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Volume change of bulk simple metals and simple metal clusters due to spin polarization

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Abstract

The stabilized jellium model (SJM) provides us with a method for calculating the volume changes of different simple metals as functions of the spin polarization, ζ, of the delocalized valence electrons. Our calculations show that for bulk metals, the equilibrium Wigner–Seitz (WS) radius, $\bar{r}_s^B(\zeta)$, is always an increasing function of the polarization, i.e., the volume of a bulk metal always increases as ζ increases, and the rate of increase is higher for higher-electron-density metals. Using the SJM along with the local spin-density approximation, we have also calculated the equilibrium WS radius, $\bar{r}_s(N, \zeta)$, of spherical jellium clusters, at which the pressure on the cluster with given number of total electrons N with spin configuration ζ vanishes. Our calculations for Cs, Na, and Al clusters show that $\bar{r}_s(N, \zeta)$ as a function of ζ behaves differently depending on whether N corresponds to a closed-shell or an open-shell cluster. For a closed-shell cluster, it is an increasing function of ζ over the whole range $0 \leqslant \zeta \leqslant 1$, whereas for open-shell clusters it has a decreasing behaviour over the range $0 \leqslant \zeta \leqslant \zeta_0$, where ζ_0 is a polarization such that the cluster has a configuration consistent with Hund's first rule. The results show that for all neutral clusters with the ground-state spin configuration, ζ_0, the inequality $\bar{r}_s(N, \zeta_0) \leqslant \bar{r}_s^B(0)$ always holds (self-compression) but, at some polarization $\zeta_1 > \zeta_0$, the inequality changes direction (self-expansion). However, the inequality $\bar{r}_s(N, \zeta) \leqslant \bar{r}_s^B(\zeta)$ always holds and equality is achieved in the limit $N \to \infty$.

1. Introduction

The jellium model (JM) with spherical geometry is the simplest model used in the theoretical study of simple metal clusters [1–3]. In the spherical JM, the ions are smeared onto a uniform positive charge background sphere of density $n = 3/4\pi r_s^3$ and radius $R = (zN)^{1/3} r_s$ where z and N are the valence of the atom and the number of constituent atoms of the cluster, respectively. In simple JM calculations the value of r_s is taken to be the bulk value of the Wigner–Seitz (WS) radius of the metal. In some calculations involving metal surfaces, one may use the diffuse JM to take account of the ion relaxations at the surface of the metal [4]. However, it is a well-known fact [5,6] that the simple JM yields negative surface energies at high

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electron densities ($r_s \leqslant 2$), and negative bulk moduli for $r_s \approx 6$. Also, using the simple JM, it is not possible to find realistic sizes and energetics for metal clusters. These drawbacks have their roots in the mechanical instability [7,8] of the simple JM system. That is, the bulk jellium system is stable only for $r_s = 4.18$. In 1990, Perdew *et al* introduced the stabilized jellium [8] model (SJM) by adding two corrections to the simple JM energy. The first correction subtracts the spurious self-energy of each WS cell from the JM energy, and the second correction adds to the energy the effect of the difference between the potentials that an electron 'sees' from the discrete pseudoions and from the jellium background. The second correction introduces the core radius parameter, r_c, of the pseudopotential which can be adjusted, for each metal, in such a way that the stability of the bulk metal is achieved at its observed r_s-value for the valence electrons. Using the value r_c^B for the core radius (which stabilizes the unpolarized bulk system) in the SJM energy functional of a spin-polarized bulk system or a cluster, it is possible to find the equilibrium r_s-value for any given spin polarization ζ.

In the present work, using the above-mentioned method, we have calculated the changes in the equilibrium r_s-values due to polarization for bulk Cs, K, Na, Li, Ga, Al, and for Cs, Na, Al clusters, in the framework of the local spin-density approximation (LSDA). Our calculations show that for the bulk system the volume is always an increasing function of the polarization and the rate of increase is higher for higher-electron-density metals. This result is an improvement over our earlier work [9] in which we had roughly assumed the same increment for different metals (see equation (19) of reference [9]). Also, we have solved the self-consistent Kohn–Sham (KS) equations [10] for Cs, Na, and Al clusters of different sizes in the spherical SJM and obtained the equilibrium sizes of the clusters for each spin configuration consistent with Pauli's exclusion principle. The results show that in a closed-shell cluster with N total electrons and polarization ζ, the equilibrium WS radius $\bar{r}_s(N, \zeta)$ is an increasing function of ζ over the whole range $0 \leqslant \zeta \leqslant 1$ whereas, for an open-shell cluster (except for the two nearest neighbours of a closed-shell cluster), it has a decreasing behaviour over $0 \leqslant \zeta \leqslant \zeta_0$, and an increasing behaviour over $\zeta_0 \leqslant \zeta \leqslant 1$. Here, ζ_0 corresponds to an electronic spin configuration for which Hund's first rule is satisfied. This behaviour is a direct consequence of assuming a spherical geometry for the jellium background, which has been shown [11] to apply to simple JM 'generic clusters'. By 'generic cluster' we mean a system composed of $N_\uparrow$ up-spin and $N_\downarrow$ down-spin valence electrons ($N_\uparrow + N_\downarrow = N$) and a simple jellium spherical background of radius $R = N^{1/3} r_s$, in which the parameter r_s takes a value that minimizes the total energy (equations (10), (11)) of the system with an specified electronic configuration (for details see reference [11]). Here, also, we have shown that the equilibrium r_s-values for a neutral cluster are always smaller than that of the bulk metal with the same value of the polarization ζ. This effect, which is due to the surface tension, becomes more significant for smaller clusters. This result is in contrast to the result obtained for 'generic clusters' (see figures 4 and 5 of reference [11]). For 'generic clusters' we had shown that the simple JM always predicts equilibrium r_s-values which are larger than the bulk value. These opposite behaviours are compared in figure 5 of this work—see later. Further, we have shown here that for an N-electron neutral cluster there exists a polarization value ζ_1 beyond which the equilibrium r_s-value of the cluster exceeds the bulk r_s-value of unpolarized metal. This is called self-expansion [12–14] and for two different neutral clusters with the same number of electrons N, the ζ_1-value of the higher-electron-density metal is smaller than that of the lower-density metal.

