We report measurements of excess electron mobility in dense Argon gas at the two temperatures $T = 152.15$ and $162.30$ K, fairly close to the critical one ($T_c = 150.7$ K), as a function of the gas density $N$ up to $14$ atoms-nm$^{-3}$ ($N_c = 8.08$ atoms-nm$^{-3}$). For the first time a maximum of the zero-field density-normalized mobility $\mu_0 N$ has been observed at the same density where it was detected in liquid Argon under saturated vapor pressure conditions. The existence of the $\mu_0 N$ maximum in the liquid is commonly attributed to electrons scattering off long-wavelength collective modes of the fluid, while for the low-density gas a density-modified kinetic model is valid. The presence of the $\mu_0 N$ maximum also in the gas phase raises therefore the question whether the single scattering picture valid in the gas is valid even at liquid densities.

Key words: electron mobility, kinetic theory, dense gases, multiple scattering effects, disordered systems.
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1 Introduction

The study of the transport properties of excess electrons in dense nonpolar gases gives important pieces of information on the nature, dynamics, and energetics of the states of excess electrons in disordered systems.

In the neighborhood of the critical point of the liquid–vapor transition the density can be varied in a large interval with a reasonably small change of

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pressure and therefore it is relatively easy to investigate how the nature of the electronic states evolve starting from the dilute gas regime, where the kinetic theory is appropriate, towards the liquid regime.

The central quantity of interest is the electron mobility $\mu$. It is defined as the ratio of the mean velocity $v_D$, acquired by an electron drifting in the medium under the action of an externally applied and uniform electric field, and the strength of the field $E$: $\mu = v_D / E$. Its zero-field limit, $\mu_0 = \lim_{E \to 0} \mu$, is related to the fundamental properties of the $e-$atom interaction. In the low density regime, the kinetic theory relates $\mu_0$ to the electron–atom momentum transfer scattering cross section $\sigma_{mt}$ according to the following equation [1]

$$\mu_0 N = \frac{4e}{3(2\pi m)^{1/2} (k_B T)^{5/2}} \int_0^\infty \frac{\epsilon}{\sigma_{mt}(\epsilon)} e^{-\epsilon / k_B T} d\epsilon$$

where $N$ is the number density of the gas, $e$ and $m$ are the electron charge and mass, respectively. $T$ is the gas temperature and $\epsilon$ the electron energy. $\mu_0 N$ is the zero-field density-normalized mobility.

For a given electron–atom cross section, Eq. (1) predicts that $\mu_0 N$ depends only on the gas temperature and is independent of the gas density. In contrast with the prediction of the classical kinetic theory [1], the electron mobility shows a strong dependence on the density of the medium [2]. It is therefore important to study the effect of the environment on the electron–atom scattering mechanisms in a relatively dense phase.

Large deviations from the classical prediction, called anomalous density effects, have been observed even in the simplest systems represented by the noble gases [2]. In gases, such as He [3] and Ne [4,5], where the short–range repulsive exchange forces dominate the electron–atom interaction, there is a negative density effect, namely, $\mu_0 N$ decreases with increasing $N$ and eventually drops rapidly to very low values because of the formation of localized electron states at high enough densities and in the liquid [6,7].

The situation in Ar is different. Here, the $e-$atom scattering at low energies is essentially determined by the long–range attractive polarization interaction because the atomic polarizability of Ar is quite large. Owing to this feature, $\mu_0 N$ shows a positive density effect, i.e., it increases with increasing $N$ [8]. A further relevant feature of Ar and of the heavier noble gases is that in the liquid the electron mobility has a value comparable to that in the crystalline state [9]. It is commonly believed that this characteristics of the mobility is due to the existence, also in the liquid, of a conduction band. Therefore, it is interesting to investigate, as a function of the density of the medium, the transition from the classical single scattering situation in the dilute gas to the
multiple scattering scenario at higher densities and the eventual formation of extended (or localized) electron states in the liquid.

The explanation of the different density effects in the mobility is commonly based on the realization that the average interatomic distance at high densities becomes comparable to the electron de Broglie wavelength $\lambda$. In this situation, the conditions for single scattering break down and quantum effects become important. Moreover, also the mean free path $\ell$ becomes comparable to $\lambda$ and multiple scattering effects come into play, too [2].

Recent and accurate measurements of mobility in Ne [4,5] and Ar [10,11] have put into evidence that the different behavior of the mobility in different gases can be rationalized into a unified picture, where all the multiple scattering effects are taken into account in a heuristic way. A model (henceforth known as the BSL model) has been developed that incorporates all features of the several models proposed to interpret the different density effects and merges the several multiple scattering effects into the single scattering picture of kinetic theory [10].

