

Theoretical results for the density dependence of the electron affinity of nonpolar liquids Ar, Kr, and Xe

P. Stampfli and K. H. Bennemann

Theoretical Physics, Freie Universität Berlin, Arnimallee 14, 1 Berlin 33, Germany

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Previous simple theories for the binding energy of excess electrons in liquid Ar, Kr, and Xe, which corresponds to the electron affinity, could not get good agreement with experimental results for the whole range of liquid densities. Here, we present an improvement of these theories yielding results for the electron affinity of liquid rare gases, which agree well with experiments at all densities, including the solid phase. This theory is quite universal and can also be directly applied to the electron affinity of liquids of nonpolar molecules.

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I. INTRODUCTION

The observed mobilities of excess electrons in liquid Ar, Kr, and Xe are rather high [1–5]. From this, one concludes that these electrons are in a delocalized quasifree state, which is part of a conduction band. In general, the electron affinity of the liquid corresponds to the bottom of the conduction band, denoted here as $E(\equiv V_o)$, and can be measured from the shift in the threshold of the photoelectric effect at immersed metal electrodes [3]. At low densities, one observes a roughly linear increase in the electron affinity for an increasing density of the atoms. At larger densities, a maximum is obtained in the electron affinity and the electron affinity then decreases for further increasing densities. Finally, the electron affinity of the solid rare gas is significantly lower than for the liquid rare gas.

Previously, Springett, Cohen, and Jortner [6] have presented a theory for the electron affinity of liquid rare gases. They have been using a simple continuum approximation for the attractive polarization interaction between the electron and the rare-gas atoms. The repulsive interaction has been modeled by a hard-sphere potential with an adjustable radius R_h , which is related to the strength of the repulsion. In order to avoid numerical calculation as much as possible, they had to use a very simple ansatz for the wave function of the electron and they have made a somewhat rough estimate for its energy. Further, an inflated solidlike atomic lattice has been used instead of a more realistic liquid structure. They obtained the correct magnitude for the electron affinity, but the resulting overall agreement with experiment has been rather poor. Only a monotonous increase of the electron affinity has been obtained with increasing atomic density and the experimentally observed maximum could effectively not be reproduced. Note that this theory wrongly gives a higher electron affinity for the solid rare gases than for the liquid. The disagreement is especially strong for argon [1,4,7].

The properties of excess electrons in liquid He and Xe have also been examined in a computer-simulation work [8]. It has been found, in agreement with the experiment,

that excess electrons mix with the xenon atoms and that no separation occurs. This is in contrast to the results for liquid helium, which forms a void bubble containing the excess electron [6]. However, no reliable results for the electron affinity have been obtained.

Quite recently, Plenkiewicz, Plenkiewicz, and Jay-Gerin [9] have obtained theoretical results for the electron affinity of liquid Ar and Kr, which are in good agreement with experiment. However, their work requires a high-precision atomic pseudopotential, which has to be determined for each element or molecule separately and which demands a considerable amount of numerical calculations. They have been using a realistic model for the liquid structure only for the calculation of the polarization interaction. Then, somewhat inconsistently, they have determined the electronic wave function and energy E using the same Wigner-Seitz approximation for the unit cell as Springett, Cohen, and Jortner [6], which corresponds to an inflated solidlike atomic lattice instead of a more realistic liquid structure.

We propose an improvement of earlier theories using a numerical solution for the electronic wave function and energy. In addition, a more realistic model is used for the structure of the liquid. Thus, reasonably good agreement is obtained with the electron affinity for all densities of the liquid. Note that we retain the simplicity of Springett's theory. Thus this theory for the density dependence of the electron affinity can be applied quite easily to any nonpolar liquid.

II. THEORY

We first discuss the theory for the electron affinity of solid rare gases. Then we present the atomic structure of the liquid and its influence on the electron affinity.