The structure of this paper is as follows. In section 2 we first show the method by which one can calculate the changes in r_s-values due to spin polarization for different bulk metals. We then explain how to apply the method to metal clusters in order to calculate the equilibrium r_s-values for different spin configurations. In section 3 we present the results of our calculations and, finally, the work is concluded in section 4.

2. Calculational scheme

In the context of the SJM, the average energy per valence electron in the bulk with density parameter r_s and polarization ζ is given by [9]

$$\varepsilon(r_s, \zeta, r_c) = t_s(r_s, \zeta) + \varepsilon_{xc}(r_s, \zeta) + \bar{w}_R(r_s, r_c) + \varepsilon_{\mathrm{M}}(r_s) \tag{1}$$

where

$$t_s(r_s, \zeta) = \frac{c_k}{r_s^2}\left[(1+\zeta)^{5/3} + (1-\zeta)^{5/3}\right] \tag{2}$$

$$\varepsilon_{xc}(r_s, \zeta) = \frac{c_x}{r_s}\left[(1+\zeta)^{4/3} + (1-\zeta)^{4/3}\right] + \varepsilon_c(r_s, \zeta) \tag{3}$$

$$c_k = \frac{3}{10}\left(\frac{9\pi}{4}\right)^{2/3} \qquad c_x = \frac{3}{4}\left(\frac{9}{4\pi^2}\right)^{1/3}. \tag{4}$$

All equations throughout this paper are expressed in Rydberg atomic units. Here t_s and ε_{xc} are the mean non-interacting kinetic energy and the exchange–correlation energy per particle, respectively. For ε_c we use the Perdew–Wang parametrization [15]. Here, ε_{M} is the average Madelung energy, $\varepsilon_{\mathrm{M}} = -9z/5r_0$, and r_0 is the radius of the WS sphere, $r_0 = z^{1/3}r_s$. We set for monovalent metals $z = 1$, and for polyvalent metals we set $z^* = 1$. That is, for polyvalent metals we replace each Wigner–Seitz cell by z cells, each having a volume $4\pi r_s^3/3$. This improves the results for polyvalent metals in which the band-structure effects make an important contribution to the bulk modulus (for details see reference [8]). In equation (1), $\zeta = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$ in which $n_\uparrow$ and $n_\downarrow$ are the spin densities of the homogeneous system with total density $n = n_\uparrow + n_\downarrow$. The quantity $\bar{w}_R$ is the average value (over the WS cell) of the repulsive part of the Ashcroft empty-core [16] pseudopotential:

$$w(r) = -\frac{2z}{r} + w_R \qquad w_R = +\frac{2z}{r}\theta(r_c - r) \tag{5}$$

and is given by $\bar{w}_R = 3r_c^2/r_s^3$ where z is the valence of the atom, and $\theta(x)$ is the ordinary step function which assumes the value of unity for positive arguments and zero for negative values.

The core radius is fixed at the bulk value, r_c^B, by setting the pressure of the unpolarized bulk system equal to zero at the observed equilibrium density $\bar{n} = 3/4\pi[\bar{r}_s^B(0)]^3$:

$$\left.\frac{\partial}{\partial r_s}\varepsilon(r_s, 0, r_c)\right|_{r_s=\bar{r}_s^B(0), r_c=r_c^B} = 0. \tag{6}$$

Here, $\bar{r}_s^B(0) \equiv \bar{r}_s^B(\zeta = 0)$ is the observed equilibrium density parameter for the unpolarized bulk system, and takes the values 2.07, 2.19, 3.28, 3.99, 4.96, 5.63 for Al, Ga, Li, Na, K, Cs, respectively. The derivative is taken at fixed r_c, and the solution of the above equation gives r_c^B as a function of $\bar{r}_s^B(0)$:

$$r_c^B[\bar{r}_s^B(0)] = \frac{1}{3}[\bar{r}_s^B(0)]^{3/2}\left\{\left[-2t_s(r_s, 0) - \varepsilon_x(r_s, 0) + r_s\,\frac{\partial}{\partial r_s}\varepsilon_c(r_s, 0) - \varepsilon_{\mathrm{M}}(r_s)\right]_{r_s=\bar{r}_s^B(0)}\right\}^{1/2}. \tag{7}$$

Inserting r_c^B from equation (7) into equation (1), the equilibrium r_s-value of the polarized bulk system, $\bar{r}_s^B(\zeta)$, is obtained by solving the equation

$$\left.\frac{\partial}{\partial r_s}\varepsilon(r_s, \zeta, r_c^B)\right|_{r_s=\bar{r}_s^B(\zeta)} = 0. \tag{8}$$

The derivative is taken at fixed ζ and r_c^B. The solution gives the equilibrium density parameter $\bar{r}_s^B(\zeta)$ as a function of the polarization. In this procedure, by taking a constant value for the core radius of the pseudopotential, we have assumed that the core region of an atom is rigid and does not change in the process of the spin polarization of the delocalized valence electrons. This approximation works well when the distance between the neighbouring atoms is sufficiently larger than the extension of the core-electron-orbital wave functions.