Three main multiple scattering effects have been identified and all of them stem from the fact that the electron mean free path becomes comparable to its wavelength and that the latter may also become larger than the average interatomic distance if the density is large enough. The first effect is a density-dependent quantum shift $V_0(N)$ of the ground state energy of an excess electron immersed in the medium. According to the SJC model [12] $V_0(N)$, can be written as

$$V_0(N) = U_P(N) + E_k(N)$$

$U_P$ is a potential energy contribution arising from the screened polarization interaction of the electron with the surrounding atoms. $E_k(N)$ is a kinetic energy term, essentially due to excluded volume effects because the volume accessible to electrons shrinks as the density is increased. Owing to its nature, $E_k$ is positive and increases with increasing $N$. An expression for it is obtained by imposing on the electron ground-state wave function the conditions of average translational simmetry about the equivalent Wigner–Seitz (WS) cell centered about each atom of the gas. $V_0$ may be either $>0$ (this is the case of He [13] and Ne [14]) or $<0$ (as for Ar [15,16]), depending on the relative sizes of $U_P$ and $E_k$. However, the experimental mobility results indicate that only the kinetic energy term $E_k$ has to be added to the true electron kinetic energy when the scattering properties (namely, the cross sections) have to be calculated. Differently stated, the bottom of the electron energy distribution function is shifted by the amount $E_k$ [5].

The second multiple scattering effect is an enhancement of electron backscat-
tering due to quantum self-interference of the electron wave function scattered off atoms located along paths which are connected by time-reversal symmetry [17]. This phenomenon is closely related to the weak localization regime of the electronic conduction in disordered solids and to the Anderson localization transition [18]. It depends on the ratio of the electron wavelength to its mean free path \( \lambda/\ell = N\sigma_{mt}\lambda \). For Ar, at the density of the experiments, \( N\sigma_{mt}\lambda < 1 \). Therefore, a linearized treatment of this effect due to Atrazhev et al. can be adopted [19]. The net result is that the scattering cross section is enhanced by the factor \( 1 + N\sigma_{mt}\lambda/\pi \).

Finally, the third multiple scattering effect is due to correlations among scatterers. The electron wave packet encompasses a region containing several atoms, especially at low temperature and high density, and is scattered off all of them simultaneously. The total scattered wave packet is obtained by summing up coherently all partial scattering amplitudes contributed by each atom. The net result is that the cross section is weighted by the static structure factor of the fluid which is related to the gas isothermal compressibility [20].

In the density-modified kinetic model (BSL model) [10], the density-normalized mobility is calculated according to the classical kinetic theory equations [1] with the modifications necessary to take into account the mentioned multiple scattering effects

\[
\mu N = - \left( \frac{e}{3} \right) \left( \frac{2}{m} \right)^{1/2} \int_0^\infty \frac{\epsilon}{\sigma_{mt}^* (\epsilon + E_k)} \frac{dg}{d\epsilon} d\epsilon
\]

\( g(\epsilon) \) is the Davydov–Pidduck electron energy distribution function [21,22]

\[
g(\epsilon) = A \exp \left\{ - \int_0^\epsilon \left[ k_B T + \frac{M}{6mz} \left( \frac{eE}{N\sigma_{mt}} \right)^2 \right]^{-1} dz \right\}
\]

where \( M \) is the Ar atomic mass. \( g \) is normalized as \( \int_0^\infty z^{1/2} g(z) dz = 1 \).

The multiple scattering effects act by dressing the cross section so that the effective momentum-transfer scattering cross section is given by [10]

\[
\sigma_{mt}^* (w) = \mathcal{F}(w) \sigma_{mt} (w) \left[ 1 + \frac{2\hbar N \mathcal{F}(w) \sigma_{mt} (w)}{(2mw)^{1/2}} \right]
\]

\( w = \epsilon + E_k(N) \) is the electron energy shifted by the kinetic zero-point energy contribution \( E_k \). The group velocity of the wave packet is \( v = [2(w - E_k)/m]^{1/2} \) and it only contributes to the energy equipartition value arising from the gas
temperature [22]. The Lekner factor $\mathcal{F}$ [20] takes into account correlations among scatterers

$$\mathcal{F}(k) = \frac{1}{4k^4} \int_0^{2k} q^4 S(q) \, dq$$

(6)

with $k^2 = 2mc/h^2$. This is equivalent to the formulation given elsewhere [30]. An expression for the static structure factor in the Ornstein–Zernicke form in the near–critical region of Ar has been found in literature [23]

$$S(q) = \frac{S(0) + (qL)^2}{1 + (qL)^2}$$

(7)

where $S(0)$ is related to the gas isothermal compressibility $\chi_T$ by the relation $S(0) = Nk_B T \chi_T$ and the correlation length $L$ is defined as $L^2 = 0.1l^2 [S(0) - 1]$. $l \approx 10$ Å is the so-called short–range correlation length [23].

