

Resonant low-energy electron attachment to O₂ impurities in dense neon gas

A. F. Borghesani

CNISM Unit, Department of Physics and Astronomy
University of Padua, Italy

E-mail: armandofrancesco.borghesani@unipd.it

Abstract. We report measurements of resonant low-energy electron attachment to O₂ molecular impurities in neon gas in the temperature range $45\text{ K} \leq T \leq 101\text{ K}$. The attachment frequency ν_A shows a well defined peak as a function of the density N when the electron energy is resonant with the 4th vibrational level of O₂⁻. For $T = 45\text{ K}$ a second peak has been detected at a much larger density, which is due to the formation of ions in the 5th vibrational level. The temperature dependence of the first peak can be explained by the ionic bubble model by computing the electron excess free energy as a function of T and N . The peak shape is rationalized by taking into account the density dependent shift of the electron energy distribution function and the density of states of excess electrons in a disordered medium, and by assuming that electrons sample the gas density over a region of the order of the ionic bubble radius.

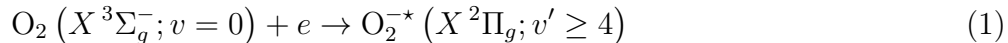
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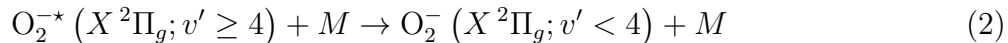
1. Introduction

Low-energy electron attachment to O₂ molecules is a phenomenon which is relevant in several processes involving the interaction of radiation with matter [1]. For instance, its important rôle in the physico-chemical processes occurring in the upper atmosphere [2,3], in electrical discharges [4,5], in low temperature plasmas [6], in the damage of DNA by low-energy electrons [7,8] is well documented.

The physical attachment process of low-energy (thermal) electrons has been quite extensively investigated, both in dilute gaseous environments [9–11] as well as in moderately dense ones [12–14]. The electron attachment to the O₂ molecule in its vibrational ground state $v = 0$ is a three-body process usually described in terms of the so called Bloch-Bradury (BB) two-stage mechanism [15]. At some specific energy resonant electron capture proceeds via the formation of a temporary negative-ion nuclear-excited Feshbach resonant state [1,16]. The kinetic energy of the captured electron couples with the molecular vibrations and leads to the formation of an ion in a vibrational excited state with quantum number v' according to the reaction



The metastable ion, which otherwise would rapidly undergo a quick unimolecular decomposition, can be stabilized in a dense gaseous environment by collision with a third body M , typically a host atom that carries away the excess energy [17].



The potential energy curves of the neutral molecule and of its anion are shown in Fig. (1). The negative-ion state lies energetically below the ground state of the parent molecule and exhibits a positive electron affinity ($\epsilon_A \approx 0.46$ eV [9,19–21]). The electron attachment turns out to be a resonant process because the energy ϵ of the colliding

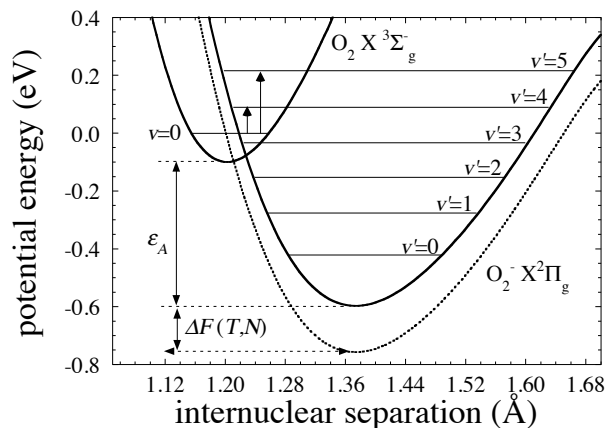


Figure 1. Potential energy curves for O₂ and O₂⁻ [18]. The O₂⁻ curve is shifted with N by ΔF , the excess free energy (dotted line). At zero density $-\Delta F = \epsilon_A$, where ϵ_A is the electron affinity. The arrows indicate the transitions to the two first vibrational levels of the ion available for attachment (see text).

electron must equal the energy difference between the energy of the excited ion state $\epsilon_{v'} - \epsilon_A$ and that of the ground state of the neutral molecule ϵ_{gs} , $\epsilon_{Rv'} = \epsilon_{v'} - \epsilon_A - \epsilon_{\text{gs}}$. The resonances have shown a doublet structure due to spin-orbit coupling in the molecular ion [22, 23]. The energies of the center of the $v' = 4$ and $v' = 5$ resonances are approximately located at $\epsilon_{R4} = 90$ meV and $\epsilon_{R5} = 210$ meV above the neutral ground state, respectively [19, 24, 25]. In Fig. (1) the arrows show the energy difference for the two first available ion states with $v' = 4$ and $v' = 5$.

In a dense gas, which is archetypal to a disordered system, it is known that the average energy of an excess electron is shifted with respect to the thermal energy by the multiple scattering induced, density-dependent energy at the bottom of the conduction band $V_0(N)$ [26]. Thus, the resonant character of the attachment process gives the researchers the unique possibility to directly investigate the energetics of an excess electron in a dense disordered medium, thereby yielding useful pieces of information on the electron density of states (DOS) and energy distribution function.

The first experimental evidence of resonant electron attachment to O₂ in dense helium gas was produced by Bartels [27]. At $T = 77$ K a sharp peak in the attachment frequency ν_A was observed at a density $N_4 \approx 30 \times 10^{26} \text{ m}^{-3}$ as well as the low-density shoulder of a second peak at higher densities. As the thermal energy amounts to only a few meV, the most important contribution to the resonance energy is believed to be due to $V_0(N)$, which, at the densities of the experiment, can be expressed by the Fermi shift [28]

$$V_0(N) = \frac{2\pi\hbar^2}{m}Na \quad (3)$$

in which a is the electron-atom scattering length, $\hbar = h/2\pi$, h is the Planck's constant, and m is the electron mass. At the density N_4 of the first peak, the Fermi shift exactly equals the energy for the $v' = 4$ resonance, $V_0(N_4) = \epsilon_{R4}$.

An unexpected increase of N_4 with the temperature T was later discovered in helium in the range $50 \text{ K} < T < 100 \text{ K}$ by using a square-wave technique. The shape of the peak was semiquantitatively reproduced by taking into account both the density dependent energy shift of the excess electrons and the effect of the density fluctuations on the electron DOS [29].

Finally, the temperature dependence of N_4 in helium was measured in a wider temperature range by using a pulsed Townsend photoinjection technique [30]. The results confirmed those of the previous experiments. The presence of a peak in the attachment frequency was rationalized as the result of the multiple scattering induced shift of the electron energy distribution function and of the quantum nature of the electron-atom interaction [31, 32]. In this experiment the researchers were also able to observe the almost complete second attachment peak caused by attachment to the $v' = 5$ ion state. At the same time it was shown that in Argon gas no attachment peaks are present because the resonance condition is never met owing to the much larger atomic polarizability of the Argon atoms with respect to helium atoms that leads to $V_0(N) < 0$ [33].

It is to be noted that in all of the cited experiments the attachment peak does not show the expected spin-orbit split doublet structure of the ion vibrational levels. This absence has also been noticed in several other crossed beam experiments in which the electron attachment to Oxygen clusters formed by nozzle expansion is investigated [34–37] and, up to now, no explanation has ever been given [38]. For this reason, in the following the energies at the center of the resonances are taken as the resonance energies.