The SJM energy for a spin-polarized system with boundary surface is [8]

$$E_{\mathrm{SJM}}\left[n_\uparrow, n_\downarrow, n_+\right] = E_{\mathrm{JM}}\left[n_\uparrow, n_\downarrow, n_+\right] + (\varepsilon_{\mathrm{M}}(r_s) + \bar{w}_R(r_s, r_c^B)) \int \mathrm{d}\boldsymbol{r}\; n_+(\boldsymbol{r}) + \langle \delta v \rangle_{\mathrm{WS}}(r_s, r_c^B) \int \mathrm{d}\boldsymbol{r}\; \Theta(\boldsymbol{r})\,[n(\boldsymbol{r}) - n_+(\boldsymbol{r})] \tag{9}$$

where

$$E_{\mathrm{JM}}\left[n_\uparrow, n_\downarrow, n_+\right] = T_s\left[n_\uparrow, n_\downarrow\right] + E_{xc}\left[n_\uparrow, n_\downarrow\right] + \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\; \phi([n, n_+]; \boldsymbol{r})\,[n(\boldsymbol{r}) - n_+(\boldsymbol{r})] \tag{10}$$

and

$$\phi([n, n_+]; \boldsymbol{r}) = 2\int \mathrm{d}\boldsymbol{r}'\; \frac{\left[n(\boldsymbol{r}') - n_+(\boldsymbol{r}')\right]}{|\boldsymbol{r} - \boldsymbol{r}'|}. \tag{11}$$

Here, $n = n_\uparrow + n_\downarrow$ and n_+ is the jellium density. $\Theta(\boldsymbol{r})$ takes the value of unity inside the jellium background and zero outside. The first and second terms in the right-hand side of equation (10) are the non-interacting kinetic energy and the exchange–correlation energy, and the last term is the Coulomb interaction energy of the system. The quantity $\langle \delta v \rangle_{\mathrm{WS}}$ is the average of the difference potential over the Wigner–Seitz cell and the difference potential, δv, is defined as the difference between the pseudopotential of a lattice of ions and the electrostatic potential of the jellium positive background. The effective potential, used in the self-consistent KS equations, is obtained by taking the variational derivative of the SJM energy functional with respect to the spin densities as

$$v_{eff}^\sigma([n_\uparrow, n_\downarrow, n_+]; \boldsymbol{r}) = \frac{\delta}{\delta n_\sigma(\boldsymbol{r})}(E_{\mathrm{SJM}} - T_s) = \phi([n, n_+]; \boldsymbol{r}) + v_{xc}^\sigma([n_\uparrow, n_\downarrow]; \boldsymbol{r}) + \Theta(\boldsymbol{r})\langle \delta v \rangle_{\mathrm{WS}}(r_s, r_c^B) \tag{12}$$

where $\sigma = \uparrow, \downarrow$. By solving the KS equations

$$(\nabla^2 + v_{eff}^\sigma(\boldsymbol{r}))\phi_i^\sigma(\boldsymbol{r}) = \varepsilon_i^\sigma \phi_i^\sigma(\boldsymbol{r}) \qquad \sigma = \uparrow, \downarrow \tag{13}$$

$$n(\boldsymbol{r}) = \sum_{\sigma=\uparrow,\downarrow} n_\sigma(\boldsymbol{r}) \tag{14}$$

$$n_\sigma(\boldsymbol{r}) = \sum_{i(occ)} \left|\phi_i^\sigma(\boldsymbol{r})\right|^2 \tag{15}$$

and finding the self-consistent values for ε_i^σ and ϕ_i^σ, one obtains the total energy.

In our spherical JM, we have

$$n_+(\boldsymbol{r}) = \frac{3}{4\pi r_s^3}\theta(R - r) \tag{16}$$

in which $R = (zN)^{1/3} r_s$ is the radius of the jellium sphere, and $n(\boldsymbol{r})$ denotes the electron density at point $\boldsymbol{r}$ in space. Using equation (21) of reference [8], this average value is given by

$$\langle \delta v \rangle_{\mathrm{WS}}(r_s, r_c^B) = \frac{3(r_c^B)^2}{r_s^3} - \frac{3}{5r_s}. \tag{17}$$

Applying equation (9) to a metal cluster which contains $N_\uparrow$ spin-up and $N_\downarrow$ spin-down electrons—a total of N $(=N_\uparrow + N_\downarrow)$ electrons—the SJM energy becomes a function of N, $\zeta \equiv (N_\uparrow - N_\downarrow)/N$, r_s, and r_c^B. The equilibrium density parameter, $\bar{r}_s(N, \zeta)$, for a cluster is the solution of the equation

$$\frac{\partial}{\partial r_s} E(N, \zeta, r_s, r_c^B)\bigg|_{r_s=\bar{r}_s(N,\zeta)} = 0. \tag{18}$$

Here again, the derivative is taken at fixed values of N, ζ, and r_c^B. For an N-electron cluster, we have solved the KS equations [10] self-consistently for various spin configurations and r_s-values and obtained the equilibrium density parameter, $\bar{r}_s(N, \zeta)$, and its corresponding energy, $\bar{E}(N, \zeta) \equiv E(N, \zeta, \bar{r}_s(N, \zeta), r_c^B)$ for each allowed spin configuration.