Experiments in Ne at $T \approx 45$ K [4,5] and in Ar at $T = 162.7$ K up to $N \approx 6.5$ atoms·nm$^{-3}$ [10] proved that the kinetic energy shift can be calculated according to the Wigner–Seitz model [24] as $E_k = E_{WS} \equiv \hbar^2 k_0^2 / 2m$, where the wavevector $k_0$ is obtained by self–consistently solving the eigenvalue equation

$$\tan [k_0 (r_s - \tilde{a}(k_0))] - k_0 r_s = 0$$

(8)

$r_s = (3/4\pi N)^{1/3}$ is the radius of the WS cell and $\tilde{a}$ is the hard–core radius of the Hartree–Fock potential for rare gas atoms. In the BSL model, according to a suggestion found in literature [12], $\tilde{a}$ is estimated from the total scattering cross section as $\tilde{a} = \sqrt{\sigma_T / 4\pi}$.

The BSL model has been successfully used to analyze the experimental data in Ar at $T = 152.5$ K up to $N \approx 10$ atoms·nm$^{-3}$ [11] by assuming that for the highest densities the WS model for the calculation of $E_k$ is inappropriate and $E_k$ must be deduced from the experiment.

It is natural to ask if the reason of the deviation of the experimentally determined $E_k$ values from the WS model is that the BSL model has been used beyond its limits of applicability, or if different mechanisms become active for momentum transfer processes at high $N$. It is known, in fact, that in liquid Ar the mobility of thermal electrons shows a maximum not very distant from the highest density investigated in previous experiments [11]. The mobility maximum occurs practically at the same density where $V_0(N)$ has a minimum [15]. The existence of this maximum, that indicates a situation of minimum scattering, has been interpreted within the deformation–potential theory [25,26].
Intrinsic density fluctuations of the fluid modulate the energy $V_0$ at the bottom of the conduction band. The spatial disuniformity of the ground–state energy of electrons is the source of scattering. This is an intrinsic multiple–scattering theory because electrons are scattered off long–wavelength collective modes of the fluid. These sorts of phononic models [25–27] do correctly predict the existence of the mobility maximum at the right value $N \approx 12.5$ atoms·nm$^{-3}$, but they fail to predict the density- and electric field dependence of the $\mu N$ data as the BSL model does.

Owing to these reasons, we have investigated an extended density range in Ar at $T = 152.15$ K up to a maximum density $N = 14$ atoms·nm$^{-3}$, well above the density of the mobility maximum in liquid, in order to see if the mobility maximum is a feature typical of the liquid only or if it appears also in the gas. In the latter case, there would be sound motivations to extend the density-modified kinetic approach even to the liquid [28–30].

2 Experimental Details

The electron mobility measurements have been carried out by using the well–known pulsed photoemission technique [5,31]. A swarm of electrons drifts in the gas under the action of an externally applied uniform electric field. The time $\tau_e$ spent by the particles crossing the drift distance $d$ is measured and the drift velocity is calculated as $v_D = d/\tau_e$. The mobility is simply obtained as $\mu = v_D/E$, where $E$ is the strength of the electric field. A simplified schematics of the experimental apparatus is shown in Fig. 1. A high–pressure cell is mounted on the cold head of a cryocooler inside a triple–shield thermostat. The cell can be operated in the range $25 < T < 330$ K and its temperature can be stabilized within $\pm 0.01$ K. The cell can withstand pressures up to 10 MPa and the pressure $P$ is measured with an accuracy of $\pm 1$ kPa. The gas density $N$ is calculated from $T$ and $P$ by means of an accurate equation of state [32].

A parallel–plate capacitor is contained in the cell and is powered by a D.C. high–voltage generator [33]. A gold–coated fused silica window is placed in the center of one of the plates and can be irradiated with a short pulse ($\approx 4 \mu s$) of VUV light produced by a Xe flashlamp. Thus, a bunch of electrons, whose number ranges between 4 and 400 fC depending on the gas pressure and on the applied electric field strength, is photoinjected into the drift space. During the drift motion of the charges towards the anode a current is induced in the external circuit. In order to improve the signal–to–noise ratio the current is integrated by a passive RC network. The resulting voltage signal is amplified and recorded by a digital oscilloscope. The drift time is obtained by analyzing the signal waveform with a personal computer. Typical signal waveforms are shown in Fig. 2. The estimated error on the mobility is less than 5%.

