \text{cm} \cdot \text{s})^{-1}$

Moreover, our results are in disagreement with the kinetic theory, even though more complete interaction potentials are considered. In fact, according to the theory [1] the zero-field mobility is given by

$$\mu_0 N = \frac{3e}{16} \left(\frac{2\pi}{Mk_B T} \right)^{1/2} \frac{1}{\bar{\Omega}^{(1,1)}(T)} \tag{1}$$

where $\bar{\Omega}^{(1,1)}(T)$ is the collisional integral given by

$$\bar{\Omega}^{(1,1)}(T) = \frac{1}{2(k_B T)^3} \int_0^\infty d\varepsilon \varepsilon^2 e^{-\varepsilon/(k_B T)} Q_D(\varepsilon) \tag{2}$$

Q_D is the momentum transfer scattering cross section, which can be calculated easily from the interaction potential. We have used a realistic model potential built according to semiempirical rules found in the literature [6, 7, 10]. It consists of an usual 12-6 Lennard-Jones potential and includes a r^{-4} contribution to account for the polarization induced by the ion,

$$V(r) = \frac{V_0}{2} \left[(1 + \gamma) \left(\frac{r_m}{r} \right)^{12} - 4\gamma \left(\frac{r_m}{r} \right)^6 - 3(1 - \gamma) \left(\frac{r_m}{r} \right)^4 \right] \quad (3)$$

The well depth V_0 and the coordinate of the minimum of the potential r_m for He and Ne are 31.7 and 168 meV and 3.53 and 2.80 Å, respectively. The parameter γ gives the relative weight of the r^{-6} and r^{-4} contributions. We used $\gamma = 0.8$, according to some suggestions given in the literature [10]. We have used here a spherically symmetric potential owing to several considerations. First, even though the O_2^- ion has an anisotropic polarizability ($|\alpha_{||} - \alpha_{\perp}|/\bar{\alpha} \approx 60\%$), the anisotropy in the interaction potential amounts to a maximum of only $\approx 10\%$ in correspondence of the potential well [6]. Moreover, our values of T and E/N are so small that only the long-range part of the potential is probed in the scattering process. On the other hand, T is high enough so that many rotational degrees of freedom of the ion are excited. This means that the ion is rotating between collisions, and therefore the use of a spherical average of the potential should be well suited. As a final remark, it is known that the use of isotropic potentials to describe the scattering of anisotropic molecules (and in one case, even polar) off a spherically symmetric ion is in disagreement by $\approx 10\%$ with the experimental results [11]. On one hand, however, we are in a more fortunate case because we are considering spherically symmetric atoms scattering off an anisotropic ion. On the other hand, we are searching for a large factor of 2 correction. Therefore, as a first approximation, we use spherical potentials.

In Fig. 4, the predictions of Eq. (1) are shown as a dashed line for He and as a solid line for Ne. Note the strong disagreement of the prediction of kinetic theory with the experimental data. Since ion mobility measurements carried out at densities at least 2 orders of magnitude smaller than those in this experiment agree with kinetic theory [1], we believe that even at the lowest densities investigated in this experiment, the conditions for the applicability of kinetic theory are not fulfilled, even though the mean free path of the ion is greater than the atomic or ionic diameter, is comparable to or larger than the mean interatomic distance, and the gas density is so low that higher-order collisions are very improbable.