Rare-gas atoms condense in a face-centered-cubic structure, which is a dense packing of spheres. The electron at the bottom of the conduction band has a wave function of wave vector $\mathbf{k}=\mathbf{0}$, thus both the electronic potential and wave function have the full symmetry of the atomic lattice and they need only be discussed in one elementary cell around one of the atoms. This cell is

roughly approximated by a sphere of radius R_s , which has the same volume. If ρ is the density of the atoms, then

$$R_s = \left[\frac{3}{4\pi\rho} \right]^{1/3}. \quad (1)$$

The electronic potential $V(\mathbf{r}) = V_r(\mathbf{r}) + V_p(\mathbf{r})$ consists of a repulsive interaction $V_r(\mathbf{r})$ of short range with the atom at $\mathbf{r}=0$ in the same cell and a polarization interaction $V_p(\mathbf{r})$ with the atoms of polarizability α . As proposed by Springett, Cohen, and Jortner [6], we decompose the polarization interaction into an interaction with the atom (at $\mathbf{r}=0$) in the same cell, which has a potential $-\frac{1}{2}\alpha e^2 r^{-4}$, and an interaction with all other atoms outside the cell. The polarization outside the cell is estimated by approximating the liquid as a dielectric continuum. The dielectric constant ϵ is obtained from the Clausius-Mossotti relation [10] as

$$\epsilon = 1 + \frac{4\pi\rho\alpha}{1 - 4\pi\rho\alpha/3} \quad (2)$$

and the polarization energy of the dielectric [11] is approximately $-\frac{1}{2}e^2(1-\epsilon^{-1})R_s^{-1}$. Note that this result is equivalent to the corresponding expression used by Springett, Cohen, and Jortner [6]. The repulsive interaction is not well known and is often, as a somewhat crude approximation, replaced by a hard-core repulsion

$$V_r(r) = \begin{cases} \infty & \text{for } r < R_h \\ 0 & \text{for } r > R_h, \end{cases} \quad (3)$$

where R_h is an adjustable parameter. With these approximations the electronic potential is

$$V(\mathbf{r}) = V_r(r) - \frac{1}{2}\alpha e^2 r^{-4} - \frac{1}{2}e^2(1-\epsilon^{-1})R_s^{-1}. \quad (4)$$

The electronic wave function ψ is roughly spherically symmetric in the cell around $r=0$ and we can use an approximate form $\psi \cong f(r)/r$. The energy E of the electron is then determined by the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V(r) \right] f(r) = E f(r) \quad (5)$$

together with the appropriate boundary conditions. Periodicity demands that the normal component of the gradient of ψ vanishes at the surface of the cell, thus we obtain the condition

$$\frac{d}{dr} \psi(R_s) \cong -\frac{f(R_s)}{R_s^2} + \frac{1}{R_s} \frac{d}{dr} f(R_s) = 0. \quad (6)$$

The appropriate boundary condition around the center of the cell is $f(R_h) = 0$, if a hard-core repulsion [Eq. (3)] is used. Alternatively, regularity at $r=0$ results in the condition $f(0) = 0$ for a general finite repulsive potential V_r . Note that Eqs. (1)–(6) determine the electron affinity of solid rare gases only up to the unknown parameter R_h .

The eigenvalue problem defined by Eqs. (5) and (6) can only be solved numerically. Springett, Cohen, and Jortner proposed an approximate analytical function

$f(r) = \sin[\kappa(r - R_h)]$, which obeys the boundary condition at the center of the cell. The boundary condition at the surface [Eq. (6)] determines κ via the nonlinear equation

$$\tan[\kappa(R_s - R_h)] = \kappa R_s \quad (7)$$

and the resulting estimate for kinetic energy T of the electron is $T = \frac{1}{2}\hbar^2\kappa^2 m^{-1}$. This approximation is quite good at high densities ρ , such that the spatial variation of $V(\mathbf{r})$ is small in comparison to T . But even using this ansatz, it is not possible to obtain an analytical result for the expectation value U of the potential energy V , because of the r^{-4} term. Therefore Springett, Cohen, and Jortner assumed (somewhat arbitrarily) that the density $|\psi|^2$ of the electron is roughly constant in the region $R_s/2 < r < R_s$ and zero for $r < R_s/2$. Thus they obtained the estimate

$$\begin{aligned} U + \frac{1-\epsilon_i^{-1}}{2R_s} e^2 &= -\frac{\alpha e^2}{2} \left[\int_{r < R_s} d^3r r^{-4} |\psi|^2 \right] \\ &\quad \times \left[\int_{r < R_s} d^3r |\psi|^2 \right]^{-1} \\ &\cong -\frac{12\alpha}{7R_s^4} e^2, \end{aligned}$$

which gives the approximate result

$$E \cong T + U = \frac{\hbar^2}{2m} \kappa^2 - \frac{12\alpha}{7R_s^4} e^2 - \frac{1-\epsilon_i^{-1}}{2R_s} e^2. \quad (8)$$