Several problems, however, remained unsolved in the helium experiment [30]. In particular, the shape of the first peak could not easily be reproduced by the use of the shifted thermal distribution function. Actually, the gas is a highly disordered system and the electrons sample the gas density over a small volume, whose size is of the order of the electron thermal wavelength or mean free path. In such small a volume fluctuations strongly influence the electron DOS leading to a broadening of the energy distribution function. Its computation is still a not completely solved issue. The use of a percolation model [39–41] led to an improvement of the simulation of the peak shape though the agreement with the experimental data was not sufficiently satisfactory.

Aiming at the solution of the several problems raised by the measurements in helium gas, we have carried out measurements in dense neon gas over a reasonably wide temperature range. Neon has been chosen because the electron-atom is still dominated by the short-range repulsive exchange forces but the polarization interaction with the host atoms is much stronger than in helium. Thus, the electron-atom scattering cross section is much smaller and more rapidly energy dependent than for helium [42] and the self energy $V_0(N)$ is still positive though smaller.

Moreover, the temperature of the investigated isotherms ($45 \text{ K} \leq T \leq 100 \text{ K}$) are much closer to the critical temperature $T_c = 44.4 \text{ K}$ than it was in the helium experiment. So, fluctuations are expected to be more effective in modifying the electron energy distribution function.

In this paper we report the experimental results of the electron attachment measurements in neon gas and their rationalization.

2. Experimental details

The experimental apparatus and technique have thoroughly been described in literature [43]. We only recall here the main features. The experimental cell can be filled with the gas up to a pressure $P \approx 10 \text{ MPa}$ and its temperature is controlled within 0.01 K . Isolated bunches of typically 10^5 to 10^6 electrons of $\approx 4 \mu\text{s}$ duration are injected into the gas by photoelectric effect and drift under the action of a uniform electric field. Owing to attachment, the induced electron current decreases exponentially with time $I(t) = I_0 e^{-\nu_A t}$. The current is integrated by a passive integrator in order to improve the signal-to-noise ratio. The numerical analysis of the recorded voltage signal yields the electron and ion drift times, and the attachment frequency ν_A [44].

Molecular Oxygen is already present in trace in the gas as an impurity. Its

concentration is of some parts per million which is sufficient to carry out attachment frequency measurements. Residual impurities such as water vapor, hydrocarbons, and carbon dioxide are removed by recirculating the gas through a liquid N₂-cooled, active-charcoal trap [45]. As the O₂ impurity content cannot be easily controlled [29], we adopted the following procedure. For each experimental run, the cell is filled at constant temperature up to the highest pressure with gas of unknown impurity concentration C . The gas is then progressively spilled out of the cell in a stepwise way so that C remains constant and measurements can be done at the desired P down to the lowest one. Measurements carried out at the same T over overlapping pressure intervals allowed to merge data taken in different runs because $\nu_A/N \propto C$.

The depletion of the electron population because of attachment does not affect its distribution function. At a typical density of $N \approx 40 \times 10^{26} \text{ m}^{-3}$ and with a typical ion concentration $C \approx 10^{-5}$, the electron mean free path is roughly one order of magnitude smaller than the average ion-ion distance [46]. Thus, in a mean electron-oxygen collision time electrons are thermalized by several collisions with the host atoms. Moreover, the attachment does not practically change the O₂ number density N_{O_2} . Actually, in the drift space of volume $v \approx 5 \times 10^{-6} \text{ m}^3$, there are $\approx 10^{17}$ O₂ molecules which are many orders of magnitude more than the number of injected electrons.

3. Experimental results

The measurements are carried out in the temperature range $46.5 \text{ K} \leq T \lesssim 150 \text{ K}$. The maximum density attained for each T is limited by the maximum pressure the cell can withstand. On each isotherm, ν_A is measured on several isopycnals as a function of the applied electric field E of low strength. The reduced electric field strength E/N never exceeds $\approx 5 \text{ mTd}$ ($1 \text{ mTd} = 10^{-24} \text{ V m}^2$). The field is so weak as not to significantly heat the electrons and does not modify their distribution function with respect to that at thermal equilibrium. As a consequence, ν_A does not depend on E/N . A typical example is shown in Fig. (2).

3.1. Density dependence of the 1st peak of ν_A/N

At all temperatures, except the highest for $T \approx 150 \text{ K}$ for which the maximum pressure was not sufficient to reach the necessary density values, ν_A shows a well defined peak as a function of N . In order to get rid of the dependence of ν_A on both the concentration and absolute number of O₂ impurities, it is customary to plot the reduced attachment frequency ν_A/N normalized to unity at the maximum. By so doing, it is possible to directly compare the neon results with those obtained in helium. In Fig. (3) $(\nu_A/N) / (\nu_A/N)_m$ for the neon case is plotted for $T = 59.8 \text{ K}$. For the sake of comparison the data obtained in helium [30] for the close temperature $T = 54.5 \text{ K}$ are also plotted.

Two striking differences can be noticed between neon and helium. First of all, the peak density N_4 in neon is much higher than in helium. This is not surprising because

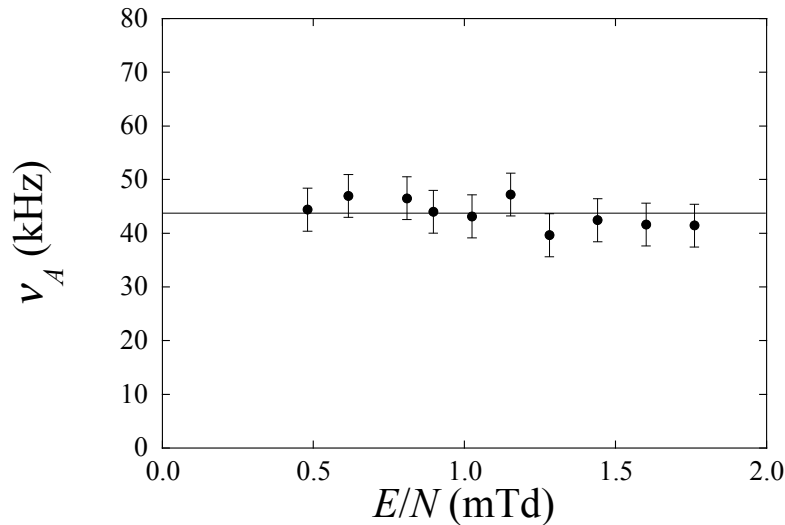


Figure 2. ν_A vs E/N for $N = 31.2 \times 10^{26} \text{ m}^{-3}$ at $T = 150.2 \text{ K}$.

$V_0(N)$ is much larger in helium [47] than in neon [48] and a higher density value is required for neon to reach the value ϵ_{R4} . Secondly, the width of the attachment peak in neon is much larger than in helium at nearly the same temperature. The peak half width at half height W is quite well correlated with the long wavelength limit of the static structure factor $S(0)(N, T) = Nk_B T \chi_T$, in which χ_T is the gas compressibility, evaluated at the density of the peak maximum, as shown in Fig. (4). The neon experiment is carried out much closer to the critical temperature than the helium one. Actually, $y = |T - T_c|/T_c \approx 5 \times 10^{-2}$ for neon and $y \approx 9$ for He. We thus draw the conclusion that the density fluctuations play a much more important rôle in neon than in helium and will have to be properly accounted for.