3.2. High-Density, Low-Temperature Results in Ne

In Fig. 5, we report the zero-field density-normalized mobility $\mu_0 N$ of Ne at $T=45.0$ K (filled symbols) [12]. The critical temperature of Ne is $T_c=44.38$ K. At this temperature we have been able to reach densities much higher than critical, $N_c=144.4 \times 10^{20} \text{ cm}^{-3}$, therefore spanning a density range from fairly dilute gas to liquid, where hydrodynamics determines the ion motion. $\mu_0 N$ is nearly constant for $N < (120 - 130) \times 10^{20} \text{ cm}^{-3}$, increases approximately linearly with N up to $N \approx 200 \times 10^{20} \text{ cm}^{-3}$, and finally, saturates to a constant value for $N > 200 \times 10^{20} \text{ cm}^{-3}$. Such a behavior is rather complex, but it is very similar to that of cations Ar⁺, N₂⁺, and CH₄⁺ in their parent gases [4]. For hydrodynamics to be valid the mean free path of the gas atoms must be smaller than the ion size. This seems to be the case. In fact, for $N=240 \times 10^{20} \text{ cm}^{-3}$ the Ne mean free path ℓ_{Ne} equals approximately 1.7 Å with a Ne-Ne cross section $Q_{\text{Ne}}=24 \text{ Å}^2$ as deduced from viscosity data [13]. The hard-sphere O₂⁻-Ne interaction diameter can be estimated to be 3.2 Å. Moreover, molecular dynamics calculations [14] have shown that the strong attractive force exerted by the ion on the polarizable atoms leads to the formation of a tightly packed solvation shell around the ion. If this shell consists of one complete layer of Ne atoms clustered around the ion, the outer diameter of this cluster can be estimated to be 8.8 Å [7]. The hydrodynamic mobility is given by the Stokes formula for a sphere of radius R , $\mu = e/6\pi\eta R$, where η is the gas viscosity and the factor 6π follows

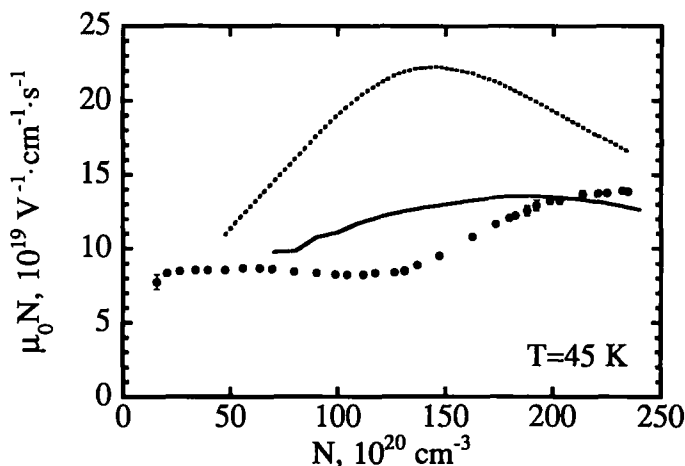


Fig. 5. Density-normalized mobility $\mu_0 N$ for Ne at $T=45.0$ K (filled symbols). Upper curve: Stokes formula for an ion radius $R \approx 4 \text{ Å}$. Lower curve: Stokes formula for $R \approx 4 \text{ Å}$ but corrected for electrostriction.

from the sticky boundary conditions [15]. Using $R \approx 4 \text{ \AA}$ and interpolating literature data for the Ne viscosity [16], we get the upper dashed curve in Fig. 5, which disagrees with experimental data up to a factor ≈ 3 . We believe that this disagreement may be attributed to the fact that the Stokes formula is deduced for a spatially uniform fluid. This is not true when there is such a strong interaction between the moving charged particle and the polarizable fluid atoms, especially close to the critical point where the gas compressibility is large. The effect of electrostriction is to enhance the local density and viscosity around the ion and the Navier–Stokes equations have to be solved accounting for this spatial dependence of N and η [17, 18]. The density profiles can be calculated by enforcing local thermodynamic equilibrium and inverting the resulting equation,

$$[K(N)]^2 \int_{N_\infty}^N \left(\frac{\partial P}{\partial N} \right) d \ln N = \frac{1}{2} \frac{\alpha e^2}{(4\pi\epsilon_0)^2 r^4} \quad (4)$$

where P is the gas pressure, K is the relative dielectric constant of the gas, and N_∞ is the density of the unperturbed gas. Some density profiles are shown in Fig. 6. For unperturbed gas densities lower than N_c there is a region where the profiles are very steep as a consequence of the large gas compressibility. Moreover, as $N_\infty < N_c$ the spatial extent of the perturbation produced by the ion grows larger. The viscosity profiles are obtained

