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I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

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INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY
c/o INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS 34100 TRIESTE (ITALY) VIA GRIGNANO, 9 (ADRIATICO PALACE) P.O. BOX 586 TELEPHONE 040-224572 TELEFAX 040-224575 TELEX 460449 APH I

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"Image Plane Position from Stabilized Jellium Model"

A. KIEJNA
University of Wroclaw
Institute of Experimental Physics
Ul. Cybulskiego 36
Wroclaw 50-205
POLAND

These are preliminary lecture notes, intended only for distribution to participants.

Image plane position from stabilized jellium model

A. Kiejna
Institute of Exp. Physics, Univ. of Wroclaw
Poland

The centre of mass $d_\perp(0)$ of the screening charge $\delta n(\vec{r})$ induced at the surface.

$$d_\perp(0) = \frac{\int x\, \delta n(\vec{r})\, d^3r}{\int \delta n(\vec{r})\, d^3r} = x_0$$

brings important information on the response of metal electrons to electric fields

For the interpretation of surface excitation spectra the values of $d_\perp$ determined from the jellium model are used.

$d_\perp$ is model sensitive !

that z_0 may be defined as the position of the center of mass of the surface charge density induced by a small static uniform external field. Their results have been obtained within the framework of LDA and linear response theory (RT).

The RT method has been applied by Ossicini et al. [10] and by Serena et al. [5], too. The surface density has been calculated by Ossicini et al. in a self-consistent way. An analytical pair-correlation function served to describe NLXC effects. In the self-consistent calculation of Serena et al. [5] the NLXC effects have been taken into account by the potential given in eq. (5). This potential has been obtained in a heuristic way. The XC hole is considered to be located on the image plane.

The results concerning $z_0(r_s)$ of the above mentioned three calculations are compared to those obtained within the framework of the second commonly used method, the so called image tail (IT) method. According to this method the image plane position should be determined from the image tail of $V_{xc}(z)$.

To determine $z_0(r_s)$ also an IT calculation has been carried out by Ossicini and Bertoni [11]. Appelbaum and Hamann [12] determined z_0 from the image potential due to a point charge external to the jellium. In their variational calculation the surface charge induced by the external point-like

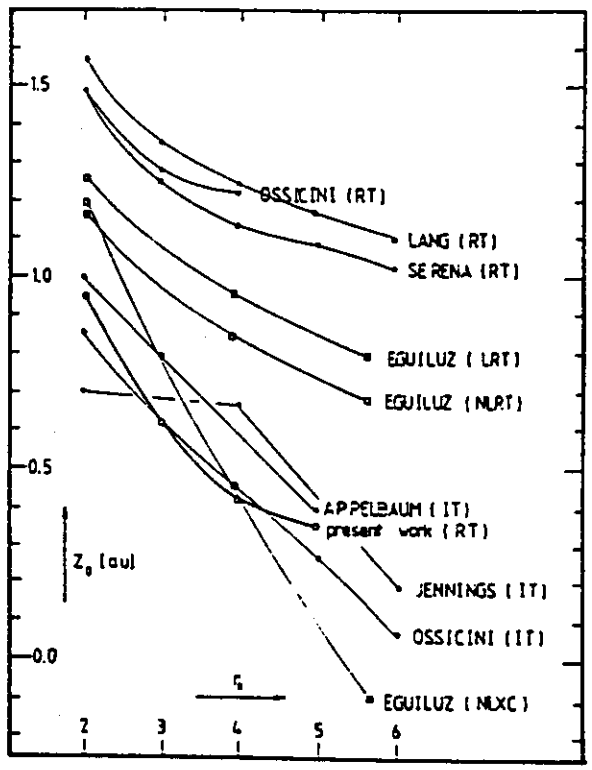


Fig. 1. Dependence of the image plane position relative to the jellium edge as a function of r_s. For detailed explanation, see the text.