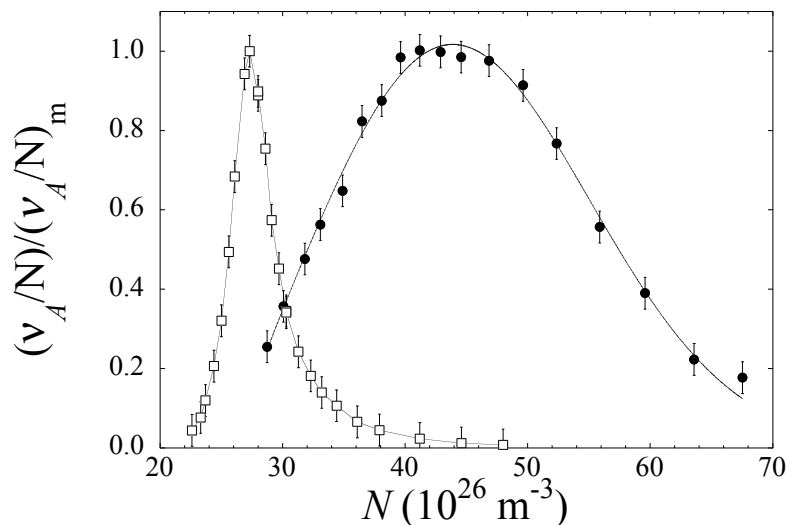


Figure 3. Normalized ν_A/N vs N in Ne for $T = 59.8 \text{ K}$ (closed points) and in He for $T = 54.5 \text{ K}$ (open points) [30]. The lines are only a guide for the eye.

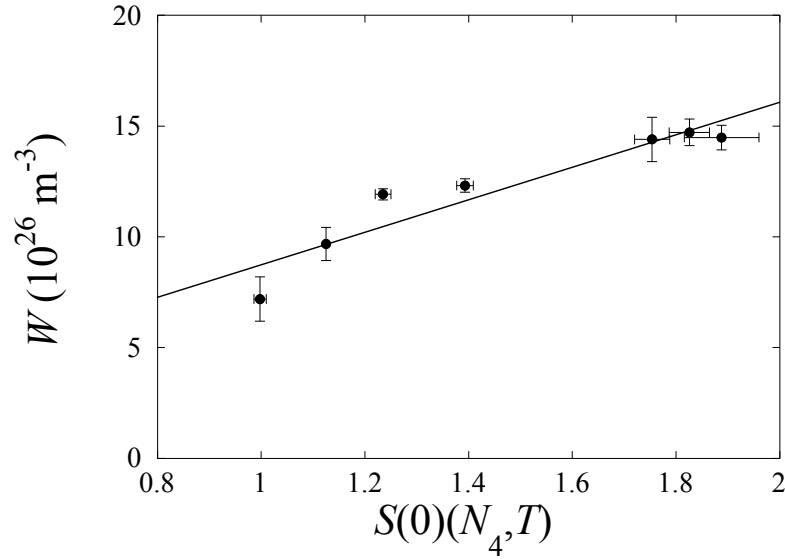


Figure 4. Correlation between W and $S(0)(N_4, T)$ in neon gas. The line is a guide for the eye only.

3.2. The 2nd ν_A/N peak at high density on the lowest isotherm

On the lowest isotherms $T = 46.5, 47.7,$ and 48.4K , also a second peak at higher densities is present, as shown in Fig. (5). This is due to attachment to the $v' = 5$ ion level. For a comparison also the data obtained in He [30] are presented. The 2nd peak in neon occurs at the much higher density N_5 and is much broader than in helium. Once more, the phenomenology can be qualitatively explained by both the smaller V_0 and by the greater closeness to the critical point of neon. We note that the ratio of the densities

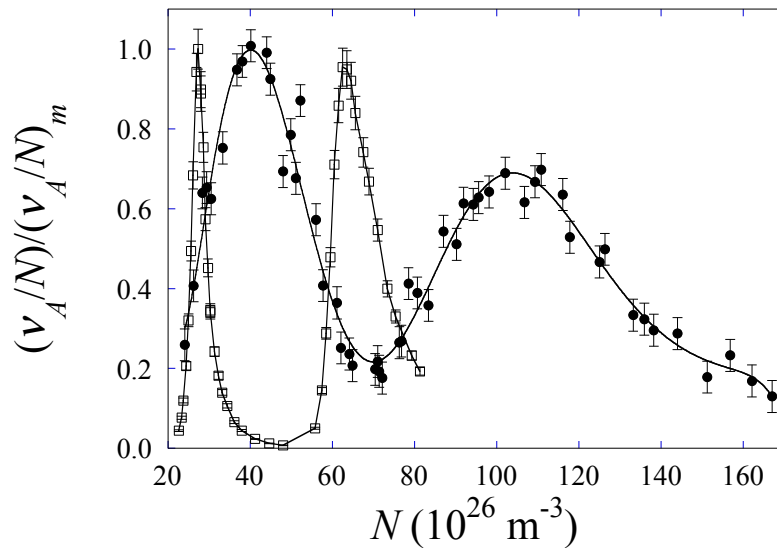


Figure 5. Normalized ν_A/N in neon for $T = 46.5, 47.7,$ and 48.4K (closed points). For a comparison, the $T = 54.5\text{K}$ data in helium are also plotted (open points) [30]. The lines are a guide to the eye only.

of the 2nd to the 1st peaks $N_5/N_4 = 2.5$ is almost equal to the ratio $\epsilon_{R5}/\epsilon_{R4} = 2.4$ of the resonance energies of the two first accessible ion vibrational levels, as is to be expected if Eq. (3) is valid. It is also to be emphasized that the 2nd peak in both gases occurs in a density region in which the phenomenon of electron self-trapping is present [48, 49].

3.3. Temperature dependence of N_4

The density N_4 of the 1st peak maximum shows an almost linear, positive dependence on the temperature T , as shown in Fig. (6). This kind of behavior was also detected in helium [30]. For the sake of comparison the results of helium are also shown in the figure. The detailed rationalization of the positive slope lines will be given in the discussion of the ionic bubble model [31, 32]. Suffices it here to say that, on the basis of energy conservation $\epsilon_{R4} = V_0(N) + (3/2)k_B T$ ($k_B T/2$ in the case of helium), the negative slope lines are obtained.

4. Discussion

The rationalization of the experimental results should answer the following questions: i) why are there peaks in the reduced attachment frequency at a specific density, ii) what does determine their shape, and iii) why does the peak density increase with temperature.