Note that this overestimates the magnitude of U at high atomic densities, because the density of the excess electron close to the atom is overestimated (see Fig. 1). Similarly, the magnitude of U is underestimated at low atomic densities in comparison to a more exact calculation.

To calculate the electron affinity of liquid rare gases, one has to make a model of its atomic structure. In the simplest approximation, which has also been used by Springett, Cohen, and Jortner [6] and Pleniewicz, Pleniewicz, and Jay-Gerin [9], the high density ρ of the solid is simply replaced by the lower density of the liquid.

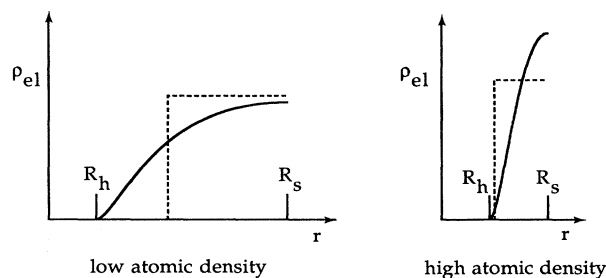


FIG. 1. Illustration of the density of the excess electron (continuous line) around a rare-gas atom at $r=0$. R_h is the radius of the hard-core repulsive potential and R_s is the radius of the unit cell. The dashed line represents the approximation used by Springett, Cohen, and Jortner (Ref. [6]) for calculating the polarization energy.

Thus the atomic lattice of the solid is just expanded. It should be noted that this is a very unrealistic model for the liquid structure, which is even in contradiction with the lack of rigidity of the liquid phase. In fact, a decrease of the density of a liquid is mainly due to a decrease of the average number of nearest-neighbor atoms of an atom and the increase of average bond lengths is rather small. Thus we propose an alternative model, which approximates the effect of a decreasing atomic density ρ as being due to an increasing number of vacant lattice sites.

In this model, the basic lattice itself is kept constant at the density ρ_s of the solid rare gas and the relative number of occupied lattice sites is simply given by ρ/ρ_s . The energy of the electron is obtained as a correctly weighted average, $E = (w_o E_o + w_v E_v)/(w_o + w_v)$, where E_o is the electronic energy at an occupied lattice cell, E_v is the energy at a vacant cell, and w_o and w_v are corresponding weights, which are composed of the relative numbers of occupied sites (ρ/ρ_s) or vacant sites ($1 - \rho/\rho_s$) and the density of the electron at each of these sites. The lattice is the same as for the solid, thus an elementary lattice cell is approximated by a sphere of radius

$$R_s = \left[\frac{3}{4\pi\rho_s} \right]^{1/3}, \quad (9)$$

which is independent of the actual atomic density ρ of the liquid.

The energy E_o at an occupied cell is calculated from Eqs. (2)–(6) and (9) and the weight w_o results from the wave function $\psi \cong f(r)/r$ as

$$w_o = 4\pi \frac{\rho}{\rho_s} \int_{R_h}^{R_s} [f(r)]^2 dr. \quad (10)$$

Note that the Clausius-Mossotti relation depends only on the validity of the Lorentz-Lorentz relation [11], thus Eq. (2) for the dielectric constant remains a valid approximation. The electronic potential V at a vacant site results from the polarization of the surrounding atoms and is approximately constant, $V \cong -\frac{1}{2}e^2(1 - \epsilon^{-1})R_s^{-1}$. Thus we assume, as an approximation, that the wave function ψ is constant in vacant cells. From continuity at the boundary between cells it follows that $\psi(r) \cong R_s^{-1}f(R_s) = \text{const.}$ This results in