3. Results

In figure 1 we have shown the r_c^B-values obtained from the application of equation (7) to different r_s-values. Different metals are indicated by the full squares. It is seen that the plot shows a linear behaviour for metals with relatively low electron density. Inserting these values of r_c^B into equation (1) and solving equation (8) for different values of the polarization, ζ, we have obtained the equilibrium r_s-values for different bulk metals at various polarizations. The values obtained at $\zeta = 1$ are 2.62, 2.72, 3.69, 4.36, 5.28, and 5.93 for Al, Ga, Li, Na, K, and Cs, respectively. The result for all polarizations $(0 \leqslant \zeta \leqslant 1)$ is shown in figure 2.

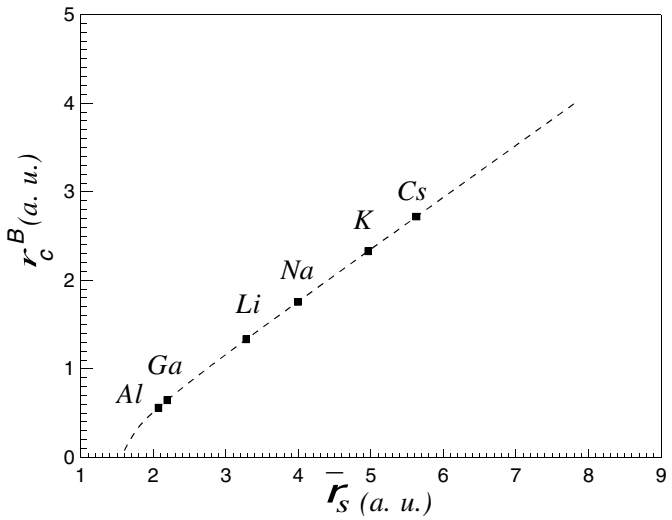


Figure 1. The pseudopotential core radius, r_c^B, in atomic units as a function of the equilibrium r_s-value of the bulk metal. The full squares indicate different metals (see also table 1 of reference [8]). The plot shows a linear behaviour at rather low densities.

In figure 2, we have plotted the changes in the equilibrium r_s-values relative to the unpolarized value as a function of the polarization for different metals. The results show an increasing behaviour for all metals but the rate of increase is higher for higher-electron-density metals. This property can easily be explained in terms of the short-range Pauli repulsive force between parallel-spin electrons which is due to the antisymmetry of the many-electron wave function. In other words, each electron creates a Fermi hole around itself which is

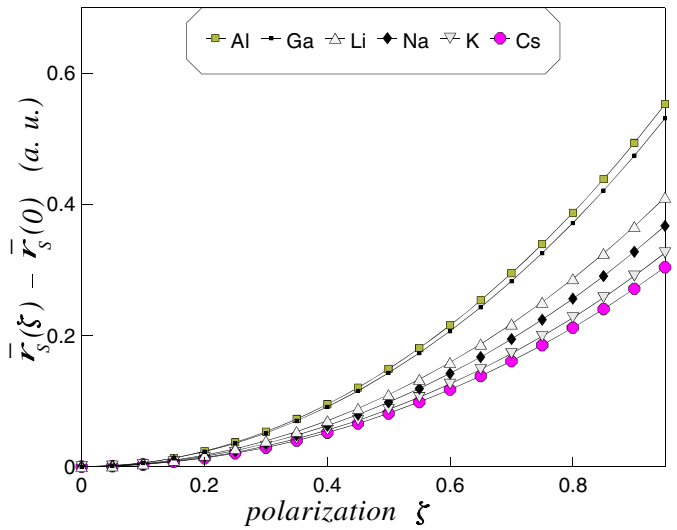


Figure 2. The changes in the equilibrium WS radius relative to the unpolarized value, $[\bar{r}_s^B(\zeta) - \bar{r}_s^B(0)]$, in atomic units, for different metals as functions of the polarization, ζ. All have increasing behaviours and the rate of increase is higher for higher-electron-density metals.

due to the repulsion of other electrons with the same spin polarization [17]. By increasing the polarization, we increase the number of potentially repelling up-spin electrons. Now, as soon as the characteristic volume $(4\pi/3)R_P^3 N_\uparrow$ exceeds the equilibrium volume of the spin-compensated system, the volume of the system starts to increase. Here, R_P is taken as a measure of the effective range of the Pauli force. For metals with very low electron density this condition will never be met and, therefore, no excess repulsive force will act on the electrons to increase the volume. The volumes of these metals are not sensitive to the spin polarization. However, on the other hand, for metals with sufficiently higher electron density this condition will be met at some value for $N_\uparrow$. Obviously, for a higher-electron-density system this condition will be met for a smaller value of $N_\uparrow$, and therefore smaller polarization. Hence, for the same value of the polarization, the volume change of the higher-electron-density metal will be greater than that of the lower-electron-density metal. This explains qualitatively the higher rate of increase for Al and the lower rate of increase for Cs metals.

Figure 3 shows a plot of $\langle \delta v \rangle_{WS}(\bar{r}_s^B(0), r_c^B[\bar{r}_s^B(0)])$, obtained from equations (17) and (7), as a function of the bulk equilibrium WS radius, $\bar{r}_s^B(0)$. The full squares correspond to different metals. The value of $\langle \delta v \rangle_{WS}$ for Na is vanishingly small because the equilibrium r_s-value of sodium is very close to 4.18, at which this average vanishes. For values of r_s greater than 4.18, the correction to the KS effective potential is positive (see equation (12)) and this decreases the well depth and cause the electrons to relax outward to make the pressure on the system (due to jellium model) to vanish. In this case, the leakage of the electrons across the jellium boundary surface is increased relative to the simple JM case. On the other hand, for $r_s < 4.18$ the potential depth is increased by the correction and the electrons should decrease their relative mean distance to make the pressure on the jellium system vanish. Therefore, the leakage of the electrons decreases relative to the simple jellium model case.