4.1. Relationship between ν_A/N and the shifted equilibrium distribution function

Owing to the quite short autoionization lifetime of O_2^- in dense gas $\tau_a \approx 2 \times 10^{-12}$ s [13], the capture cross section $\sigma(\epsilon)$ is strongly peaked at the resonance energy $\epsilon_{Rv'}$ and its

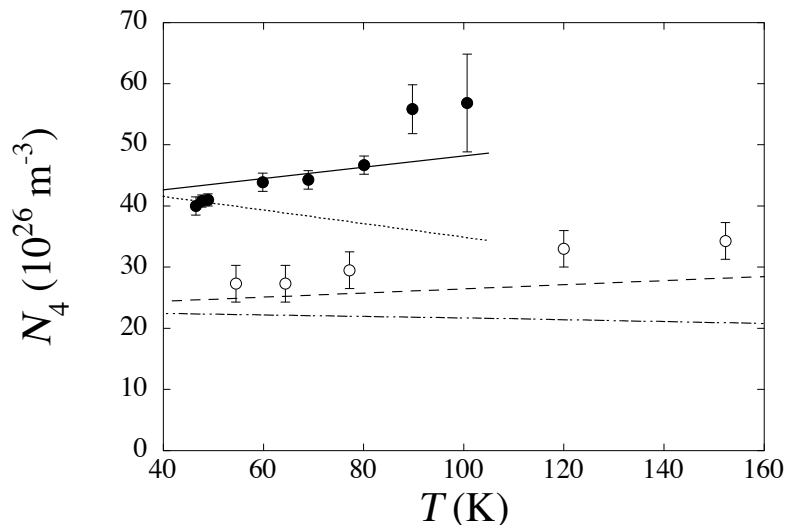


Figure 6. N_4 vs T in neon (closed points) and in helium [30] (open points). Solid and dashed lines: prediction of the ionic bubble model (Eq. (7), see text). Dotted and dash-dotted lines: energy conservation condition (see text).

width is $\Delta\epsilon \sim \hbar/\tau_a \approx 0.3$ meV, to be compared with the width of the electron energy distribution function $\simeq 4k_B T \approx 16$ meV for $T = 46$ K. For this reason the attachment frequency ν_A can be written as [29]

$$\nu_A = p_s \sigma_c C N w(\epsilon_{Rv'}) \mathcal{F}(\epsilon_{Rv'}, T, N) \quad (4)$$

in which p_s is the stabilization coefficient, $\sigma_c = \int \sigma(\epsilon) d\epsilon$ is the integrated capture cross section, C is the O₂ concentration. The electron velocity w and the Maxwell-Boltzmann(MB) equilibrium distribution function \mathcal{F} are to be evaluated at the resonance energy. \mathcal{F} explicitly depends on the gas density N because of the shift $V_0(N)$ [29, 43, 50]. The stabilization coefficient can be written as

$$p_s = \frac{k_s N}{\tau_a^{-1} + (k_s + k_d) N} \quad (5)$$

in which k_s and k_d are the rates of collisional stabilization and dissociation, respectively. $(k_s + k_d)$ can be estimated from the measurements of the O₂⁻ ion mobility μ in dense neon gas [51–53] as $(k_s + k_d) = (e/M\mu N)$ where M is the atomic mass of neon. At the typical density of the 1st peak, $N \approx 40 \times 10^{26} \text{ m}^{-3}$, and $\tau_a (k_s + k_d) N \gtrsim 8$. Thus, p_s can be assumed to be practically density independent. As a consequence,

$$\frac{\nu_A}{N} = D \mathcal{F}(\epsilon_R, N, T) \quad (6)$$

in which D is a constant.

According to classical Kinetic Theory [54], \mathcal{F} should be independent of density. However, it is now very easy to intuitively grasp the basic features of the attachment peak formation if the density dependent shift of the distribution function is taken for granted. Let us inspect Fig. (7) and consider the 1st peak. The MB equilibrium distribution function is shifted by the amount $V_0(N)$. The reduced attachment frequency

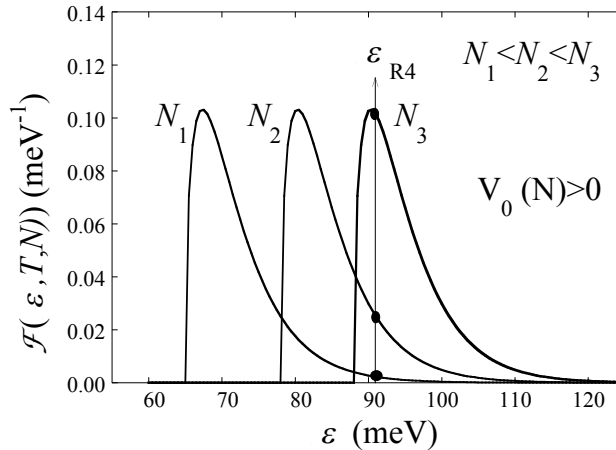


Figure 7. Qualitative picture of the sampling of the shifted MB distribution at constant resonance energy ϵ_{RA} .

is sampling \mathcal{F} at the constant energy ϵ_{R4} . Thus, by increasing N , at first the low-density shoulder of ν_A/N reproduces the high-energy tail of \mathcal{F} . For $N = N_4$ the maximum of \mathcal{F} occurs for ϵ_{R4} and ν_A/N goes through a maximum, as well. Eventually, for higher N , the shift V_0 is such that ϵ_{R4} falls in the low-energy tail of \mathcal{F} , which is reflected in the high-density tail of the ν_A/N .

This naïve approach has worked quite well for helium because the temperatures were much higher than the critical one and fluctuations did not play a major rôle. In neon, however, the situation is more complicated. Actually, if one would simply solve the resonance condition $\epsilon_{R4} = V_0(N_4) + (3/2)K_B T$ for N_4 , one would obtain $N_4 \approx 73 \times 10^{26} \text{ m}^{-3}$ for $T = 46.5 \text{ K}$, to be compared with the experimental value $N_4 \approx 40 \times 10^{26} \text{ m}^{-3}$. This discrepancy can be traced back to two main reasons. First of all, the quantum nature of the electron-host atom interaction that leads to the formation of an empty cavity around the ion is neglected. The second reason is that fluctuations, so very important in neon, are also neglected. They lead to a DOS broadening that results in a shift of the \mathcal{F} maximum to lower energies, thereby reducing the required density contribution from V_0 . Evidently, these two mechanisms act simultaneously. We will try to disentangle their effects by first treating the effect of the formation of the void around the ion within the so called *ionic bubble* model [31, 32] and, then, the computation of the distribution function in a disordered medium will be dealt with in the Eggarter's *fluctuational model* [39–41].

4.2. Predictions of the ionic bubble model

The time required for the formation and expansion of a cavity around the ion in neon gas is not known. However, experimental as well as theoretical estimates of the bubble formation time in liquid helium and neon [55, 56] suggest that the formation time is of the order of $\approx 1 \text{ ps}$, comparable to or even shorter than the autoionization lifetime τ_a . Thus, the cavity around the ion can form before autoionization occurs.

Owing to its relatively small binding energy, the weakly bound outer electron in the ion is localized in a region larger than the electronic shell of the molecule and can be treated as if it were a quasifree electron which strongly interacts with the host atoms. As a result of the competition between the short-range exchange repulsive interaction and the long-range attractive polarization one an empty cavity is formed around the ion. A denser layer outside of the cavity is also formed because of electrostriction [57] but, as the neon polarizability is relatively small, it will be neglected for the sake of simplicity. Due to the presence of $V_0(N)$, the binding energy is changed in a cavity whose radius is comparable to the spatial extent of the electron wave function. The optimum cavity radius R_b is determined by minimizing the free energy excess ΔF , i.e., by optimizing the difference between the increase of the binding energy of the electron in the ion and the energy spent to expand the cavity itself. The details of the computation and minimization of the excess free energy are described in Appendix A.

