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Physica A 293 (2001) 59–70

PHYSICA A

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# Sum-rule approach in the theory of charged self-compressed dielectric droplets

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Received 13 November 2000

## Abstract

The formal density-functional theory for neutral droplets that experience a spontaneous deformation is developed. The perturbative analytical expressions for the size corrections to the chemical potential, surface tension, and atomic density are derived from the condition of mechanical equilibrium, using a power series expansion in the inverse of droplet radius  $R$ . In this way, the determination of these corrections is reduced to a calculation of the quantities for a liquid with a flat surface. It is shown that the size compression and tension of density occur in the  $1/R$  and  $1/R^2$  orders, respectively. The sizes of charged, rigid and elastic, the so-called critical clusters, for which the binding energy is close to zero, are calculated for  $\text{Ar}_N^-$ ,  $\text{Kr}_N^-$ ,  $\text{Xe}_N^-$  and  $\text{Ar}_N^+$ ,  $\text{Ne}_N^+$ ,  $\text{He}_N^+$ . The results show significant contribution of self-compression to the binding energy of excess electron and a negligible influence on the positron binding. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 36.40.-c; 36.40.Wa; 61.46.+w; 71.24.+q

Keywords: Rare-gas atoms; Dielectric droplets; Binding energy; Self-deformed clusters

## 1. Introduction

Excess charged particles and polarization interactions with medium in which they are solvated are of great importance in physical chemistry and biology. The interaction of electrons with the rare-gas atoms, which are characterized by large polarizabilities,

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exhibits an attractive character that overcomes the repulsive short-range interaction and makes their localization (binding) in clusters possible [1,2]. Negative cluster's ions were discovered experimentally in a dense xenon [3,4]. In helium, where atomic polarizability is very small, electrons are localized in bubble-like structures. Recently, such electronic bubbles were observed even in the helium microdroplets [5]. The interaction of positrons with atoms, owing to the absence of the exchange interaction, demonstrates always an attractive character [6,7]. Positron clusters were reported for all dense rare-gas atoms [8]. The mass-spectrometry experiments allowed to discover the existence of xenon clusters which contain nearly dozen of atoms and are charged by only one excess electron [9]. They have a noticeable lifetime and are called "critical" clusters. The size dependence of the electron affinity and critical size of xenon solid clusters were examined within the continuum model [10,11], and also by taking full account for the atomic structure [12] of clusters.

In this work we point out the importance of elastic effects in the determination of the droplet's energetics and propose an improvement on earlier theories. We develop a formal density-functional theory for finite classical system in order to account for the self-deformation of the droplet. For smallest clusters, the theory based on the continuum model, retains simplicity of the method developed for rigid clusters [10]. Furthermore, we calculate critical sizes for single-charged elastic clusters.

The analytical sum-rule approach, developed for neutral metallic clusters [13,14], describes the influence of self-compression upon ionization potential only in terms proportional to first order in  $1/R$ . As will be shown, for dielectric clusters this approach is more progressive and the corrections, proportional to  $1/R^2$ , are obtained. In the following section we briefly present the density-functional theory of self-deformed cluster.

## 2. Density-functional theory

Consider a classical, dense vapour at temperature  $T$ , and of chemical potential  $\mu$ , consisting of  $N$  atoms in a box of volume  $\mathcal{V}$ . The free energy of droplet–vapour system,  $F = F[\rho(r, R)]$ , is a functional of the inhomogeneous atomic concentration  $\rho(r, R)$ , with  $R$  being the cluster radius. In the framework of the density-functional theory, the free energy can be written in the form

$$F = \int d^3r (f + g(\nabla\rho)^2), \quad (1)$$

where  $f \equiv f[\rho(r, R)]$  is the energy density of the quasi-homogeneous part of the functional,  $g \equiv g[\rho(r, R)]$  gives the first inhomogeneity term represented by the first gradient term.