$$w_v = \frac{4\pi}{3} \left[1 - \frac{\rho}{\rho_s} \right] R_s [f(R_s)]^2 \quad (11)$$

and

$$E_v = -\frac{1}{2}e^2(1 - \epsilon^{-1})R_s^{-1}. \quad (12)$$

Obviously, this ansatz for the wave function ψ is not very accurate, but we argue (based on the Rayleigh-Ritz variational principle) that the resulting energy E should represent a rough upper limit for the energy of the excess electron. Noting that $E_o - E_v$ is independent of ρ , we rewrite E as

$$E(\rho) = \frac{w_o}{w_o + w_v} (E_o - E_v) - \frac{1}{2}e^2(1 - \epsilon^{-1})R_s^{-1}. \quad (13)$$

The qualitative dependence of the energy E on the density ρ follows directly from this equation. The first term represents the interaction of the excess electron with an atom in the same elementary cell (if occupied) and makes a positive contribution to E . The second term is the polarization energy of the surrounding environment and makes a negative contribution. At low densities ρ the second term is larger in magnitude than the first one and both are roughly proportional to ρ . Thus the electron affinity ($-E$) first increases linearly with ρ . At high densities, the second term saturates and the first term continues to increase, thus the electron affinity has a maximum and then decreases for further increasing densities. Further, we note that the results of Eq. (13) depend mainly just on the electron affinity of the solid, its atomic density ρ_s , and the polarizability α of the atoms or molecules. Then, the details of the atomic pseudopotential only have a small influence on the electron affinity via Eq. (10) and the result of this model is quite universal.

III. RESULTS

We use in our calculation the following parameters. The polarizability of a xenon atom is 4.04 \AA^3 , 2.48 \AA^3 for a krypton atom, and 1.64 \AA^3 for an argon atom [12]. The radius R_h of the hard-core repulsion has been adjusted, such that our calculation reproduces the electron affinity of solid rare gases as measured in the experiment [7]. The energy E of the excess electron is -0.57 eV at a temperature of 160 K in solid Xe, -0.4 eV at 114 K in solid Kr, and 0.0 eV at 82 K in solid Ar. The atomic densities of the solid are obtained from an appropriate extrapolation of experimental results [13] as $1.58 \times 10^{22} \text{ cm}^{-3}$ for Xe, $2.01 \times 10^{22} \text{ cm}^{-3}$ for Kr, and $2.46 \times 10^{22} \text{ cm}^{-3}$ for Ar. This determines uniquely R_h for each element, the resulting values are 1.152 \AA for Xe, 0.982 \AA for Kr, and 0.883 \AA for Ar. Note that these values are somewhat smaller than values suggested previously [5] and which have been obtained from Springett's theory.

The results of our calculation for the energy E of an excess electron in liquid Xe, Kr, and Ar are given in Figs. 2, 3, and 4, respectively, together with the experimental measurements of various groups. The continuous line is obtained using the vacancy model [Eqs. (9)–(13)] and the dashed line is obtained using the model of the expanded solid [Eqs. (1)–(6)] for the structure of the liquid. The dotted line results from the approximations [Eqs. (1), (7), and (8)] introduced by Springett, Cohen, and Jortner [6]. Our calculation agrees qualitatively and quantitatively rather well with the experiments. The linear increase of the electron affinity ($A \equiv -E$) at small densities, its maximum at larger densities, and its decrease towards the high density of the solid are obtained correctly. Quantitatively, the agreement is especially good for Xe. For Kr and Ar, there seems to be a systematic deviation between experiment and theory. This could be due to the actual atomic structure of the liquid, which deviates from the simple models presented here. Note that the experiments have been done at rather high temperatures. Thus, large local fluctuations of the atomic density become possible. These fluctuations should have a strong effect on the en-