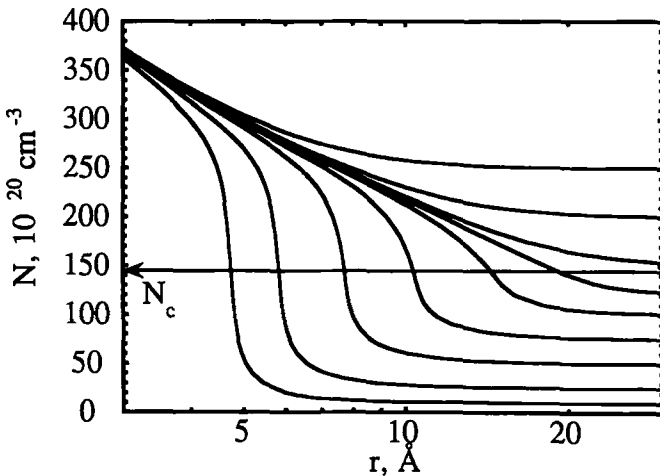


Fig. 6. Gas density profiles around the ion in presence of electrostriction. The unperturbed gas densities are, from the bottom, (10, 25, 50, 75, 100, 120, 150, 200, 250) $\times 10^{20} \text{ cm}^{-3}$.

by exploiting the experimentally observed dependence of η on N . The Stokes formula can be then cast in the following form [18],

$$\mu = \frac{e}{6\pi\eta_\infty FR} \quad (5)$$

where η_∞ is the viscosity of the unperturbed fluid and F is obtained by direct solution of the Navier–Stokes equations. The factor F depends on the ion radius. In Fig. 5 (solid line) we show the mobility calculated from Eq. 5, where the factor F has been computed by assuming the same ion radius $R = 4 \text{ \AA}$. By so doing we obtained a better agreement with the experiment. The residual disagreement could be attributed to the fact that such steep density profiles are not very realistic and might be in contrast with the assumption of local thermodynamic equilibrium. Moreover, we remind that the η values might be inaccurate by as much as 20–30%, because in literature there are no viscosity data for the temperature of our experiment that has been carried out very close to the critical temperature. Therefore, we used data for the closest temperature available, thus neglecting the critical enhancement of η .

4. CONCLUSIONS

We have carried out measurements of the drift mobility of O_2^- ions in He and Ne gas at moderate densities, in a region where there is lack of both experimental data and theoretical development. Our results show that in this density range the kinetic theory is not able to reproduce the experimental data, even though the ionic mean free path is still much larger than the atomic size.

On the other hand, in the high-density region the hydrodynamic theory can describe relatively well the gross features of the ionic drift mobility if it takes into account the effects of electrostriction.

Measurements in noble gases of higher polarizability should give a deeper clarification of the issue.

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REFERENCES

1. E. A. Mason and E. W. McDaniel, *Transport Properties of Ions in Gases* (Wiley, New York, 1988).
2. G. R. Freeman and D. A. Armstrong, in *Advances in Atomic and Molecular Physics*, Vol. 20, D. Bates and B. Bederson, eds. (Academic, New York, 1985), p. 267.

3. A. F. Borghesani, L. Bruschi, M. Santini, and G. Torzo, *Phys. Rev.* **A37**:4828 (1988).
4. N. Gee, S. S.-S. Huang, T. Wada, and G. R. Freeman, *J. Chem. Phys.* **77**:1411 (1982).
5. A. F. Borghesani and M. Santini, *Meas. Sci. Technol.* **1**:939 (1990).
6. F. Chiminello, Thesis (University of Padua, Padua, 1993), unpublished.
7. D. Neri, Thesis (University of Padua, Padua, (1991), unpublished.
8. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
9. A. K. Bartels, Ph.D. Thesis (University of Hamburg, Hamburg, 1971), unpublished.
10. G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces. Their Origin and Determination* (Oxford University Press, Oxford, 1981).
11. L. A. Viehland, *Chem. Phys. Lett* **144**:552 (1988).
12. A. F. Borghesani, D. Neri, and M. Santini, *Phys. Rev.* **E48**:1379 (1993).
13. G. H. Wannier, *Statistical Physics* (Dover, New York, 1966).
14. E. L. Pollock and B. J. Alder, *Phys. Rev. Lett.* **41**:903 (1978).
15. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena* (Wiley, New York, 1960).
16. V. A. Rabinovitch, V. I. Nedostup, A. A. Vasserman, and L. S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton, and Xenon* (Hemisphere, Washington, D.C., 1988).
17. K. R. Atkins, *Phys. Rev.* **116**:1339 (1959).
18. R. M. Ostermeier and K. W. Schwarz, *Phys. Rev.* **A5**:2510 (1972).