The grand free energy is found by minimizing the functional

$$\Omega_{\mathcal{V}}[\rho, \psi] = F[\rho] - \mu \int d^3r \rho(\mathbf{r}) + \frac{\hbar^2}{2m} \int d^3r |\nabla\psi|^2 + \int d^3r |\psi(\mathbf{r})|^2 V(\mathbf{r}) \quad (2)$$

with respect to variation of  $\rho(\mathbf{r})$  and the wave function  $\psi(\mathbf{r})$ , subject to conditions

$$\int d^3r |\psi(\mathbf{r})|^2 = 1, \quad \text{and} \quad \int_{\mathcal{V}} d^3r \rho(\mathbf{r}) = N \gg 1. \quad (3)$$

Here

$$V(\mathbf{r}) = \int d^3r' v(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}'), \quad (4)$$

where  $v(\mathbf{r})$  is the electron/positron–atom interaction potential. By varying  $\Omega_{\mathcal{V}}[\rho, \psi]$  with respect to  $\psi(\mathbf{r})$ , while using a Lagrange multiplier one gets the standard Schrödinger equation for  $\psi(\mathbf{r})$

$$\left( -\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (5)$$

and the Euler–Lagrange equation can be written in the form

$$\begin{aligned} \mu(r, R) = \frac{\delta F[\rho]}{\delta(\rho, R)} = \frac{\partial f}{\partial \rho} - \frac{\partial g}{\partial \rho} (\nabla \rho)^2 - 2g \left( \Delta \rho + \frac{2}{r} \nabla \rho \right) \\ + \int d^3r' |\psi(\mathbf{r}')|^2 v(\mathbf{r}' - \mathbf{r}). \end{aligned} \quad (6)$$

For the equilibrium concentration profile  $\rho(r, R)$ , we have  $\mu(r, R) \equiv \mu(R)$ . For a given  $\rho(r)$  we look for the lowest-energy solution to Eq. (5). Let us denote the energy in this state by  $E[\rho]$ . For the equilibrium profile  $\rho(r, R)$ , the functional  $\Omega_{\mathcal{V}}[\rho(r, R), \psi] = E + F - \mu N$  has a minimum and is equal to the Gibbs grand potential  $\Omega = -P\mathcal{V}$ , where  $P$  is the pressure in the box.

We consider the case of weak perturbation of the atomic distribution  $\rho(r)$  by an excess quantum particle. The effect of the correction can be estimated a posteriori and such an estimate is made at the end of this section.

By definition, the surface free energy per unit area,  $\gamma$ , and surface tension  $\tau$  (or stress, for a solid [15,16]) are given by

$$\gamma = \frac{1}{A} \{ F[\rho(r, R)] - F[\rho_0^+] \theta(r - R) - F[\rho_0^-] \theta(R - r) \} \quad (7)$$

and

$$\tau = \gamma + A \frac{d\gamma}{dA}, \quad (8)$$

where  $A = 4\pi R^2$  is the area of “equimolecular surface” of the cluster, which is defined by the condition

$$4\pi \int_0^\infty dr r^2 [\rho(r, R) - \rho_0^+ \theta(r - R) - \rho_0^- \theta(R - r)] = 0. \quad (9)$$

Here  $\rho_0^+$  is the atomic concentration in the uniform condensed matter,  $\rho_0^-$  the density of uniform vapour beyond the surface, and  $\theta(-x)$  the Heaviside step function. In the following, we employ the expansion of the quantities  $Y \equiv \rho, \mu, \gamma, \tau$  in powers of the inverse radius  $1/R$ ,

$$Y = \sum_{k=0}^{\infty} \frac{Y_k}{R^k}. \quad (10)$$

The zeroth-order terms in (10) are relevant to a system with planar boundary. A necessary condition for this expansion to become possible is that the density of the system be “leptodermous”, i.e., essentially constant in the bulk and dropping to zero in a relatively narrow region around the surface [17].

Inserting this expansion into (6) and (9), one can compile the terms having equal powers of  $1/R$ , getting a set of equations for  $\rho_k$  and  $\mu_k$ . The equations for  $k = 0, 1, 2$  have the form

$$\mu_0 = \frac{\partial f_0}{\partial \rho_0} - \frac{\partial g_0}{\partial \rho_0} (\nabla \rho_0)^2 - 2g_0 \Delta \rho_0, \quad (11)$$

$$\mu_1 = \frac{\partial^2 f_0}{\partial \rho_0^2} \rho_1 - 2 \frac{\partial g_0}{\partial \rho_0} (\nabla \rho_0 \nabla \rho_1 + \rho_1 \Delta \rho_0) - \frac{\partial^2 g_0}{\partial \rho_0^2} \rho_1 (\nabla \rho_0)^2 - 2g_0 (\Delta \rho_1 + 2\nabla \rho_0), \quad (12)$$