Fig. 2. Signal waveforms induced by electrons uniformly drifting in a gas. At left: pure gas, at right: gas containing a few p.p.m. of O\textsubscript{2} electron–attaching impurities.

The gas used is ultra–high purity Argon with a nominal O\textsubscript{2} content of 1 part per million. Further purification is accomplished by recirculating the gas in a closed loop through a LN2–cooled activated–charcoal trap and a commercial Oxisorb cartridge. The final O\textsubscript{2} amount is estimated to be a fraction of a part per billion.
We have carried out measurements at two different temperatures in the neighborhood of the critical temperature, namely, at $T = 162.30$ K and $T = 152.15$ K ($T_c = 150.7$ K). We have investigated the dependence of the density–normalized mobility $\mu N$ as a function of the density–reduced electric field strength $E/N$ and of the density $N$. The density range explored encompasses the critical density $N_c = 8.08$ atoms $\cdot$ nm$^{-3}$. In Fig. 3 we show sample $\mu N$ data at $T = 162.30$ K. These data agree well with previous measurements at $T = 162.7$ K [10]. The data for $T = 152.15$ K are qualitatively similar to those shown in Fig. 3.

The behavior of the reduced mobility $\mu N$ of excess electrons in Ar as a function of the reduced electric field is quite complicated, although it is now well understood for not too high densities ($N < 7.0$ atoms $\cdot$ nm$^{-3}$) [10]. At low field strength $\mu N$ is a constant independent of $E/N$. This constant value is the zero–field density–normalized mobility $\mu_0 N$ and pertains to thermal electrons. In fact, at such low fields, the energy gained by electrons from the field is negligible in comparison with their thermal energy. According to the prediction of the classical kinetic theory [1], $\mu_0 N$ should be constant and independent of $N$, while, experimentally, a completely different behavior of $\mu_0 N$ is observed, as it is easily realized by observing Fig. 3.
At small and medium \( N \), \( \mu N \) displays a maximum as a function of \( E/N \) in the range \( (2 \leq E/N \leq 4) \times 10^{-24} \text{ V m}^2 \), whose position depends on the density. Since the maximum is observed from the dilute gas up to the present densities, it is obvious that it has to be attributed to the Ramsauer–Townsend minimum of the \( e–\text{Ar} \) atomic momentum–transfer scattering cross section, which is located at an electron energy \( \epsilon_{RT} \approx 230 \text{ meV} \) \([35,36]\). When \( E/N \) has the value \( (E/N)_{\text{max}} \) corresponding to the mobility maximum, the average electron energy is equal to the energy of the Ramsauer minimum \( \langle \epsilon \rangle = \epsilon_{RT} \). For larger \( N \), the mobility maximum at \( (E/N)_{\text{max}} \) gradually disappears.

Finally, for even larger \( E/N \geq 4 \times 10^{-24} \text{ V m}^2 \), the \( \mu N \) curves for all densities merge into a single curve that is well described by the classical kinetic equations with the given cross section. For large \( E/N \), the behavior of \( \mu N \) becomes therefore independent of density and is easily explained in terms of the BSL model. At low \( E/N \), i.e., at small electron energies \( \epsilon \), the de Broglie wavelength of the electron, \( \lambda = h/\sqrt{2m\epsilon} \), is pretty large and the electron wave packet is so much extended as to encompass many atoms at once. In this situation, multiple scattering effects are very important. As the mean electron energy \( \langle \epsilon \rangle \) is increased by increasing \( E/N \), the extension of the electron wave function, as measured by \( \lambda \), decreases and the importance of multiple scattering is reduced. Therefore, the experimental points converge to the prediction of the classical kinetic theory. This behavior is present also in the liquid \([11]\) and has been observed also in Neon gas \([5]\), where the energy dependence of the cross section is completely different from that of Ar and where the temperature of the experiment (\( T \approx 45 \text{ K} \)) was much lower than in the present case.

As already observed for several temperatures \([10,11]\), the mobility maximum related to the Ramsauer minimum of the cross section shifts to lower \( E/N \) values as the density is increased, as shown in Fig. 4, where the reduced field of the mobility maximum, \( (E/N)_{\text{max}} \), is plotted as a function of \( N \) for \( T = 152.15 \text{ K} \). This behavior is also consistent with previous measurements in gaseous Ar at room temperature for densities up to 2 atoms \( \cdot \text{ nm}^{-3} \) \([34]\). On approaching the critical density, for \( N > 6.0 \text{ atoms} \cdot \text{ nm}^{-3} \), the decrease of \( (E/N)_{\text{max}} \) proceeds at a much faster rate than before, until, for \( N \approx N_c = 8.08 \text{ atoms} \cdot \text{ nm}^{-3} \), \( (E/N)_{\text{max}} \to 0 \) and the mobility maximum disappears, as can be seen in Fig. 3.