The image plane position is a decreasing function of r_s (for jellium).

Jellium model of metal

The ions smeared into a positive background

$$n_+(\vec{r}) = \bar{n}\,\theta(\vec{r}), \qquad \theta(\vec{r}) = \begin{cases} 1 & \text{inside} \\ 0 & \text{outside} \end{cases}$$

where

$$\bar{n} = \frac{3}{4\pi r_s^3} = \frac{k_F^3}{3\pi^2}.$$

The total energy of jellium, as a functional of the electron density $n(\vec{r})$, is

$$E_{jell}[n, n_+] = T_s[n] + E_{xc}[n] + \frac{1}{2}\int d^3r\, \phi([n, n_+]; \vec{r})[n(\vec{r}) - n_+($$

where

$$\phi([n, n_+]; \vec{r}) = \int d^3r' \frac{[n(\vec{r}') - n_+(\vec{r})]}{|\vec{r}' - \vec{r}|}$$

is the electrostatic potential.

$T_s[n]$ – noninteractic kinetic energy which can be evaluated exactly by the K-S method

$$T_s[n] = \sum_i \int d^3r\, \frac{1}{2}\left|\nabla \psi_i(\vec{r})\right|^2$$

$$n(\vec{r}) = \sum_i \left|\psi_i(\vec{r})\right|^2$$

where ψ_i are self-consistent orbitals.

$E_{xc}[n]$ - exchange-correlation energy in the LDA

$$E_{xc}[n] = \int d^3r\, n(\vec{r})\, \varepsilon_{xc}(n(\vec{r}))$$

where

$$\varepsilon_{xc}(n) = -\frac{3}{4\pi}(3\pi^2 n)^{1/3} + \varepsilon_c(n)$$

The density which minimizes E_{jell} can be found from the solution of the Euler eqn.

$$\frac{\delta E_{jell}[n_-, n_+]}{\delta n(\vec{r})} = \mu$$

μ - Lagrange multiplier has sense of the chemical potential

The effective one-electron potential of the Kohn-Sham theory becomes:

$$\frac{\delta}{\delta n(\vec{r})}\left(E_{jell}[n_-, n_+] - T_s[n]\right) = \underbrace{\phi([n_-, n_+]; \vec{r}) + \mu_{xc}(n(\vec{r}))}_{v_{eff}[n; \vec{r}]}$$

where

$$\mu_{xc}(n) = \frac{d}{dn}\left(n\,\varepsilon_{xc}(n)\right)$$

The Euler eqn replaced by a self-consistent equations.

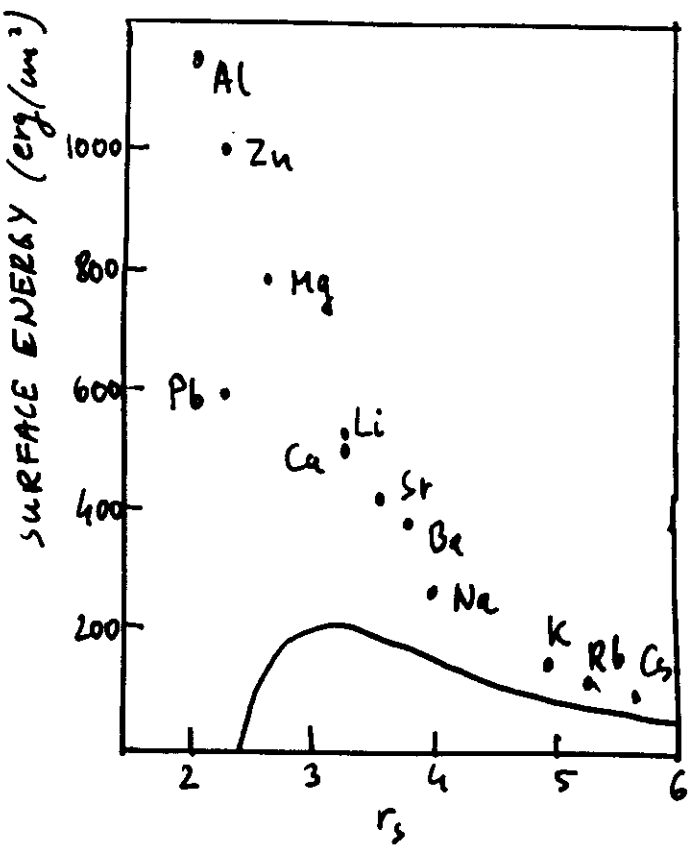
Lang & Kohn (1970)