$$\mu_2 = \frac{1}{2} \frac{\partial^3 f_0}{\partial \rho_0^3} \rho_1^2 + \frac{\partial^2 f_0}{\partial \rho_0^2} \rho_2 + \text{gradient terms}, \quad (13)$$

$$\int_{-\infty}^{\infty} dx [\rho_0(x) - \rho_0^+ \theta(-x) - \rho_0^- \theta(x)] = 0, \quad (14)$$

$$\int_{-\infty}^{\infty} dx [\rho_1(x) - 2x \rho_0^+ \theta(-x) - 2x \rho_0^- \theta(x)] = 0, \quad (15)$$

where we have changed the variable  $x = r - R$ , and we have made use of the limit  $R \rightarrow \infty$ , denoting  $\rho^+ \equiv \rho(x = -\infty)$ , and  $\rho^- \equiv \rho(x = +\infty)$ . For brevity, we use the notation  $\nabla = d/dx$  and  $\Delta = d^2/dx^2$ . The liquid under consideration occupies the half-space  $x < 0$ , and the vapour is for  $x > 0$ . It is convenient to introduce the useful definition of the “average over a planar surface”

$$\langle \mu(x) \rangle = -\frac{1}{\rho_0^+ - \rho_0^-} \int_{-\infty}^{\infty} dx \mu(x) \nabla \rho_0 \quad (16)$$

and the “first average over spherical surface”

$$\langle\langle \mu(x) \rangle\rangle = -\frac{1}{\rho_1^+ - \rho_1^-} \int_{-\infty}^{\infty} dx \mu(x) \nabla \rho_1. \quad (17)$$

By analogy with Refs. [18,19], using Eqs. (14)–(16), after cumbersome transformations, one gets the analogue of results obtained earlier, and in another form, in the framework of the van der Waals theory (see Ref. [20], where  $g_0 = \text{constant}$  was used):

$$\gamma_0 = 2 \int_{-\infty}^{\infty} dx g_0 (\nabla \rho_0)^2, \quad (18)$$

$$\gamma_1 = 4 \int_{-\infty}^{\infty} dx x g_0 (\nabla \rho_0)^2. \quad (19)$$

A similar expression was derived earlier [14,18,19] in the two-component plasma model and stabilized jellium for self-compressed metal clusters. Using Eqs. (11)–(12) and (16)–(19) one can obtain the following expressions:

$$\mu_1^\pm = \rho_1^\pm \frac{\partial^2 f_0^\pm}{\partial \rho_0^{\pm 2}}, \quad (20)$$

$$\langle \mu_1 \rangle (\rho_0^+ - \rho_0^-) = 2\gamma_0 \quad (21)$$

and

$$\mu_2^\pm = \frac{1}{2} \rho_1^{\pm 2} \frac{\partial^3 f_0^\pm}{\partial \rho_0^{\pm 3}} + \rho_2^\pm \frac{\partial^2 f_0^\pm}{\partial \rho_0^{\pm 2}}, \quad (22)$$

$$\langle \mu_2 \rangle (\rho_0^+ - \rho_0^-) + \frac{1}{2} \langle \mu_1 \rangle \left( \frac{\rho_0^{+2} \mu_1^+}{B_0^+} - \frac{\rho_0^{-2} \mu_1^-}{B_0^-} \right) = 2\gamma_1, \quad (23)$$

where  $\mu^+ \equiv \mu(x = -\infty)$ ,  $\mu^- \equiv \mu(x = +\infty)$ , and  $B_0^\pm = \rho_0^{\pm 2} \partial^2 f_0^\pm / \partial \rho_0^{\pm 2} \equiv \rho_0^{\pm 2} f_0^{\pm \prime\prime}$  is the bulk modulus (or inverse compressibility) of liquid (+) and vapour (–), respectively. In particular, Eq. (21) defines the size correction to the “atomic work function” or cohesive energy  $\varepsilon_{coh}(R) = \varepsilon_{coh0} + \varepsilon_{coh1}/R$ , where  $\varepsilon_{coh1} = -2\gamma_0/(\rho_0^+ - \rho_0^-)$ .