The observed behavior can be explained by noting that, for \( (E/N)_{\text{max}} \), the average electron energy equals that of the Ramsauer minimum of the cross section, \( \langle \epsilon \rangle = \epsilon_{RT} \). Generally speaking, it turns out that \( \langle \epsilon \rangle \) can be written in the form

\[
\langle \epsilon \rangle = \frac{3}{2} k_B T + E_k(N) + f(E/N)
\]  

(9)
where \( f(E/N) \) is a monotonically increasing function of the reduced electric field [22]. Since the density–dependent electron kinetic energy shift \( E_k(N) \) increases with increasing \( N \), \( (E/N)_{\text{max}} \) must decrease in order to fulfill the condition \( \langle \epsilon \rangle = \epsilon_{RT} \) with increasing \( N \) at constant temperature. [We will furthermore show that the change of slope of \( (E/N)_{\text{max}} \) as a function of \( N \) for \( N > 6.0 \text{ atoms} \cdot \text{nm}^{-3} \) is related to the change of slope of \( E_k(N) \) at the same density.] Eventually, for \( N > N_c \), the electron energy distribution function is so largely shifted by \( E_k \) as to sample the scattering cross section well beyond the Ramsauer–Townsend minimum. This is the reason of the disappearing of the mobility maximum.

A cornerstone for the understanding of the electron scattering in dense gases is represented by the analysis of behavior of the zero–field density–normalized mobility \( \mu_0N \) as a function of the density, because, as already pointed out, the classical kinetic theory predicts that \( \mu_0N \) is independent of \( N \), while the experiment gives a strongly density–dependent \( \mu_0N \) for every explored temperature. In Fig. 5 we therefore show the zero–field density–normalized mobility \( \mu_0N \) as a function of \( N \) for the two investigated temperatures \( T = 162.30 \text{ K} \) and \( T = 152.15 \text{ K} \). Previous data taken at \( T = 162.7 \text{ K} \) with a different apparatus [10] are reported in order to show the consistency of the present data. Moreover, also data obtained in liquid Ar [11] are shown for comparison, although it must be remembered that the measurements in the liquid are taken along the liquid-vapor coexistence line and are therefore not isothermal.

Two relevant features emerge from Fig. 5. The first one is the impres-
Fig. 5. $\mu_0 N$ as a function of $N$ for $T = 162.30$ (open squares), $T = 162.7$ (open circles) [10], and 152.15 K (closed circles). The closed squares are the results in liquid Ar [11]. The arrow indicates the value of the density $N_m$ of the $\mu_0 N$ maximum in gas. The lines are only guides for the eye.

A progressive increase of $\mu_0 N$ with increasing $N$ for both temperatures up to $N \approx 11.0 \text{ atoms} \cdot \text{nm}^{-3}$. This behavior is present also at room temperatures [8] and has been one the primary motivations for the development of multiple scattering theories. The BSL model explains quantitatively this feature of $\mu_0 N$ for $N \leq 10 \text{ atoms} \cdot \text{nm}^{-3}$. For $E/N \rightarrow 0$, electrons are in thermal equilibrium with the host gas and do not gain energy from the field. Therefore, their average energy is $\langle \epsilon \rangle \ll \epsilon_{RT}$. In this energy range, the momentum-transfer cross section decreases rapidly with increasing electron energy [35,36], as shown in Fig. 6. Roughly speaking, $\mu_0 N$ is a sort of weighted average of the inverse cross section.
section, as it can be realized by inspecting Eq. 1. To a first approximation, 
\( \langle 1/\sigma_{mt} \rangle \approx 1/\sigma_{mt} (\langle \epsilon \rangle) \). At constant \( T \), this average should be constant and 
should not depend on the density \( N \), unless \( \langle \epsilon \rangle \) depends on it. In particular, 
owing to the shape of \( \sigma_{mt}(\epsilon) \), \( \mu_0 N \) can increase with increasing \( N \) only if \( \langle \epsilon \rangle \) 
does the same. Therefore, the positive density effect of \( \mu_0 N \) supports the conclusion 
that the average electron kinetic energy includes a density–dependent 
contribution that is positive and increases with increasing \( N \), as expressed 
by Eq. 9. This conclusion immediately rationalizes the observations described 
by Christophorou et al. [34]. In fact, they note that the minimum of the in-
verse density–normalized mobility at zero–field, i.e. a quantity proportional 
to the cross section, shifts to lower energies as the density is increased. They 
calculate the average electron energy at zero field according to the Nernst–
Einstein–Townsend relation

\[ \langle \epsilon \rangle = \frac{3 D_L}{2 \mu_0} = \frac{3}{2} k_B T \]

where \( D_L \) is the longitudinal diffusion coefficient. By so doing, they neglect 
the density–dependent zero–point electron energy \( E_k(N) \), and therefore the 
Ramsauer–Townsend minimum seemingly appears at lower energies, as can be 
seen by inspecting Eq. 9 with \( E/N = 0 \), i.e. \( f(E/N) = 0 \), and by neglecting 
\( E_k \).