Once the excess free energy has been minimized with respect to the cavity radius for

all densities and temperatures yielding $\Delta F_m \equiv \Delta F(R_b, T, N)$, the resonance condition changes to

$$\epsilon_{Rv'} + \Delta F_m = V_0(N_{v'}) + \frac{3}{2}k_B T \quad (7)$$

In Fig. (6) the solid line shows how Eq. (7) predicts the change of N_4 as a function of T whereas the dotted line is obtained by only enforcing energy conservation. The agreement with the data is rather good, although it is somewhat worse at higher T . It appears that the ionic bubble model is also valid in the He case, in which it produces an even better agreement with the data than in neon, as shown in Fig. (6). It is worth emphasizing here that the position of the peak maximum is due to the combined effect of the density dependent shift of the electron energy at the bottom of the conduction band and of the fluctuations induced broadening of the electron energy distribution function. In helium the latter phenomenon is less important because of the distance from the critical temperature and can be neglected. In neon, on the contrary, owing to the greater closeness to T_c , the effect of fluctuations contributes a big deal to the location of the maximum and the ionic bubble model can only be used to predict most of the temperature dependence of the maximum location.

4.3. Shape of the attachment peak

Whereas the concept of the density dependent shift of the distribution function qualitatively rationalizes the presence of a peak in the reduced attachment frequency ν_A/N and the results of the ionic bubble model rather well explain the increase of the density of the peak maximum with T , nonetheless the explanation of the peak shape requires a detailed computation of the distribution function in a disordered medium. To this goal we have adopted the semiclassical fluctuational model [39–41]. A brief description of the model and some of its most pertinent features will be described in Appendix B. Suffices here to say that the density fluctuations lead to the appearance of a low-energy tail of the DOS, whose extension is controlled by the characteristic length L with which electrons are sampling the distribution of the host atoms. L is the most important quantity in the fluctuational model. The original suggestion to describe the electron mobility in dense helium gas at low temperature was to use a length proportional the uncertainty in the electron position according to the Heisenberg's principle $L \propto h/\sqrt{2m\epsilon}$ whereas a better agreement for the electron mobility in neon gas was given by choosing a length proportional to the electron mean free path [46].

For the present attachment experiment, in which the attaching electrons have to be somehow localized in a restricted region near the O_2 molecule, we have decided to use the thermal wavelength to characterize the sampling length

$$L = c(T) \frac{h}{\sqrt{2\pi m k_B T}} \quad (8)$$

in which c is a temperature dependent adjustable constant.

The the distribution function, whose shape depends on the choice of c , as shown in Appendix B, is evaluated at the energy $\epsilon_{Rv'}$ matching the resonance condition Eq. (7).

A proper choice of c on the several isotherms leads to satisfactory agreement of the model with the experimental data. In Fig. (8) we plot the data of the lowest isotherm about ≈ 47 K. We note that the two peaks for N_4 and N_5 are reproduced quite well

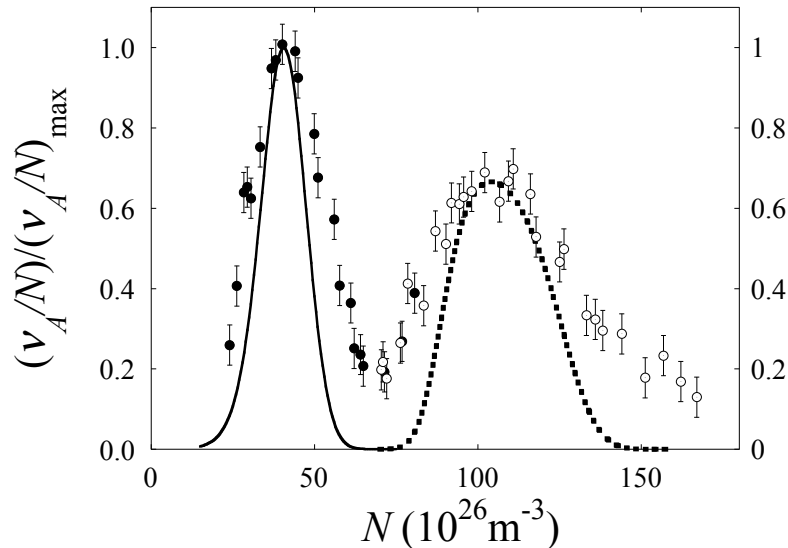


Figure 8. Normalized ν_A/N vs N for the lowest isotherms. $T = 47.7$ and 48.4 K (closed symbols). $T = 46.5$ K (open symbols). Solid line: $c = 0.145$. Dashed line: $c=0.353$.

with different c values. As the data are measured on an isotherm, the sampling length is larger when c is larger. This means that the 2nd peak is reproduced only if a larger sampling length is used than for the 1st peak. A possible rationalization of the meaning of this difference will be described later. We now note that previous electron mobility measurements [48] have shown that electrons localized in bubbles appear in significant proportion for $N \geq 95 \times 10^{26} \text{ m}^{-3}$. This means that the whole high-density tail of the 2nd attachment peak occurs in a region in which most electrons are localized in bubbles. According to literature [58] attachment from self-trapped states should be more efficient than from delocalized states as a probable consequence of the quick stabilization of the ion by the collapsing bubble [38]. This could be the reason why ν_A/N does not rapidly fall to zero at very high density. In any case the fluctuational model and the ionic bubble one are rather successful at describing also the second attachment peak.

At higher temperatures the agreement with the data is even better. For instance, in Fig. (9) we show the results for $T = 80.1$ K. Similar results are obtained for all isotherms for a proper choice of the value of the parameter c .

As a matter of fact, c turns out to be temperature dependent as well as the sampling length L . In Fig. (10) we compare the temperature dependent L that gives the better agreement with the peak shapes and the optimum ionic bubble radius R_b . In spite of the very large uncertainty in the sampling length especially at higher T , we nonetheless note that L and R_b almost have the same value and temperature dependence. Probably, the attachment process more effectively proceeds if the electron wavelength is close to

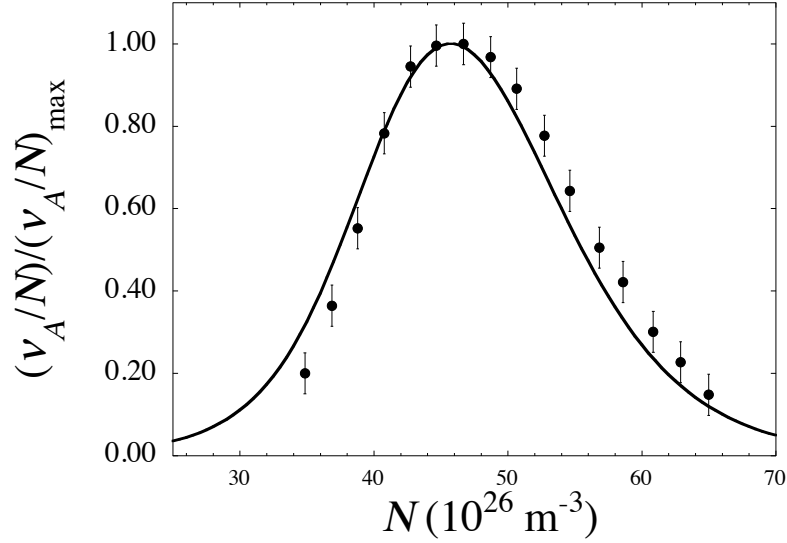


Figure 9. Normalized ν_A/N vs N for $T = 80.1$ K. Solid line: $c = 0.225$.

that of the electron bound in the ion, which is of the order of R_b . This may happen when a negative energy fluctuation of size L occurs around the molecule.