The equilibrium conditions,  $\mu_{1,2}^+ = \langle \mu_{1,2} \rangle = \mu_{1,2}^- = \langle \langle \mu_{1,2} \rangle \rangle$ , lead to cancellation of the second term in (23) and after trivial algebra we derive the desired equalities

$$\rho_1^+ = 2\gamma_0 \frac{\rho_0^{+2}}{B_0^+ (\rho_0^+ - \rho_0^-)}, \quad (24)$$

$$\rho_2^+ = \rho_1^+ (\delta - \chi), \quad (25)$$

which will be used in further calculations. The “size” coefficient  $\delta = \gamma_1/\gamma_0$  is defined by the dependence  $\gamma(R) = \gamma_0(1 + \delta/R)$ , and  $\chi = \rho_1^+ f_0^{+ \prime\prime\prime} / 2f_0^{+ \prime\prime}$ . The quantities,  $\rho_1$  and  $\rho_2$ , appearing in (24) and (25) can be calculated by solving the problem for a flat surface. It is worth mentioning that for the liquid rare gases, the value of  $\gamma_0/B_0^+$  appearing in (24) is close to one half of the Bohr radius  $a_0 = \hbar^2/me^2$ , thus giving some “fundamental” length, in analogy to liquid metals [21].

Expression (24) means that atomic concentration in the bulk of the cluster increases by  $\rho_1^+/R$  compared to the  $\rho_0^+$  case, where  $R \rightarrow \infty$ . Thus, *self-compression* is a result of surface curvature that creates an extra pressure,  $2\gamma_0/R$ , in comparison to the planar case. As is shown below, the second-order correction,  $\rho_2^+/R^2$ , has a negative sign. This points to the size *self-tension* that appears in the terms of order  $1/R^2$ .

The sign of the coefficient  $\delta$  in (25) may be determined qualitatively by the following argument. The response of a droplet to decrease in its size corresponds to that predicted by the well-known Le Chatelier’s principle. Taking into account the size dependence of surface energy, the extra pressure inside a droplet equals to  $2\gamma(R)/R$ , where  $\gamma(R) < \gamma_0$ . Consequently, the decreasing of  $\gamma(R)$  relative to  $\gamma_0$ , counteracts the increase in capillary pressure due to the diminishing of droplet size. In order to make a connection with

Ref. [9], let us restrict our consideration to the droplet–vacuum system. It means that we need to set  $\rho_0^- = 0$  in (24) and to make a substitution  $\gamma(R) \rightarrow \tau(R)$  [22,23]. Then, by the definition of surface tension (8), we have

$$\tau(R) = \tau_0 \left( 1 + \frac{\delta}{2R} \right), \quad (26)$$

where, for simplicity, we assumed that  $\tau_0 = \gamma_0$  (see discussion in Ref. [16]). Following Eq. (26), the correction  $\rho_2^+/R^2$ , defined by (25), decreases by a factor of 2.

Let us discuss the influence of localized quantum particle upon the atomic density in a cluster. In general, the corresponding component of the pressure is determined by the last two terms of Eq. (2). For a considered system, the intrinsic pressure is of the form

$$P = \frac{2\tau(R)}{R} + P_q[\psi(r), \rho(r)]. \quad (27)$$

The pressure  $P_q$  due to an excess particle is defined by the derivative of energy  $dE/dV_{cl}$  over volume of the cluster for  $E = -E_b$ , where  $E_b$  is the binding energy of particle to a cluster. For a large cluster  $\int_0^R dr 4\pi r^2 |\psi(r)|^2 \rightarrow 1$ . Taking for  $E_b$  the expression derived [24] in the effective medium approach and the pseudopotential theory of scattering,

$$E_b = E_b^0 - \frac{\hbar^2 \pi^2}{2mR^2} (1 - C\xi), \quad (28)$$

where  $E_b^0$  is the standard binding energy component that contains Born correction;

$$E_b^0 = -V_0 - \frac{e^2}{2R} \frac{\varepsilon - 1}{\varepsilon}. \quad (29)$$

Here  $V_0 < 0$  is the ground-state energy of electron in an extended dielectric medium (Ar, Kr, Xe).  $R = N^{1/3} \bar{r}$  is the cluster radius,  $N$  is the number of its atoms and  $\bar{r}$  is the average distance between the atoms of density  $\rho = (4\pi \bar{r}^3/3)^{-1}$ . The dielectric constant,  $\varepsilon = 1 + 3\alpha/(\bar{r}^3 - \alpha)$ , where  $\alpha$  is atomic polarizability, was taken in the Clausius–Mossotti approximation,  $C \approx 2.86$ , and  $\xi = L/\bar{r}$  is the small parameter [24].