The second most relevant feature is the presence of a sharp maximum of 
\( \mu_0 N \) for \( N \equiv N_m \approx 12.5 \text{ atoms} \cdot \text{nm}^{-3} \) at \( T = 152.15 \text{ K} \). [Probably, such max-
imum would exist also at the higher temperature, but the limited pressure 
range of the experimental cell (\( P \leq 10.0 \text{ MPa} \)) did not allow the investiga-
tion of larger densities at higher temperatures.] The \( \mu_0 N \) maximum occurs 
at nearly the same density where it was observed in liquid Ar [11], as also 
shown in Fig. 5. A similar behavior has been previously observed in liquid 
and gaseous CH\(_4\) [37].

It is well–known [25,27] that the maximum of \( \mu_0 N \) in liquid has been 
attributed to scattering of electrons off long-wavelength collective modes of 
the fluid. The intrinsic density fluctuations of the liquid modulate the elec-
tron energy at the bottom of the conduction band of the liquid, \( V_0(N) \), and 
the spatial fluctuations of \( V_0(N) \) act as the potential for the scattering, just 
as lattice deformation–potentials from acoustic phonons scatter carriers in 
semiconductors. Within the deformation potential theory, the potential for 
scattering is linear in the density deviations about the average value. Since it 
happens that \( V_0(N) \) has a minimum at nearly the same density, \( N_m \), where 
\( \mu_0 N \) is maximum [15], the scattering potential vanishes to first order at \( N_m \). 
Therefore, at this density the scattering of electrons is very much reduced and 
the electron mobility turns out to be maximal. For any other \( N \neq N_m \), the 
slope of \( V_0(N) \) as a function of \( N \) is nonzero and deformation potential is large
enough to efficiently scatter electrons, thus reducing their mobility.

However, a gas does not support phonons as a liquid does. Therefore, the presence of the $\mu_0N$ maximum in dense Ar gas at the same density $N_m$ as in the liquid raises the question if, beyond a given density threshold, there is a change in the physical mechanisms which determine the mobility in the gas, or, rather, if the single scattering picture of the density–modified kinetic theory can be extended to the liquid.

On one hand, one could argue that, at low and medium densities, the single scatterer approximation is valid and electrons can be described as scattering off individual atoms, though the scattering properties have to be density–modified in order to account for multiple scattering effects. On increasing the density, a conduction band might develop and electrons might be scattered off long–wavelength collective modes of the dense gas, though they might not be true phonons.

On the other hand, there are several reasons to extend the single scattering picture to the liquid. First of all, the phononic theories are developed for thermal electrons only, i.e., they make predictions only on $\mu_0N$ and completely disregard the electric field dependence of the experimental $\mu N$ data. This dependence is very important because it is intimately related to the shape of the atomic cross section. There have indeed been more or less successful attempts to use the classical kinetic theory even in the liquid [28–30], though the cross section has been taken as an adjustable parameter. Moreover, the phononic models do not even predict accurately $\mu_0N$, unless higher–order scattering processes are taken into account [26,27].

It is therefore challenging to investigate the possibility that the density–modified kinetic model can account for the $\mu_0N$ maximum and that a single–scattering picture can be retained even in the liquid, owing to its conceptual simplicity. The BSL model has been thus used for the analysis of the experimental data at high density.

First of all, we do not make any assumptions on the value of the kinetic energy shift $E_k(N)$. We treat it as an adjustable parameter to be determined by fitting the equations of the model Eqns. 3–5 in the limit $E/N \to 0$ to the experimental data. Literature data for the cross section have been used [35]. Once $E_k(N)$ has been determined by this fitting procedure, the average electron energy (Eq. 9) could be evaluated, if necessary, as

$$\langle \epsilon \rangle = E_k(N) + \int_0^\infty z^{3/2}g(z)dz$$

where $g$ is given by Eq. 4, and Eq. 9 is recovered. In Fig. 7 the resulting $E_k$
Fig. 7. Values of $E_k$ plotted as a function of $N$ for $T = 162.30$ K (open circles) and $T = 152.15$ K (closed circles). Previous values determined from data at $T = 162.7$ K [10] are shown (open squares). The solid line is the prediction of the WS model. The arrow indicates the density where $(E/N)_{\text{max}}$ changes slope.

values are shown as a function of $N$ for the two investigated temperatures. Previous determinations of $E_k$ for $T = 162.7$ K [10] are also shown for comparison to assess the consistency of these new sets of measurements with previous ones.