This point of view could explain why L is larger for the 2nd peak than for the 1st peak on the lowest isotherm. Actually, the amplitude of vibration of the $v' = 5$ level is larger than that of the $v' = 4$ one, and, presumably, the size of an actual ionic bubble should increase with the vibrational state of the ion.

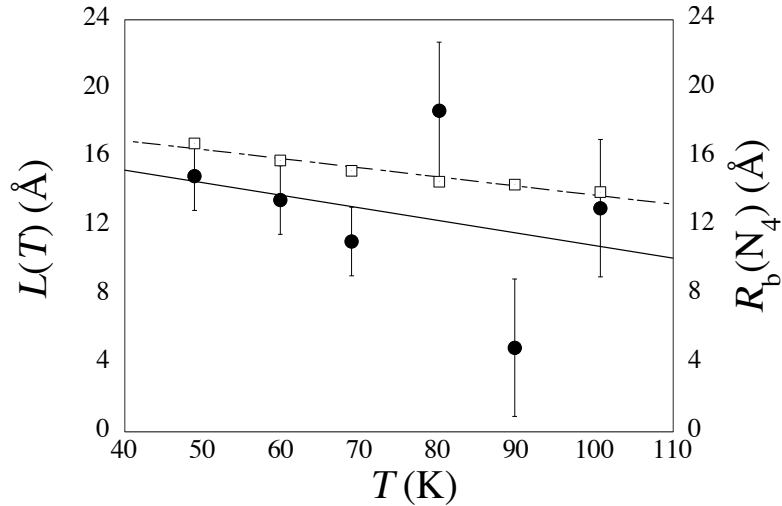


Figure 10. $L(T)$ (closed symbols, left scale) and R_b (open symbols, right scale) vs T . The lines are only a linear fit to the data and do not have any theoretical meaning.

5. Conclusions

We have shown that the phenomenon of resonant electron attachment to O₂ molecular impurities in a dense gas gives important pieces of information about the energetics and statistics of electron states in a disordered medium. Actually, the attachment frequency measurements sample the electron energy distribution function at the energy of resonance that is constant.

These new measurements in neon gas in broad density and temperature ranges once more confirm that the ground state energy of quasifree electrons in thermal equilibrium in a dense medium is offset by a density dependent contribution V_0 that is the result of multiple scattering effects and that shifts the equilibrium distribution function. This shift affects many properties of quasifree electrons, including mobility [49] and excimer formation [59]. The attachment process provides the researchers a tool to infer V_0 without the shortcomings of other techniques [29].

At the same time, we have shown that the attachment process is very sensitive to the presence of fluctuations in the system. Actually, the shape of the attachment peak is related to the DOS of electrons in a disordered system. Actually, in neon the measurements are carried out much closer to its critical temperature than in the previous experiments in helium gas.

In order to correctly describe the attachment process it is necessary to take into account the fact that the ion distorts the surrounding compliant medium giving origin to a complex structure that depends on the quantum nature of the outer electron in the ion and its interaction with the electronic clouds of the host atoms. Only if this structure is accounted for a good agreement with experiment and theory can be achieved.

Moreover, attaching molecular impurities other than O₂ of different vibrational structure such as, for instance, SF₆ could be exploited to sample the distribution function at different energies.

Finally, we would like to point out that the observation of an attachment peak from which so many pieces of information can be gathered can only happen if the electron-host atom interaction is dominated by short-range repulsive forces that lead to a positive V_0 . For negative scattering length gases as, for instance, Argon in which the long-range polarization interaction is dominant, V_0 is negative. In this case the resonance condition cannot be met and no peaks are observed although attachment still takes place.

Appendix A. Excess free energy computation in the ionic bubble model

The excess free energy of an ion surrounded by a cavity with respect to the free ion is reduced by the increase of the electron binding energy in the ion and is increased by the work done against volume and surfaces forces to expand the cavity and form an interface

$$\Delta F = -\Delta\epsilon(R, T, N) + \frac{4\pi}{3}P(N, T)R^3 + 4\pi\sigma_s R^2 + \epsilon_P \quad (\text{A.1})$$

The optimum cavity radius R_b is obtained by minimizing ΔF with respect to R , thereby yielding ΔF_m as a function of T and N . $\Delta\epsilon(R, T, N) = [\epsilon(R, T, N) - \epsilon_A]$ is the change of the electron binding energy in the ion and $\epsilon(R, T, N)$ is the lowest energy eigenvalue in the field of the ion. R is the cavity radius, $P(N, T)$ is the gas pressure given by the equation of state [60], and σ_s is the surface tension. ϵ_P is the solvation energy of the ion immersed in the medium, which, according to [61], can be estimated by the Born solvation energy

$$\epsilon_P = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 R} \left(\frac{K-1}{K} \right) \quad (\text{A.2})$$

K is the relative dielectric constant of neon and is obtained, as usual, from the neon atomic polarizability $\alpha_{\text{Ne}} = 2.66 a_0$ via the Clausius-Mossotti equation $(K-1)/(K+2) = (4\pi/3)N\alpha_{\text{Ne}}$.

The s -wave eigenvalue is obtained for all T , N , and R by numerically solving the Schrödinger equation for the electron in a rectangular well subjected to the potential

$$V(r) = \begin{cases} \infty & \text{for } r \leq R_0 \\ -\frac{1}{2} \frac{\alpha e^2}{4\pi\epsilon_0 r^4} & \text{for } R_0 < r \leq R \\ V_0(N) - \frac{1}{2} \frac{\alpha e^2}{4\pi\epsilon_0 r^4} & \text{for } r > R \end{cases} \quad (\text{A.3})$$

in which $\alpha = 10.6a_0^3$ is the polarizability of O₂ and a_0 is the Bohr radius. R_0 is the ion hard-core radius which is determined by solving the Schrödinger equation for the isolated ion with the constraint that the energy eigenvalue equals ϵ_A . The value $R_0 = 0.909a_0$ is obtained that is very close to the value $R_0 = 0.92a_0$ obtained in literature by using the variational method [31, 32]. By so doing, we implicitly neglect electrostriction and the distribution of host atoms outside the cavity.

As far as the surface term is concerned, an estimate of the surface tension σ_s can be obtained by the parachor equation [62–64] by assuming that the cavity is empty

$$\sigma_s = (\pi_c N)^4 \quad (\text{A.4})$$

in which π_c is the parachor constant whose crude estimate can be obtained from the surface tension $\sigma_t \approx 5.5 \times 10^{-3} \text{ N/m}$ [65] and density $N_t = 373.9 \times 10^{26} \text{ m}^{-3}$ at the triple point as $\pi_c = \sigma_t^{1/4} / \rho_t \approx 7.3 \times 10^{-30} \text{ N/m}^{1/4} \text{ m}^3$. In any case, although the concept of surface tension in a gas and the parachor approximation might be questionable, the contribution of the surface energy term to ΔF is rather small. For instance, for $N \approx 40 \times 10^{26} \text{ m}^{-3}$ and for a typical cavity radius $R \approx 8 \text{ \AA}$, we get $4\pi R^2 \sigma_s \approx 36 \text{ \mu eV}$.