Then, the  $P_q$  component of pressure can be written as follows:

$$P_q \rightarrow \left\{ -\frac{e^2}{8\pi R^4} \frac{\varepsilon - 1}{\varepsilon} - \frac{\hbar^2 \pi}{4mR^5} (1 - C\xi) \right\}, \quad (30)$$

which is an analogue of the Thompson equation [25]. The “surplus” pressure  $P_q$  of quantum particle introduces an additional correction to the atomic density  $\Delta\rho_q = \rho_0 P_q / B_0^+$ . Simple estimations of the particle-induced tension for Xe cluster show that for  $N > 150$  the effect is weak, but it becomes noticeable with decreasing  $N$ . However, for smallest, i.e., nearly critical clusters, the physical picture becomes simpler, because occupation probability for electron (or positron) is close to zero, and the  $P_q$  term disappears.

### 3. Critical clusters

Consider the ground state of a particle localized in a small cluster. Using (2), let us write the standard wave equation for the radial wave function

$$\frac{d^2 u(r)}{dr^2} + \frac{2m}{\hbar^2} [E - V(r)] u(r) = 0, \quad (31)$$

where the potential  $V(r) \equiv V(R, r)$ ,  $u(r) = r\psi(r)$ , and  $\psi(r)$  is the particle's wave function. The ground-state wave function is symmetrical about the centre of cluster ( $r = 0$ ), so that the boundary conditions,  $u(0) = 0$  and  $u(\infty) = 0$ , have to be satisfied.

For a decreasing cluster size, the near-surface region occupies a considerable part of its volume and electron mainly can be found outside the formal cluster boundary at the polarization tail of the potential  $V(r > R)$ . It is stipulated by the electrostatic component of  $V(r)$ , which can be calculated exactly as the interaction energy of a point charge  $e^\pm$  with the dielectric sphere of radius  $R$ . The electrostatic component of  $V(r)$  has a nonphysical singularity at the cluster boundary. This singularity at  $r = R$  is removed by the usual cut-off procedure and replaced by a constant potential. The discontinuity of  $V(r)$  is an artefact of the model and has only a small influence on  $\psi(r)$  and the binding energy [10]. On the other hand, the short-range component of  $V(r)$  can be calculated only when  $r \leq R$  [24]. Thus, we assume that the one-particle potential  $V(r)$  in (31) can be represented by the following form, similar to Heine–Abarenkov electron–ion pseudopotential for a metal:

$$V(r) = \begin{cases} -E_b^0, & r < R, \\ V_p(R + \bar{r}/2), & R < r < R + \bar{r}/2, \\ V_p(r), & r > R + \bar{r}/2, \end{cases} \quad (32)$$

where for the polarization tail  $V_p(r)$ , the cut-off at  $r = R + \bar{r}/2$  is used, and

$$V_p(r) = -\frac{e^2 \varepsilon - 1}{2 \varepsilon + 1} \frac{R}{r^2} \left\{ \frac{R^2}{r^2 - R^2} - \frac{1}{\varepsilon + 1} \left[ \ln \left( \frac{r^2}{r^2 - R^2} \right) - \sum_{k=1}^{\infty} \frac{1}{k(k\varepsilon + k + 1)} \left( \frac{R}{r} \right)^{2k} \right] \right\}, \quad r > R. \quad (33)$$

The pseudopotential (32) has the right asymptotics:  $V(r) \rightarrow V_0$  for  $R \rightarrow \infty$ , and  $V(r) \rightarrow -N\alpha e^2/2r^4$ , for  $r/R \rightarrow \infty$ . The binding energy,  $E_b$ , results from a competition of kinetic and polarization energies, and for a critical cluster is close to zero. Thus, by solving (31) with (32)–(33), we find  $V(R^*, r)$  and consequently  $N^* = (R^*/\bar{r})^3$ .

The potential in the centre of large cluster can be assumed as the nearest to the bottom of the conduction band,  $V_0$ , in an infinite liquid. For a solid state,  $V_0$  is close to zero (in particular, for solid Ar) [26,27], and by taking into account Born's size correction and self-compression, it may even become positive (i.e., more incapable of retaining an electron). On the other hand, the polarization tail,  $V_p(r)$ , in the region  $r > R$ , depends rather weakly upon cluster state (liquid or solid). Therefore, it is clear that when the first bound state appears, the electron will probably be localized outside the cluster, in a near-surface state.