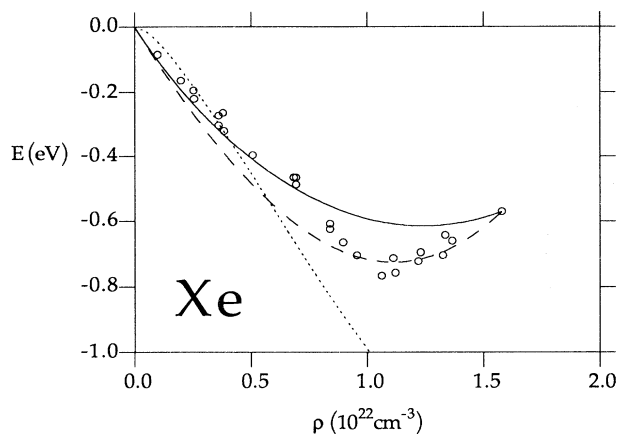


FIG. 2. Dependence of the energy E of excess electrons in liquid Xe on the density of atoms ρ . Calculated results: The continuous line refers to the vacancy model [Eqs. (9)–(13)], the dashed line to the expanded lattice model [Eqs. (1)–(6)], and the dotted line to previous calculations [approximation by Springett, Cohen, and Jortner, Ref. [6], and Eqs. (1), (7), and (8)]. Experimental results are given by circles, Ref. [5].

ergy of the excess electron, mainly due to the strong repulsive interaction. On the other hand, fluctuations might also be enhanced in the presence of excess electrons.

Note that we obtain a rather good agreement with the theoretical results of Pleniewicz, Pleniewicz, and Jay-Gerin [9], although our atomic potentials are rather different and our model requires significantly less computational work. In contrast, the approximations made by Springett, Cohen, and Jortner [6] lead to an unsatisfactory agreement with experiment. The electron affinity is both strongly underestimated at low densities and overes-

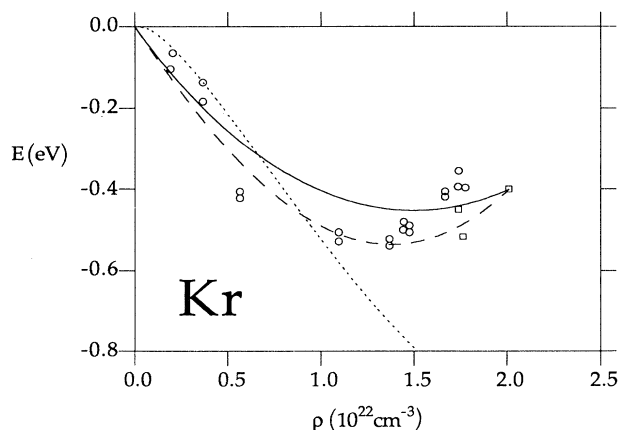


FIG. 3. Dependence of the energy E of excess electrons in liquid Kr on the density of atoms ρ . Calculated results are presented in the same way as in Fig. 2. Experimental results are given by circles (Ref. [5]) and squares (Ref. [7]).

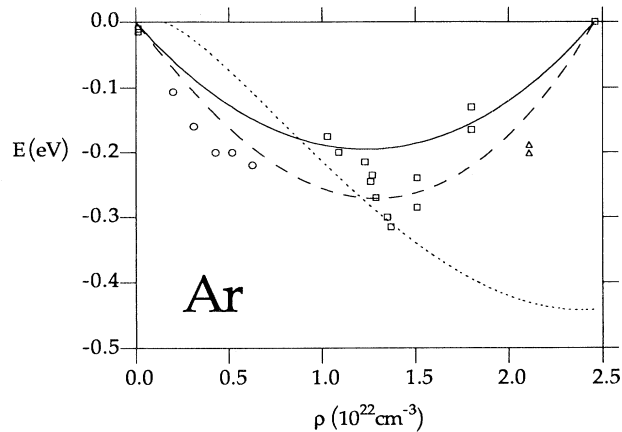


FIG. 4. Dependence of the energy E of excess electrons in liquid Ar on the density of atoms ρ . Calculated results are presented in the same way as in Fig. 2. Experimental results are given by circles (Ref. [16]), squares (Ref. [4]), and triangles (Ref. [3]).

timated at high densities for any reasonable choice of the parameter R_h of the repulsive interaction. Thus, not even the maximum of the electron affinity at liquid densities could be reproduced.