The data at $T = 162.30$ K agree very well with the data taken at $T = 162.7$ K. There are small differences between the results for $T = 152.15$ K and $T = 162.30$ K, which might be attributed to the larger gas compressibility for the temperature close to $T_c$ and to the uncertainty with which the short-range correlation length $l$ is known [23]. Nonetheless, the experimentally determined $E_k$ values agree pretty well with the prediction of the WS model (shown as a solid line in Fig. 7) for densities up to $\approx 7.0$ atoms · nm$^{-3}$. For larger $N$, starting at practically the same density where $(E/N)_{\text{max}}$ changes slope (see Fig. 4), up to $N \approx 10$ atoms · nm$^{-3}$, the values of $E_k$ that reproduce the experimental values of $\mu_0 N$ increase faster with $N$ than the prediction of the WS model. This is not a failure of the BSL model. It is just related to the fact that the WS model is only valid when $r_s \gg \tilde{a}$. Unfortunately, up to now there are no theoretical calculations of $E_k$ with which the present results can be compared.

In the density range of the present experiment, the BSL model does not reproduce only $\mu_0 N$ with the proper choice of $E_k(N)$. It also shows a high de-
degree of internal consistency because the value of \( E_k \) determined from the data at low field allows to reproduce quite accurately the full \( E/N \)-dependence of \( \mu N \). This result is shown in Fig. 8, where the curves for several densities

\[
\mu N (10^{26} \text{m}^{-1} \text{V}^{-1} \text{s}^{-1})
\]

\[
E/N (10^{-24} \text{V m}^2)
\]

Fig. 8. Comparison of the results of the BSL model with the experimental \( \mu N(E/N) \) data for some densities (dotted lines). The densities are (from top): \( N = 13.33, 9.935, 5.144, 0.502 \) atoms \( \cdot \) nm\(^{-3} \). The solid lines are obtained by using the effective cross section \( \sigma_{\text{eff}} \), as described in the text.

are compared with the prediction of the BSL model (dotted lines). The dotted curves are obtained by using the \( E_k(N) \) values determined by fitting the model to the zero-field data. It can be realized that, at small and medium \( N \), the features of the mobility are all reproduced well. Namely, the position and strength of the mobility maximum as well as its behavior as a function of the density are described accurately. The behavior at small- and high-fields of \( \mu N \) is correctly reproduced, with the curves for different densities merging into a single one at large \( E/N \). All these observations are consistent with the hypothesis that the kinetic-energy shift \( E_k(N) \) increases with increasing \( N \), and that it can grow so large as to shift the average electron energy beyond \( \epsilon_{RT} \).

However, it is also evident that, for even larger \( N (\geq 10 \) atoms \( \cdot \) nm\(^{-3} \)), the BSL model as such does neither reproduce the \( \mu_0 N \) maximum for \( N = N_m \), nor the decrease of \( \mu_0 N \) with increasing \( N \) for \( N > N_m \). On one hand, it is clear, of course, that the overall behavior of \( \mu_0 N \) as a function of \( N \) must be related to the shape of the atomic cross section and to the density-dependent quantum shift of the electron energy distribution function. Unfortunately, the scattering cross sections are known with limited accuracy as far as strength
and position of the Ramsauer minimum are concerned. Different choices of \( \sigma_{mt} \) give different strength and position of the \( \mu_0 N \) maximum [11] or they may not even give a maximum at all.