Unlike an electron, a positron will be located inside the cluster. In the large  $\text{Ar}_N$  cluster the value of  $V_0$  amounts to about  $-1$  eV, i.e., in the centre of cluster, positron feels a deep potential well. As will be seen, positrons localize in much smaller Ar clusters than electrons. This is conditioned by the relative prevalence of attraction over repulsion in the positron–atom interaction.

#### 4. Results and discussion

First, let us determine the coefficient  $\delta = c_1 + c_2$  for the calculation of  $\rho_2^+ = \frac{1}{2}\rho_1^+(\delta - \chi)$ . From the semi-empirical rule [23], derived from the vacancy formation energy and the cohesive energy results that  $c_1 = +0.5\bar{r}_0$ . The re-definition of “equimolecular surface” for icosahedral cluster [22] gives  $c_2 = -1.32\bar{r}_0$  and thus  $\delta = -0.82\bar{r}_0$ . The calculation of third-order derivative of the free energy with respect to density is a difficult problem. On the other hand, the third-order derivative in (25) can be expressed by the first derivative of the  $B_0^+(\rho_0^+)^2$  with respect to  $\rho_0^+$ . Let us make use of the well-known sum-rule for the compressibility

$$S_{k=0} = \frac{\rho_0^+ k_B T}{B_0^+}, \quad (34)$$

where  $S_{k=0}$  is the structure factor of a liquid for zeroth wave vector and for constant temperature,  $T$ . For the properties of extended liquids, the hard-sphere model gives good results; so we employed Percus–Yevick structure factor for a fluid,  $S_{HS} = (1 - \eta)^4 / (1 + 2\eta)^2$ . Here,  $\eta = \pi d^3 \rho_0^+ / 6$  is the packing fraction and  $d$  is the hard-sphere diameter. Then, we have  $\chi = (\gamma_0 / B_0^+) (\rho_0^+ / y) (\partial y / \partial \rho_0^+)$ , where  $y = k_B T / S_{HS} \rho_0^+ = B_0^+ / (\rho_0^+)^2$ . Using the experimental values for  $S_{k=0}$  at the triple point [28] we determine  $d$  and then  $\chi$ . This allows to rewrite expression (25), to a reasonable accuracy, in the following form:

$$\rho_2^+ = -\frac{1}{2} \zeta \bar{r}_0 \rho_1^+, \quad (35)$$

where  $\zeta$  is the constant (see Table 1). Comparing the values of  $\rho_1^+$  and  $\rho_2^+$  one can see that size tension has a noticeable effect on the atomic density corresponding to the smallest clusters.

Table 1

The calculated input values of  $V_0$ , and  $\zeta = L/r_0$  used for estimation of the binding energy  $E_b(N)$  of electron and positron. The data for  $\bar{r}_0$  and the values of structure factor  $S_{k=0}$  are taken from Ref. [28]. The positron scattering length at helium atom  $L_0 = -0.48a_0$  [29].  $a_0$  is the Bohr radius

Cluster	$T$ (K)	$\bar{r}_0$ ( $a_0$ )	$\zeta$	$V_0$ (eV)	$\frac{dV_0}{d\rho}$ (eV $\times a_0^3$ )	$\frac{\gamma_0}{B_0}$ ( $a_0$ )	$\zeta$
$\text{Xe}_N^-$	161.4	4.914	0.11	-0.609	1190	0.63	2.19
$\text{Kr}_N^-$	115.7	4.544	0.13	-0.454	676	0.57	2.03
$\text{Ar}_N^-$	83.8	4.251	0.18	-0.114	1191	0.49	1.94
$\text{Ar}_N^+$			-0.16	-0.977	-310		
$\text{Ne}_N^+$	24.8	3.531	-0.0076	-0.446	-17.8	0.46	1.85
$\text{He}_N^+$	4.2	4.404	-0.066	-0.259	-45.0	0.44	1.90