In figure 4, using equations (7), (8), and (17) we have plotted the variation of $\langle \delta v \rangle_{WS}(\bar{r}_s^B(\zeta), r_c^B))$ as a function of ζ for different metallic densities. For low-electron-density metals, it has a decreasing behaviour, and in the case of K metal, there is a change in the sign

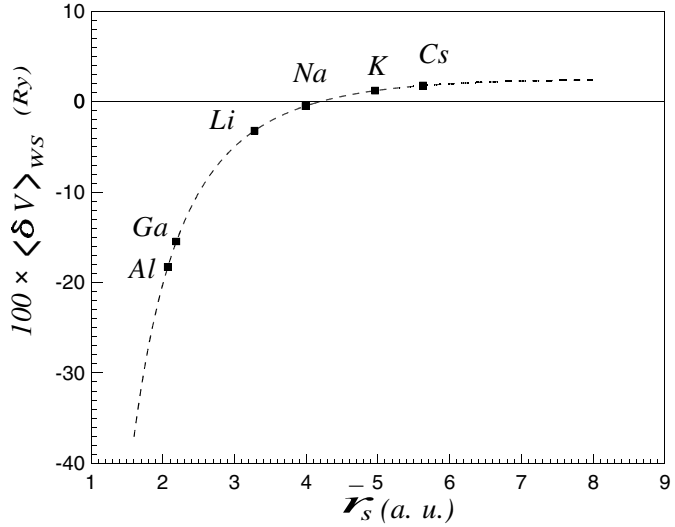


Figure 3. The average value of the difference potential, in rydbergs, as a function of the equilibrium WS radius for a bulk jellium system. The full squares correspond to different metals.

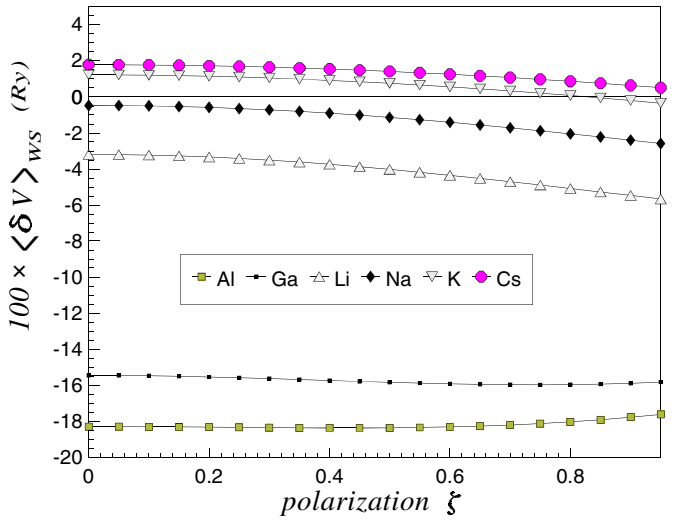


Figure 4. The average values of the difference potential, in rydbergs, as functions of the polarization for different bulk metals. The plots show decreasing behaviours for Cs, K, Na, Li over the whole range; whereas the plots for Ga and Al show decreasing behaviours at low polarizations, and increasing behaviours at higher polarizations with minima in between.

at high polarizations. However, for Al and Ga, it shows rather different behaviours. That is, Cs, K, Na, Li show a decreasing behaviour over the whole range $0 \leqslant \zeta \leqslant 1$ whereas Al and Ga have decreasing behaviours at lower polarizations and increasing behaviours at higher polarizations. These different behaviours can be explained by the detailed analysis of equation (17). The right-hand side of equation (17) has a physical minimum at $r_s = \sqrt{15} r_c^B$. In order to realize this minimum for a metal over the range $0 \leqslant \zeta \leqslant 1$, the core radius of that

metal should satisfy the inequality

$$\frac{\bar{r}_s^B(0)}{\sqrt{15}} \leqslant r_c^B \leqslant \frac{\bar{r}_s^B(1)}{\sqrt{15}}. \tag{19}$$

In the above inequality, $\bar{r}_s^B(0)$ and $\bar{r}_s^B(1)$ are the bulk equilibrium values at $\zeta = 0$ and $\zeta = 1$, respectively. Examination for different metals shows that, out of the six above-mentioned metals, only Al and Ga with respective core radius values of 0.56 and 0.65 satisfy this constraint. Comparing this figure with figure 1 of reference [9], one sees different behaviours for high-electron-density metals. The incorrect behaviour predicted by the previous [9] SSPJM has roots in the rough estimation used there for the increment in r_s due to polarization; whereas here, as shown in figure 2, the increment for each metal has been calculated separately in a self-consistent way.

In figure 5 we have compared the different behaviours of the ground-state equilibrium r_s-values predicted by the simple JM for 'generic clusters' and the SJM for Na clusters. In the limit of $N \to \infty$, the infinite 'generic clusters' approach the infinite electron gas system for which $\zeta \to 0$ and $\bar{r}_s \to 4.18$. As is shown in figure 5, the equilibrium r_s-value for the generic cluster approaches the bulk value, 4.18, from above, which does not simulate the correct behaviour for a real metal cluster. However, for the Na clusters, we see that the SJM predicts equilibrium r_s-values which are always smaller than the bulk value, 3.99. This comparison clearly shows that the simple JM overestimates the bond lengths.