In Fig. 5 we present theoretical results for the electron affinity of liquid Xe using the soft interaction potential between excess electrons and atoms proposed by Coker, Berne, and Thirumalai (see part II of Ref. [8]). Their po-

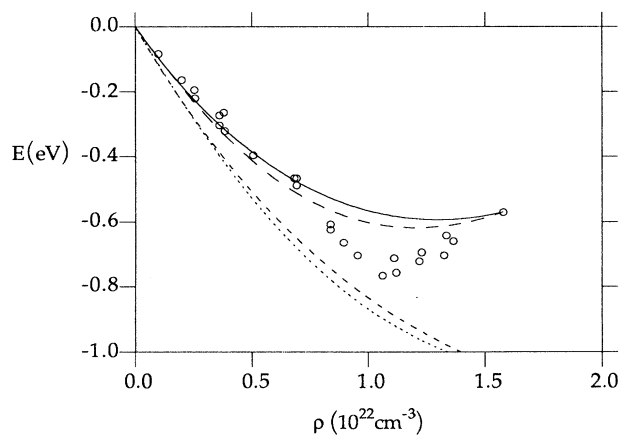


FIG. 5. Calculation of the energy E of excess electrons in liquid Xe making use of the interaction potential proposed by Coker, Berne, and Thirumalai (Ref. [8]). The short-dashed line indicates the results for the vacancy model [Eqs. (9)–(13)] and the dotted line refers to the expanded lattice model [Eqs. (1)–(6)]. Here, the original potential [Eq. (14)] has been used in both cases. Using the modified potential [Eq. (15)], one gets results indicated by the continuous line in the case of the vacancy model and the dashed line in the case of the expanded lattice model. Experimental results are given by circles (Ref. [5]).

tential has been given in the analytic form

$$V(r) = \frac{e^2\alpha}{2r^4} \left[\frac{B}{(C+r^6)} - 1 \right]. \quad (14)$$

The parameters B and C define the repulsive potential and they have been determined by extensive numerical calculations. Using this potential instead of the terms $V_r(r) - \frac{1}{2}e^2\alpha r^{-4}$ in Eq. (4), we obtain the lower set of lines. Clearly, the electron affinity is strongly overestimated at high densities. One reason for this problem might be that Coker, Berne, and Thirumulai have not used a sufficiently strong cutoff for the polarization term $-\frac{1}{2}e^2\alpha r^{-4}$ at small r . To examine this further, we have made a second calculation with the slightly modified potential

$$V(r) = \frac{e^2\alpha}{2} \left[\frac{B}{r^4(C+r^6)} - \frac{1}{(r^2+D^2)^2} \right], \quad (15)$$

where D is an adjustable parameter. A similar cutoff has also been used by Plenkiewicz, Plenkiewicz, and Jay-Gerin [9]. The upper set of lines has been obtained using the value $D = 0.41 \text{ \AA}$, which results in a good agreement with the experiment. Note that the results given by the vacancy model (solid line) are almost identical to the respective results in Fig. 2, in spite of the different atomic potentials. This demonstrates the universal behavior, which we expect on the basis of Eq. (13). Finally, we conclude that the repulsive part of the interaction potential of Eq. (14) is too weak and that appropriate corrections are necessary. This might explain some of the differences between the results of two recent calculations on the elec-

tron affinity of small clusters of xenon atoms [14,15]. Note that we do not use a similar cutoff as in Eq. (15) together with the hard-core repulsive potential [Eq. (3)] because this does not make a significant change in our results.

IV. CONCLUSIONS

Using a rather simple model, we have calculated the electron affinity of liquid rare gases and its dependence on the atomic density. The results agree rather well with the experiments. Thus, we expect that this model for the interaction between electrons and rare-gas atoms could also be used to examine the properties of excess electrons on clusters of rare-gas atoms. Additionally, this theory can also be used to examine the electron affinity of liquids of nonpolar molecules.

A similar calculation using an interaction potential introduced by Coker, Berne, and Thirumulai for excess electrons at xenon atoms results in electron affinities that are far too large. Based on this result, we expect that using this potential the electron affinity of larger clusters of Xe atoms is overestimated as soon as the excess electron is localized inside the cluster. Thus, this potential should be corrected before it is used for other calculations.

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