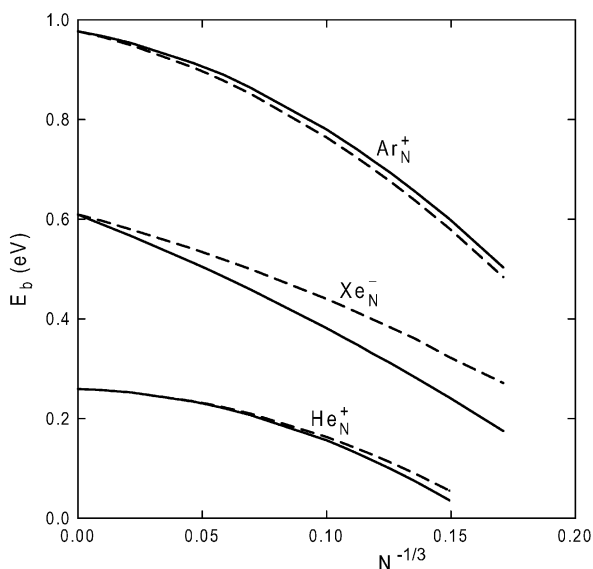


Fig. 1. The binding energy for electron and positron in rigid (dashed line) and self-compressed (solid line) clusters, calculated from Eq. (28).

It should be noted that compression of cluster leads to a rise/drop of the potential bottom,  $V_0$ , for electron/positron and to the increase of its kinetic energy owing to the decrease of cluster radius. The position of the bottom of the band shows strong dependence on the density of atoms (see Refs. [26,27] and Table 1). From now on, in order to simplify the calculations of the  $E_b^0(N)$  component in (29), for self-deformed clusters we employ the linear approximation:

$$V_0(\rho) = V_0(\rho_0) + \frac{dV_0}{d\rho}(\rho - \rho_0),$$

where  $\rho - \rho_0 = \rho_1^+/R_0 + \rho_2^+/R_0^2$ , and  $R_0 = N^{1/3}\bar{r}_0$ . Fig. 1 gives the comparison of the electron and positron binding energies, calculated from Eq. (28), for elastic, and for rigid clusters. The differences in energies are much greater than the energy,  $k_B T$ , of thermal excitation. One can see that the shrinkage of Xe and Kr clusters leads to a strong positive shift of the electron discrete energy level. This effect was not revealed by previous calculations for critical solid clusters [10,12]. For positron in the  $Ar_N$  clusters the self-compression leads to a negative shift in energy. Besides, for these clusters the  $E_b^0$  grows faster than the kinetic energy with decreasing  $R$ , therefore,  $E_b$  is bigger for self-compressed cluster than for a rigid one. For  $He_N$  this correlation breaks down. This is also reflected in the results for the critical positron clusters presented in Table 2.

The sizes of critical clusters  $N^*$  were determined by numerical solution of Eq. (31). To simplify the calculations we assume that  $V_p(r) = 0$ , for  $r > R + a$  [10]. Putting  $a = 7R$  (which is a good approximation because  $|V_p(R + a)| < 0.1$  meV, and also owing to the fact that the wave function in the region  $r > R + a$  has a purely exponential form)

Table 2

Number of atoms constituting the electron and positron critical clusters for different rare gases and two different binding potentials. The values of  $E_b$  and  $N^*$  are determined quantum-mechanically with the potential given by (32)

Cluster	Rigid		Elastic	
	$E_b$ (meV)	$N^*$	$E_b$ (meV)	$N^*$
$\text{Xe}_N^-$	0.89	5	1.1	6
$\text{Kr}_N^-$	0.13	8	0.019	9
$\text{Ar}_N^-$	0.049	22	1.0	101
$\text{Ar}_N^+$	3.2	5	4.5	5
$\text{Ne}_N^+$	0.02	19	0.07	20
$\text{He}_N^+$	0.02	20	0.0005	20