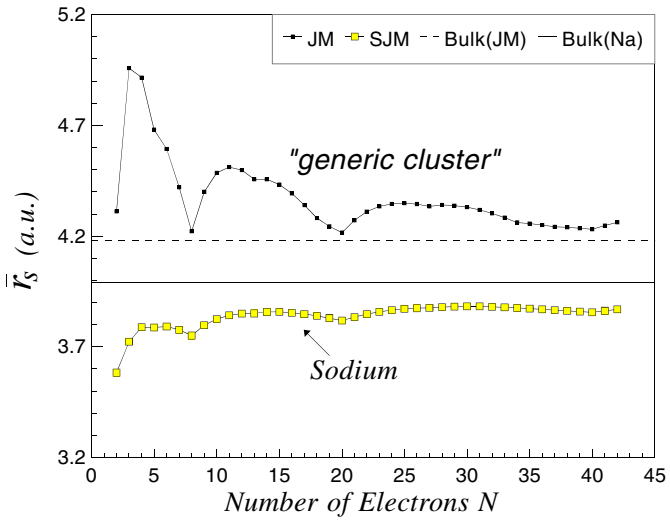


Figure 5. The equilibrium r_s-values for the ground states, in atomic units, as functions of the cluster size N. The solid squares correspond to the 'generic clusters' and the large squares correspond to the SJM results for Na clusters. The dashed and solid lines correspond to the equilibrium r_s-value of the bulk (4.18) in the simple JM and to the bulk value of sodium (3.99), respectively.

In order to find the equilibrium size of an N-electron cluster in the SJM for various spin configurations of $N_\uparrow - N_\downarrow = 0$, $N_\uparrow - N_\downarrow = 2$, $N_\uparrow - N_\downarrow = 4$, ..., $N_\uparrow - N_\downarrow = N_\uparrow$, keeping the total number of electrons, $N_\uparrow + N_\downarrow = N$, fixed, we solve equation (18) using the set of self-consistent equations (12)–(15). In the above we have assumed an even total number of electrons, N. For an odd number of electrons, the differences $(N_\uparrow - N_\downarrow)$ would also be odd numbers.

In figures 6(a)–6(c) we have plotted the equilibrium r_s-values, $\bar{r}_s(N,\zeta)$, obtained for different spin configurations, as a function of $\zeta \equiv (N_\uparrow - N_\downarrow)/N$ for Cs, Na, and Al clusters. To clarify the different behaviours of the closed-shell and open-shell clusters, we have studied the $N = 8$, 20, 40 cases which are closed-shell clusters and the $N = 27$ case which is an open-shell cluster. We have also compared the result with the bulk case. In figures 6, the dashed lines correspond to the equilibrium WS radius of the unpolarized bulk metal, $\bar{r}_s^B(0)$. For all the closed-shell clusters, $\bar{r}_s(N,\zeta)$ is an increasing function of ζ while for the open-shell cluster, $N = 27$, it is decreasing over $0 \leqslant \zeta \leqslant 7/27$, and increasing over $7/27 \leqslant \zeta \leqslant 1$. Here, $\zeta_0 = 7/27$ corresponds to an electronic spin configuration for which Hund's first rule is satisfied. That is, the configuration in which the up-spin shell with $l = 3$ is half-filled ($1s^2 1p^6 1d^{10} 2s^2 1f^7$). This difference between closed-shell and open-shell clusters can be explained as follows. For an open-shell cluster if one increases the spin polarization from a possible minimum value consistent with the Pauli exclusion principle, one should make a spin flip in the last incomplete shell. Because of high degeneracy for the spherical geometry, this spin flip in the last shell does not appreciably change the kinetic energy contribution to the total energy, but does appreciably change the exchange–correlation energy which in turn gives rise to a deeper effective potential that makes the KS orbitals more localized and therefore leads to a smaller size for the cluster. On the other hand, in closed-shell clusters increase in the polarization is always accompanied by transitions of electrons to unoccupied shells that have larger kinetic energies which leads to larger cluster sizes.

In figures 6 we notice that as the size of the cluster increases, the plot of $\bar{r}_s(N,\zeta)$ resembles much more the bulk function $\bar{r}_s^B(\zeta)$ and approaches it so that, as is expected, we have

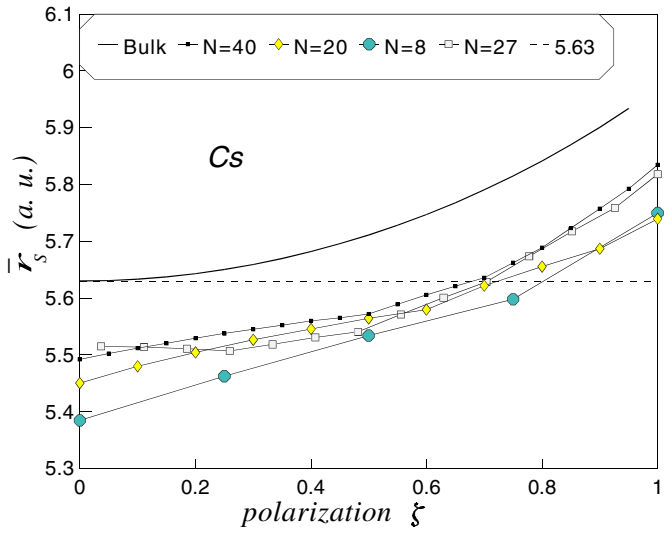
$$\lim_{N\to\infty} \bar{r}_s(N,\zeta) = \bar{r}_s^B(\zeta). \tag{20}$$