$V_0(N)$ was computed in Ref. [48]. For the present computational purposes it can be extremely well approximated up to the highest densities by a 3rd order polynomial

$$V_0(N) = 7.096 \times 10^{-4} N + 6.743 \times 10^6 N^2 - 7.883 \times 10^{-9} N^3 \quad (\text{A.5})$$

if N is expressed in units of 10^{26} m^{-3} and V_0 is in eV.

In Fig. (A1) the results for ΔF are shown as a function of R on some isopycnals for $T = 46.5 \text{ K}$. The curves are labelled by the density values in units of 10^{26} m^{-3} . All

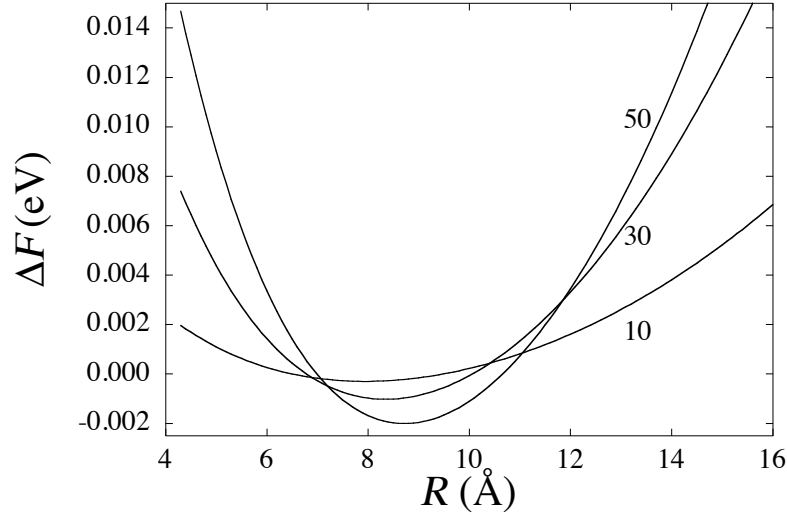


Figure A1. ΔF vs R on some isopycnals for $T = 46.5$ K. The curves are labelled with the density value in units of 10^{26}m^{-3} .

curves show a minimum as a function of the bubble radius R that gets deeper as the density is increased. The minimization procedure yields ΔF_m and the optimum bubble radius R_b as a function of N for each isotherm. ΔF_m is plotted as a function of N for the investigated isotherms in Fig. (A2). By inspecting Fig. (A2) we note that, at constant N , ΔF_m increases with increasing T leading to an increase of the density N_4 required by the resonance condition Eq. (7). This increase is shown as the solid line in Fig. (6) for neon.

As a byproduct of the computations also the optimum ionic bubble radius R_b is obtained. It is plotted as a function of N for the different isotherms in Fig. (A3). The

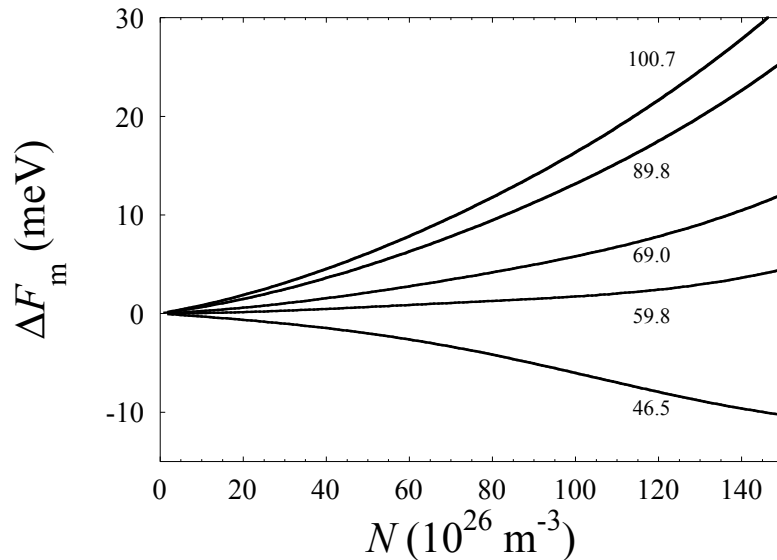


Figure A2. ΔF_m vs N on the investigated isotherms. The curves are labelled with the value of T .

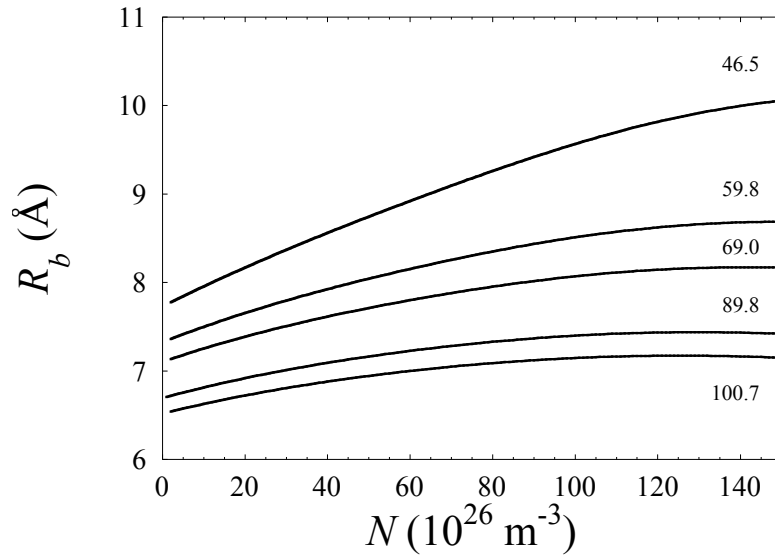


Figure A3. R_b vs N . The curves are labelled by the temperature value.

optimum radius R_b for a given N is larger at lower T mainly because it compensates for the lower pressure. Moreover, it has to be noticed that R_b shows a maximum at high N that shifts to lower density as T is increased. This behavior depends on both the density dependence of pressure and of the superlinear density dependence of $V_0(N)$.

We finally note that this approach only gives the optimum state that minimizes the excess free energy and does neither give any pieces of information on the fluctuations of the free energy nor on the distribution of the bubble radii.

Appendix B. The fluctuational model

Here, we briefly describe the main features of the fluctuational model with some results pertinent to the problem of attachment. The motion of quasifree electrons through a disordered medium of scatterers is converted to their motion in a smooth effective potential by averaging the scatterers distribution by dividing the medium into boxes of side L and averaging over them. The average potential is $V_0(N)$ which fluctuates because the density is fluctuating within the volume of size L^3 . The sampling length L can be considered as the scale of the autocorrelation of the potential. In each box, the DOS is assumed to be that relative to a freely propagating particle with energy above the local value of V_0 . The total DOS is obtained by summing over all cells. By assuming that the fluctuations are normally distributed if L is not too small, the variance of the potential is given by

$$\sigma_V^2(N) = \frac{N}{L^3} S(0) \left[\frac{\partial V_0(N)}{\partial N} \right]^2 \quad (\text{B.1})$$

and the ensemble averaged DOS is

$$g(\epsilon, N) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sigma_V^{1/2} \mathcal{H}(x) \quad (\text{B.2})$$

in which $x = [\epsilon - V_0(N)]/\sigma_V$. The function $\mathcal{H}(x)$ is given by

$$\mathcal{H}(x) = (2\pi)^{-1/2} \int_0^{\infty} z^{1/2} e^{-[(x-z)^2/2]} dz \quad (\text{B.3})$$

The resulting DOS shows a low energy tail of non propagating electron states that is due to those boxes in which the fluctuations lead to a lower-than-average density.