On the other hand, the use of an effective density–modified scattering cross section \( \sigma^*_mt \) has proven so powerful giving a nice agreement between model and data up to fairly large densities that it is interesting to extend this paradigm to higher densities. According to a suggestion proposed in literature [11,28], at high \( N \) a good agreement between data and model can be obtained by scaling \( \sigma^*_mt \) by a factor \( c_0(N) \). The adjustable parameter \( c_0 \) depends only on \( N \), but it is independent of \( E/N \) and of the electron energy. Therefore, it has no influence on the dependence of \( \mu N \) on \( E/N \) at constant density. While \( c_0 \) is introduced as an adjustable parameter, the energy shift \( E_k \) is no longer determined from the experimental data. Instead of \( E_k \) it is rather used the value \( E_{WS} \) given by the WS model and calculated according to Eq. 8 (solid line in Fig. 7). \( \sigma^*_mt \) is everywhere replaced by \( \sigma_{eff} = c_0(N) \sigma^*_mt \) and \( c_0 \) is so adjusted as to reproduce the behavior of \( \mu_0 N \) as a function of \( N \). \( c_0 \) turns out to be of order unity \( c_0 \approx O(1) \). With this choice the electric field dependence of \( \mu N \) is reproduced even at the highest densities. The shape of the effective cross section at thermal energies \( \sigma_{eff} = c_0(N)\sigma^*_mt [ (3/2)k_BT + E_{WS}(N) ] \) is shown in Fig. 9. The energy scale on the upper horizontal axis has been obtained by converting density to energy by means of the WS model Eq. 8. By comparing Fig. 9 to Fig. 6 there is undoubtely a strong similarity between \( \sigma_{eff} \) and the atomic cross section \( \sigma_{mt} \). In particular, it is interesting the presence of a Ramsauer–type minimum also in the effective cross section. Moreover, the strength of \( \sigma_{eff} \) is very close to its atomic companion, though the position

![Fig. 9. Effective scattering cross section \( \sigma_{eff} = c_0(N)\sigma^*_mt \) as a function of \( N \) (lower scale) and energy (upper scale). The upper scale has been obtained by converting density to energy by means of the WS model.](image-url)
of the minimum occurs at a somewhat lower energy and the minimum itself appears to be narrower. This feature might be due to the use of the WS model for the $N \rightarrow \epsilon$ conversion. If the experimentally determined values of $E_k(N)$ had been used instead of the WS model, the $\sigma_{ef}$ minimum would be broader and shifted to larger energies because $E_k(N) > E_{WS}$ for $N \geq 7 \text{ atoms} \cdot \text{nm}^{-3}$.

This effective cross section can be compared with the effective one $\langle \sigma_L \rangle$ obtained in liquid Ar by Christophourou et al. [34]. Even there, $\langle \sigma_L \rangle$ appears to be much narrower and its minimum occurs at an energy much smaller than in the atomic one. An agreement with the two effective cross sections could be obtained by adding $E_k(N)$ to and by using $F(k)$ rather than $S(0)$ in the data of Christophorou.

4 Conclusions

In this paper measurements of the excess electron mobility in dense Ar gas in the neighborhood of the liquid–vapor critical point are presented. The most important result of the present experiment is the observation of a sharp maximum of the zero-field density-normalized mobility $\mu_0N$ at the same density where it occurs in the liquid.

The interpretation of these measurements is challenging because two opposite points of views must be reconciled. In fact, in the low-density gas it is customary to adopt a single scattering picture, while in the dense liquid the electron transport properties are described in terms of scattering of electrons off collective excitations of the medium. The interesting point is to understand if the physical mechanisms underlying the scattering processes gradually change at some density between the dilute gas and the dense liquid or if the kinetic picture valid at low density can be still retained, with obvious modifications so as to include multiple scattering, also in the liquid phase.

To this goal, the present data have been analyzed by extending the heuristic model proposed by Borghesani et al. to explain the mobility measurements in moderately dense Ar gas [10]. The model is a density–modified kinetic model based on the classical kinetic theory [1], where density–dependent multiple–scattering effects are included in a heuristic way. The model is based on the quantum density-dependent shift of the ground state energy of the electrons in a dense and disordered medium, on the accounting for correlations among scatterers described by the static structure factor of the medium, and on the quantum self–interference of the electron wavepacket scattered off randomly located scattering centers along paths connected by time–reversal. The kinetic term of the ground state energy shift must be added to the usual kinetic energy of the electrons when the cross section and other dynamic properties of
scattering have to be evaluated. All these effects concur to dress the atomic cross section resulting in an effective density-dependent momentum transfer cross section, that nonetheless is intimately related to the atomic one.

Although the data for quite high densities fit well in this model, the description of the newly discovered feature, namely the mobility maximum, requires the introduction of a density-dependent adjustable parameter that scales the cross section. In any case, however, the kinetic picture is preserved and the resulting effective cross section turns out to be very similar to the atomic one. In particular, it shows a Ramsauer-type minimum.

The overall success of this kinetic description is striking, even more if one takes into account the limited accuracy with which the atomic cross section is known, especially in the region of the Ramsauer minimum, and the uncertainty with which the energy-dependent structure function $\mathcal{F}(\epsilon)$ is known, particularly in the neighborhood of the critical point. It also appears that more refined theoretical calculations of the kinetic energy shift at high density are needed, as well as a treatment of the effect of the density fluctuations on the electron energy distribution function.

Moreover, these data still raise the question of how to treat theoretically the scattering processes for momentum transfer at very large densities, possibly including contributions from mechanisms different from density-modified kinetic processes.
References