As we see, in all neutral clusters, the inequality

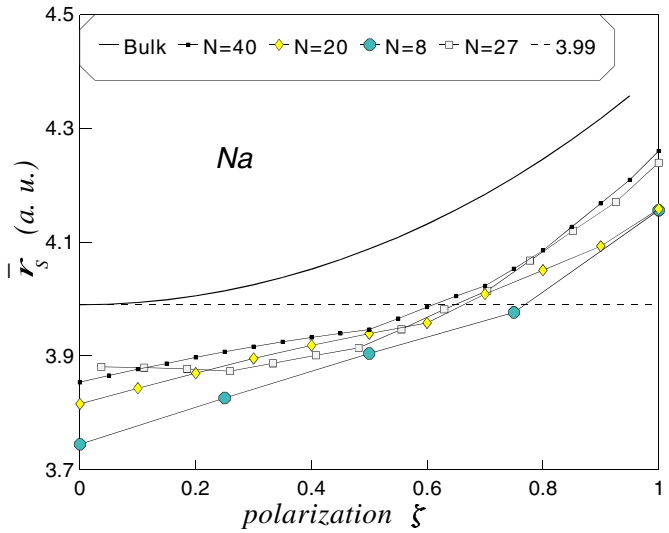
$$\bar{r}_s(N,\zeta) \leqslant \bar{r}_s^B(0) \tag{21}$$

always holds for the ground state of the cluster in which $\zeta = \zeta_0$. This effect is called self-compression [12] and is due to surface tension. Now if we increase the polarization of the cluster, $\zeta \equiv (N_\uparrow - N_\downarrow)/N$, relative to ζ_0 and obtain the equilibrium WS radius by solving equation (18), we then see that beyond some polarization, ζ_1, the inequality in equation (21) changes direction and the equilibrium r_s-value of the cluster exceeds the bulk value $\bar{r}_s^B(0)$. This is called self-expansion which originates from the Pauli force. Self-expansion is also observed in charged metal clusters [13], and originates from the Coulombic repulsion force. Here, the value of ζ_1 is shifted toward zero as the size of the cluster increases. Also, comparison of figures 6(a)–6(c) shows that for two clusters with the same N, the value of ζ_1 is smaller for higher-electron-density metal. It is also interesting to look at the plot of $\bar{r}_s(N,\zeta_0)$ as a function of N (see the lower plot in figure 5 for sodium). As we increase N from one 'magic' number to the next one, the polarization ζ_0 increases from the value of zero for the closed-shell cluster to a maximum for a half-filled-shell cluster and then decreases to zero. As we see, $\bar{r}_s(N,\zeta_0)$ for the half-filled-shell cluster is larger than those for the corresponding consecutive 'magic' numbers. In a 'magic' cluster all electronic shells are completely occupied by electrons.

In figures 7(a)–7(c), we have plotted the quantity $\langle \delta v \rangle_{\mathrm{WS}}$ for Cs, Na, Al clusters of different sizes, as a function of ζ, using the equilibrium values $\bar{r}_s(N,\zeta)$ in equation (17); and have compared with their respective bulk functions. It is seen that for metals for which the inequality in equation (20) does not hold, this quantity has a decreasing behaviour whenever $\bar{r}_s(N,\zeta)$ has an increasing behaviour, and vice versa. For Cs clusters in figure 7(a), the quantity has positive values over the whole range $0 \leqslant \zeta \leqslant 1$. In figure 7(b), for Na clusters, this quantity changes sign beyond some ζ-value. The Al clusters in figure 7(c) have negative values for $\langle \delta v \rangle_{\mathrm{WS}}$ and they show minima as discussed before.



(a)

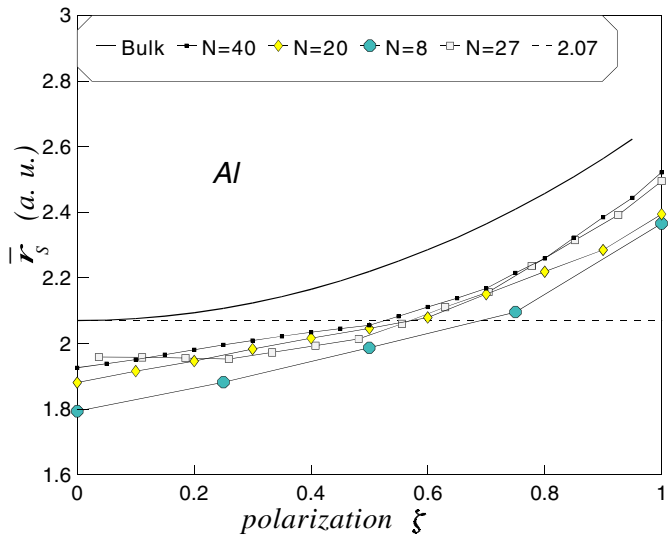


(b)

Figure 6. The equilibrium WS radius, $\bar{r}_s(N, \zeta)$, in atomic units, as functions of the polarization for (a) Cs, (b) Na, (c) Al clusters. In all closed-shell clusters (here, $N = 8$, 20, 40) $\bar{r}_s(N, \zeta)$ is an increasing function of ζ while for the open-shell cluster (here, $N = 27$) it is decreasing over $0 \leqslant \zeta \leqslant 7/27$, and increasing over $7/27 \leqslant \zeta \leqslant 1$. The solid lines correspond to the bulk $\bar{r}_s^B(\zeta)$, and the dashed lines correspond to the equilibrium value of the unpolarized bulk system, $\bar{r}_s^B(0)$.