Self-consistent equations for semi-infinite jellium:

$$\left\{ -\frac{1}{2}\frac{d^2}{dx^2} + v_{eff}[n;x] \right\} \psi_k(x) = \frac{1}{2}(k^2 - k_F^2)\,\psi_k(x)$$

$$n(x) = \frac{1}{\pi^2}\int_0^{k_F} (k_F^2 - k^2)\,|\psi_k(x)|^2\,dk$$

Jellium model leads to negative surface energies!



Why?

Jellium is stable (obeys zero pressure condition) only at $r_s = 4.2$.

At other densities the uniform electron gas is under the pressure (exerted by the uniform positive background) which allows to keep it at the specified r_s.

To stabilize it, an extra electron-ion interaction should be introduced !

Lang & Kohn → Madelung and pseudopotential corrections.

J. P. Perdew et al. PRB 42, 11627 (1990) :

Madelung and pseudopotential corrections approximated by structureless averages

⇓

stabilized jellium

$$E_{sj}[n, n_+] = E_{jell}[n, n_+] + B \int d^3r\, n_+(\vec{r}) + \langle \delta v \rangle_{ws} \int d^3r\, \theta(\vec{r}) [n(\vec{r}) - n_+(\vec{r})]$$

The constants B and $\langle \delta v \rangle_{ws}$, determined from the bulk stability condition, do not depend on the structure parameters except of r_s

Independent, equivalent model called "ideal metal" - H. B. Shore & J. H. Rose, PRL 66, 2519 (1991)

The Euler equation:

$$\frac{\delta}{\delta n(\vec{r})}\left(E_{sj}[n_1, n_+] - T_s[n]\right) = \phi([n_1, n_+]; \vec{r}) + \mu_{xc} + \langle \delta v \rangle_{ws}\,\theta(\vec{r})$$

The additional potential required to keep the electron gas in equilibrium

$$\boxed{\langle \delta v \rangle_{ws} = -\bar{n}\,\frac{d\varepsilon}{d\bar{n}}}, \qquad \varepsilon(\bar{n}) = t_s(\bar{n}) + \varepsilon_{xc}(\bar{n})$$

$$\langle \delta v \rangle_{ws} = -\frac{k_F^2}{5} + \frac{k_F}{4\pi} + \frac{r_s}{3}\,\frac{d\varepsilon}{dr_s}$$

Solve self-consistent K-S equations with v_{eff}:

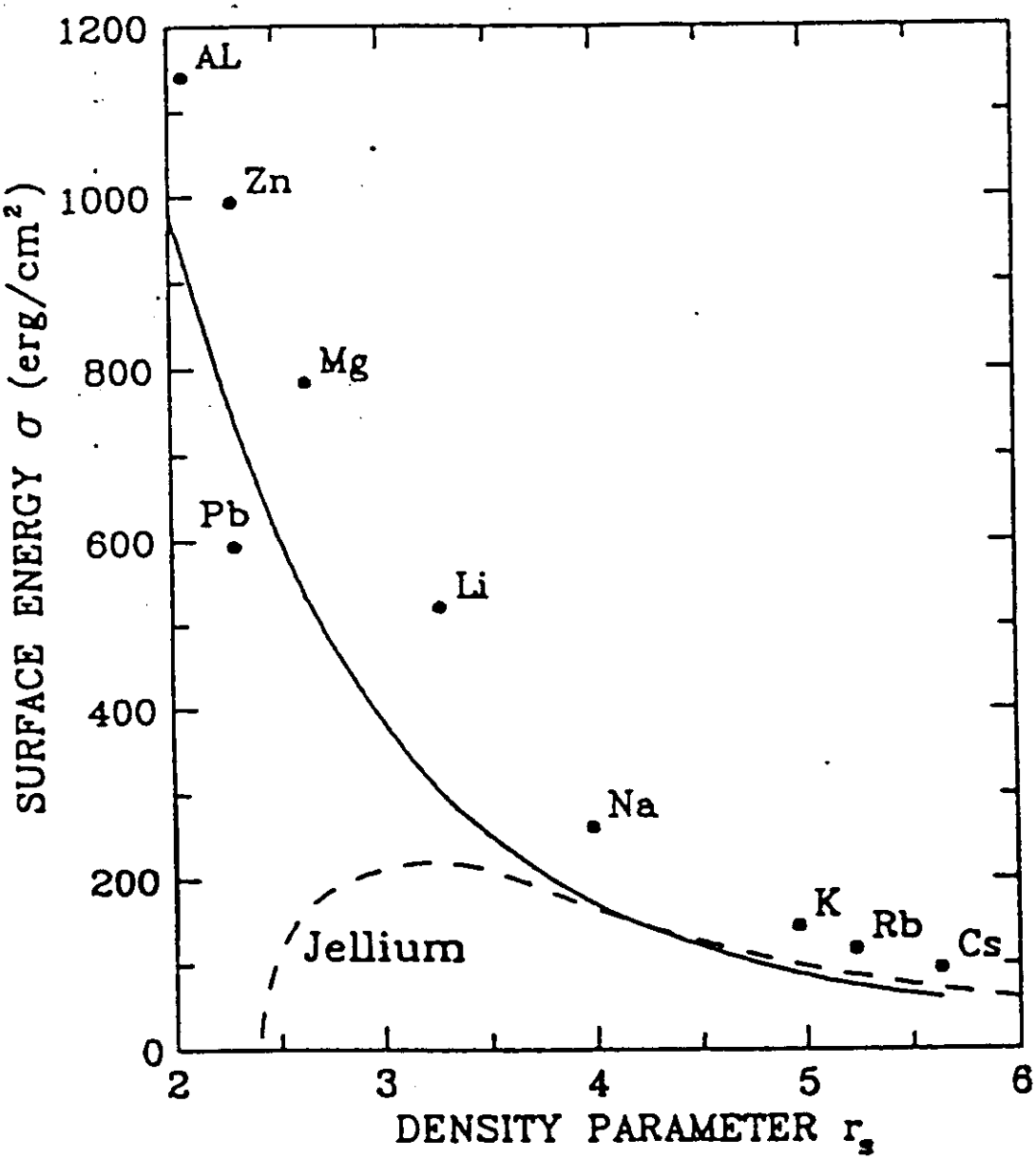
$$v_{eff}[n; x] = \underbrace{\phi([n_1, n_+]; x) + \mu_{xc}(n(x))}_{\text{jellium}} + \langle \delta v \rangle_{ws}\,\theta(-x)$$

Note that:

- similarly like for jellium no parameters except the average electron density (r_s) are introduced
- the electron density is in mechanical equilibrium at any specified electron density