Once the DOS is known, the normalized electron energy distribution function \mathcal{F} is given by

$$\mathcal{F}(\epsilon, T, N) = Q(T, N)^{-1} g(\epsilon, N) e^{-\beta\epsilon} \quad (\text{B.4})$$

in which $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, and $Q(T, N) = \int_0^{\infty} g(\epsilon, N) e^{-\beta\epsilon} d\epsilon$ is the partition function.

For the computations relative to attachment, the sampling length is chosen proportional to the electron thermal wavelength

$$L = c(T) \frac{h}{\sqrt{2\pi m k_B T}} \quad (\text{B.5})$$

The effect of the choice of c can be observed by inspecting Fig. (B1) in which the normalized distribution function computed for $T = 48.4$ K and $N = 30 \times 10^{26} \text{ m}^{-3}$ is plotted for several values of c . First of all, we note that the distribution function is mainly shifted by $V_0(N)$. In addition to that, we also notice that not only the distribution broadens as the value of c is decreased but also that its maximum shifts to lower energies. That is the reason why the attachment frequency peak position is determined in a combined way by both the shift due to $V_0(N)$ and that due to the fluctuations induced broadening of the distribution function.

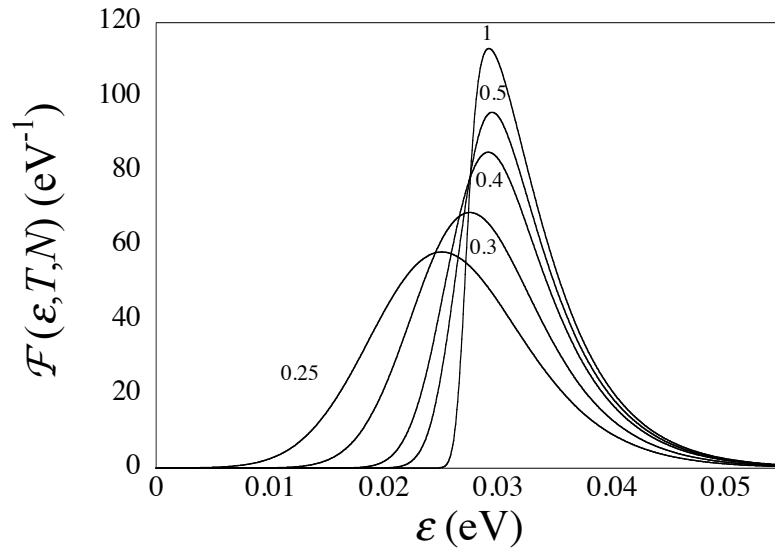


Figure B1. Normalized distribution function \mathcal{F} for $T = 48.4$ K and $N = 30 \times 10^{26} \text{ m}^{-3}$. The curves are labelled by the values of c .

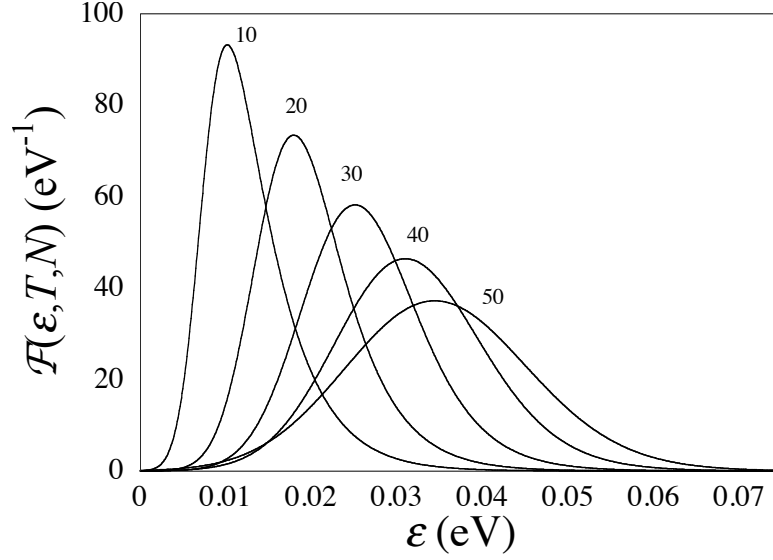


Figure B2. Normalized distribution function for $T = 48.4$ K and $c = 0.25$ for several N . The curves are labelled by the density values in units of 10^{26} m^{-3} .

The effect of the density dependent shift $V_0(N)$ on \mathcal{F} at constant sampling length can be seen in Fig. (B2) in which \mathcal{F} is plotted for several densities at constant T . The distribution function broadens by increasing N because of the increase of $S(0)$ with increasing N below the critical density, thereby leading to a larger effective potential variance.

Finally, the sensitivity of the normalized ν_A/N on the value of the sampling length can be realized by plotting the distribution function \mathcal{F} evaluated at the resonant energy ϵ_{R4} as a function of N at constant $T = 48.4$ K for several values of the parameter c in Fig. (B3). By suitably choosing c one can control both the width of the resonance curve

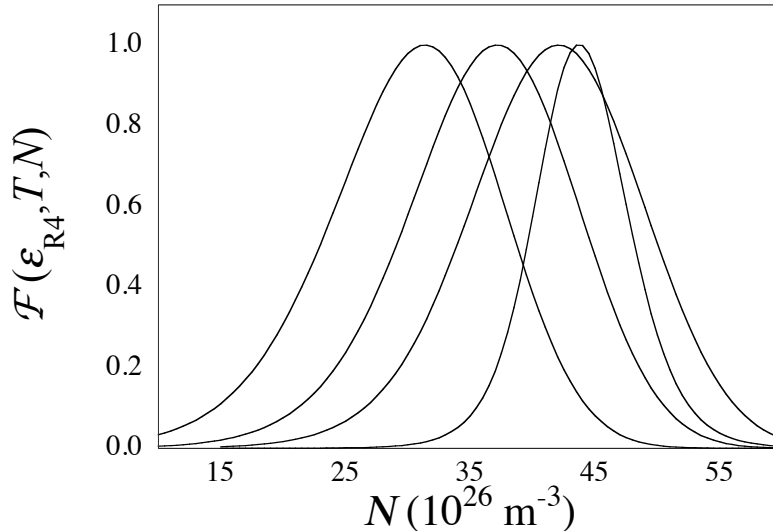


Figure B3. $\mathcal{F}(\epsilon_{R4}, T, N)$ normalized to unity at the maximum for several values of c at $T = 48.4$ K. From left: $c = 0.125, 0.1375, 0.15, 0.3$,

as well as the location of the maximum. In this way we also demonstrate that density dependent shift $V_0(N)$ of the electron ground state energy is not sufficient to explain the features of the attachment peak because of the action the fluctuations are exerting on the distribution function via the density of states.

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