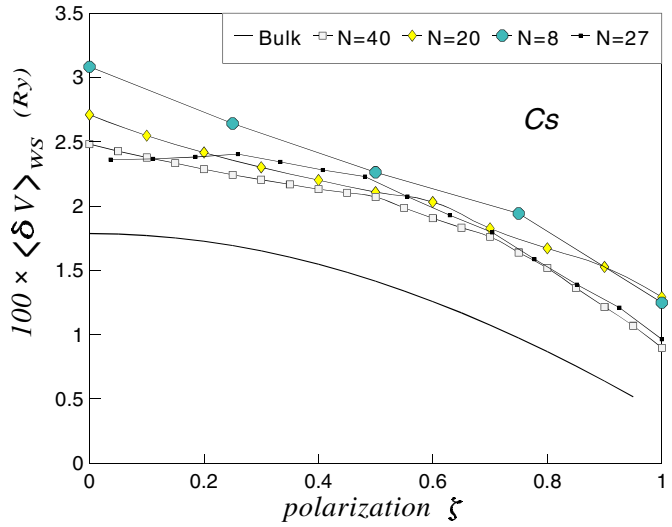
4. Summary and conclusions

In this work, we have calculated the equilibrium r_s-values of different metals as functions of their electronic spin polarizations, using the stabilized jellium model along with the local spin-density approximation. Our calculations show an increasing behaviour for the bulk Wigner–Seitz radius of the electron as a function of polarization. Also we have shown that the rate of



(c)

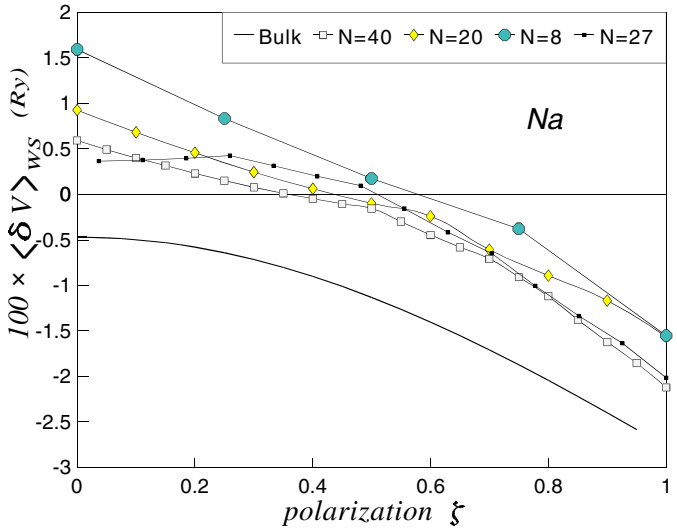
Figure 6. (Continued)



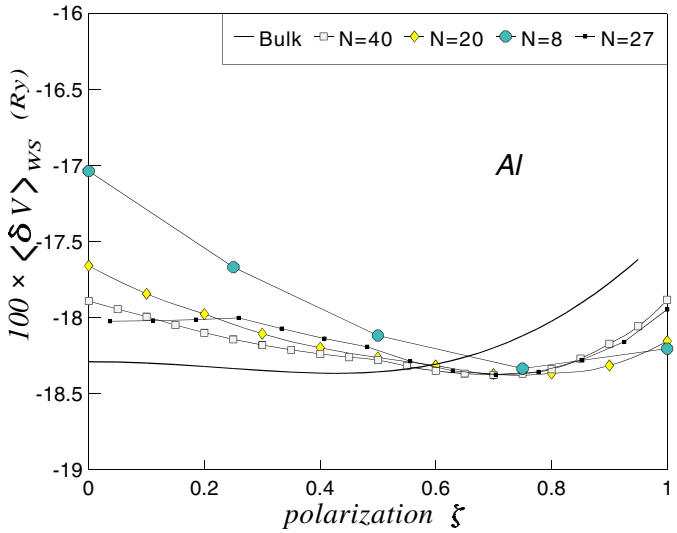
(a)

Figure 7. The average values of the difference potential, in rydbergs, as functions of the spin configurations, ζ. In (a) Cs and (b) Na, for the closed-shell clusters (here, $N = 8, 20, 40$) it shows a decreasing behaviour over the whole range, as in the bulk case which is specified by a solid line. But, in open-shell clusters (here, $N = 27$) it is increasing over $0 \leqslant \zeta \leqslant 7/27$, and decreasing over $7/27 \leqslant \zeta \leqslant 1$. In (c) Al, the same behaviours hold for lower polarizations but, as discussed in the text, there is a minimum at higher polarizations.

increase is higher for higher-electron-density metals. Calculation of the equilibrium r_s-values for closed-shell clusters shows behaviours similar to those of the corresponding bulk metals i.e., they also show increasing behaviours as functions of ζ. But, the situation is somewhat



(b)



(c)

Figure 7. (Continued)

different for open-shell clusters. The open-shell clusters show decreasing behaviour at lower polarizations and increasing behaviours at higher polarizations. The equilibrium r_s-values of the ground-state configurations of the clusters are always smaller than the bulk value. This self-compression is due to the surface tension. On the other hand, at higher polarizations, the equilibrium r_s-values exceeds the bulk value $\bar{r}_s^B(0)$, and this is called self-expansion. In conclusion, the SJM has provided a method which can be used to calculate the sizes of the simple metal clusters with minimum possible effort. More realistic results for open-shell clusters are obtained when the spherical geometry for the jellium background is replaced by spheroidal or ellipsoidal shapes. Work in this direction is in progress.

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