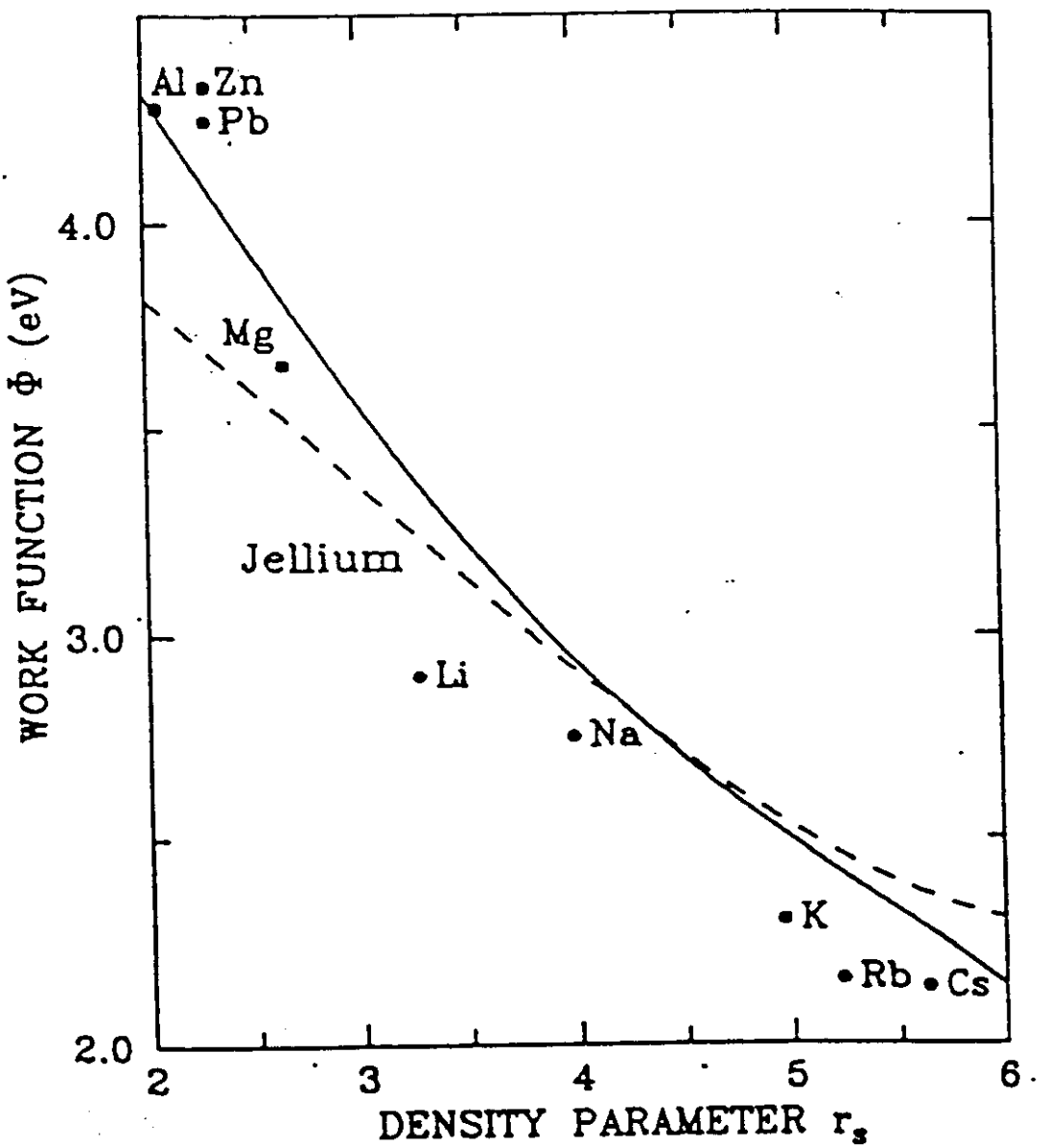
$\langle \delta v \rangle_{ws} < 0$ for $r_s < 4.2$ and $\langle \delta v \rangle_{ws} > 0$ for $r_s > 4.2$