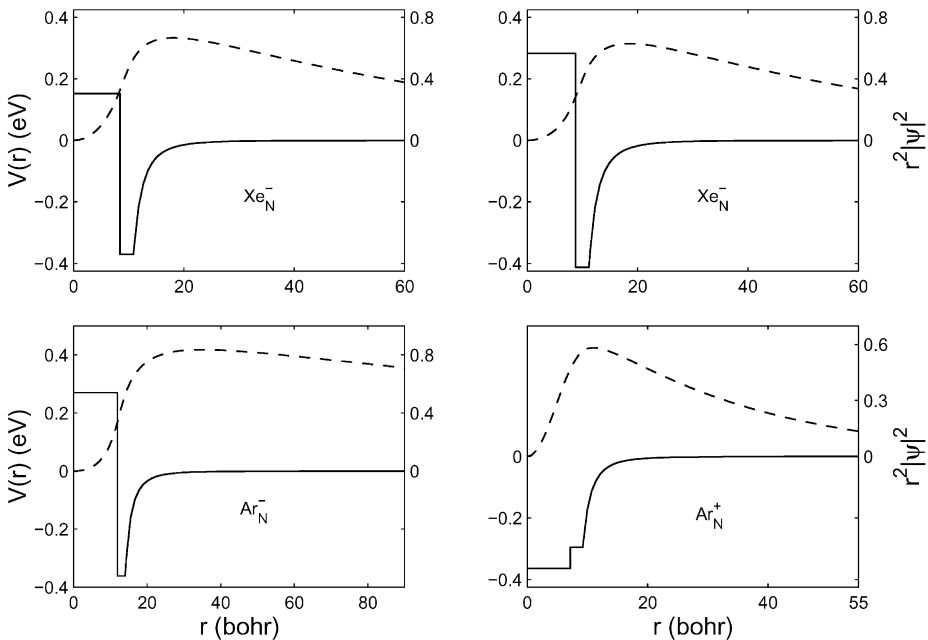


Fig. 2. The pseudopotential (solid line and left-hand side axis) and the corresponding density  $|u(r)|^2 = |r\psi(r)|^2$  (dashed line and right-hand side axis) for electron in Xe and Ar cluster: Rigid  $\text{Xe}_N^-$  (top left), elastic  $\text{Xe}_N^-$  (top right), rigid  $\text{Ar}_N^-$  (bottom left), elastic  $\text{Ar}_N^+$  (bottom right). The respective cluster's radii are  $R^* = 8.40, 8.77, 11.91,$  and  $7.27$  bohr.

we can replace the boundary condition outside the cluster from  $r = \infty$  to  $R + a$  and set

$$\frac{d}{dr} \ln u(r) = -\sqrt{\frac{2mE_b}{\hbar^2}}.$$

We determine the critical  $N^*$  by calculating the least positive value of the binding energy. The results of calculations for  $N^*$  and  $E_b$  are presented in Table 2. The actual forms of the pseudopotential (32) and the density  $|u(r)|^2$  for electron in Xe and Ar and positron in Ar critical clusters are plotted in Fig. 2.

Numerical solutions of Eq. (31) confirm the role of self-deformation. The values of  $N^*$  calculated for the rigid and elastic clusters may differ even by a factor of 4.5. This is caused by a significant magnitude of the derivative  $dV_0/d\rho$ . However, in smallest clusters the size self-compression is neutralized by the size self-tension.

Analysing the results for elastic electronic clusters, it is seen that the calculated critical number for  $\text{Xe}_N^-$  agrees with the experimental result giving  $N^* = 5-8$  [11]. The agreement with another theoretical result for solid Xe and Kr clusters ( $N^* = 8$  and 14) is also good, but not for Ar ( $N^* = 46$ ) [15]. Our calculations demonstrate the noticeable influence of self-compression, which leads to increase of  $N$  by 30–50%. In view of the latter fact, the accurate prediction of critical number  $N^*$  by the authors of Refs. [11,12] should be considered rather as fortuitous.

## 5. Summary

The problem of electron and positron droplets of polarisable fluids has been considered. We have developed formal density-functional theory of a finite classical system which allows to account for the effect of self-compression, originating from the curvature of droplet surface, and the effect of self-tension due to reduction of the droplet's size. The theory was applied to calculate the elastic effects in large as well as in critical (small) clusters. The critical sizes of clusters were determined quantum-mechanically by solving the Schrödinger equation. Our calculations show that the effects of self-compression and self-tension give a significant contribution to the critical sizes of clusters charged by electron and should be taken into consideration in any comparison of critical cluster's sizes with the measured ones. For positron-charged clusters the elastic effects are negligible. Although the method applied here is based on the concepts of surface tension and pressure and thus, it cannot pretend to the highest accuracy, it allows, however, to present a clear physical picture of the problem.

The behaviour of the one-particle potential  $V(r)$  of electronic clusters qualitatively resembles that for the positron in a metal with negative positron work function (Al, Mo, Fe, Ni). It suggests a possibility of application of our method to metallic clusters charged by positron. The results of this investigation may find application in positron diagnostics in ultradispersed media and possibly in rare-gas atoms nanotechnology.

## Acknowledgements

One of us (AK) is grateful to Prof. Bengt Lundqvist for the support and hospitality at Chalmers at the final stage of this work.

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