A. Kiejna (1992)



Stabilized jellium

A. Kiejna (1992)



Stabilized jellium

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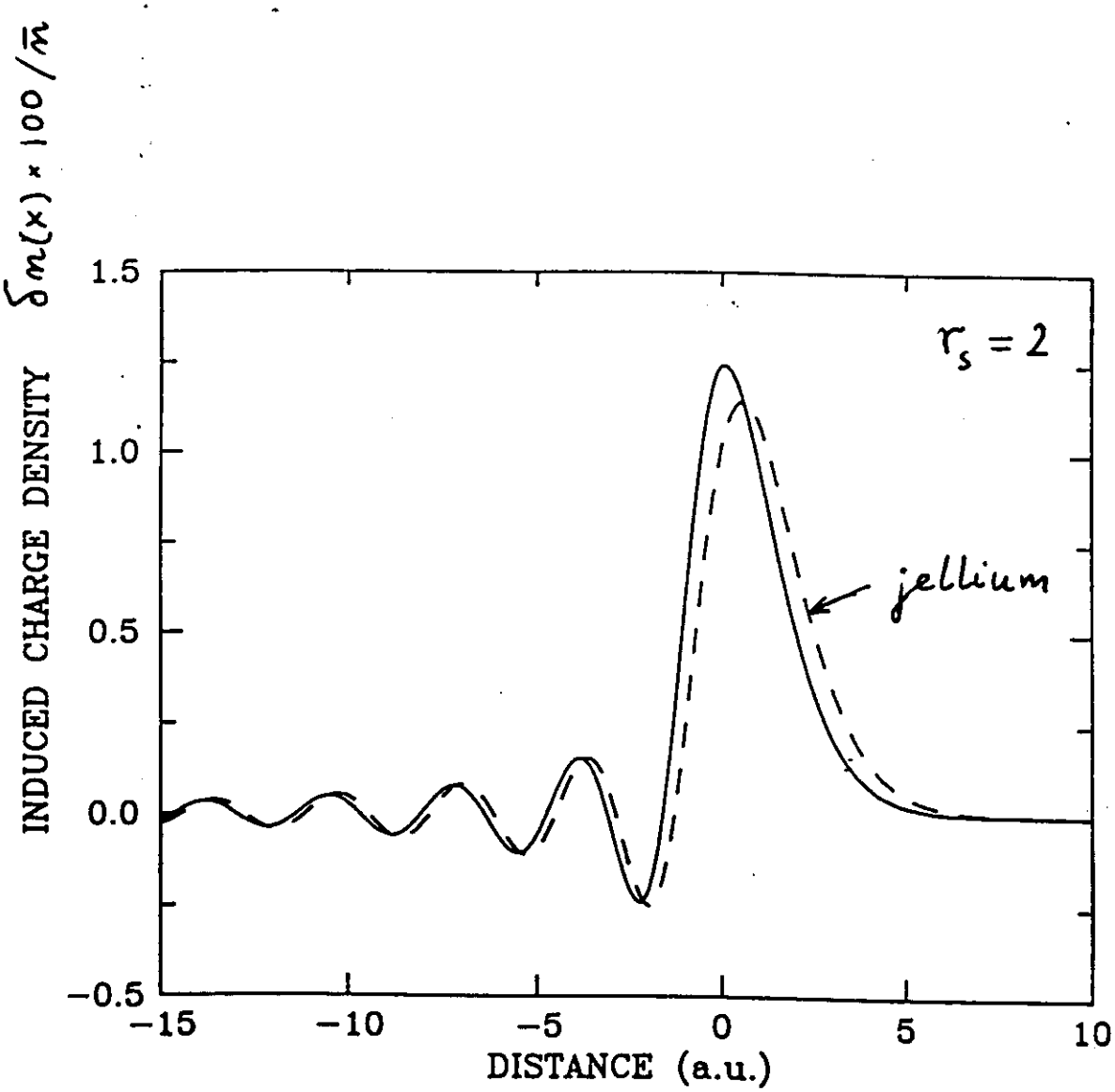

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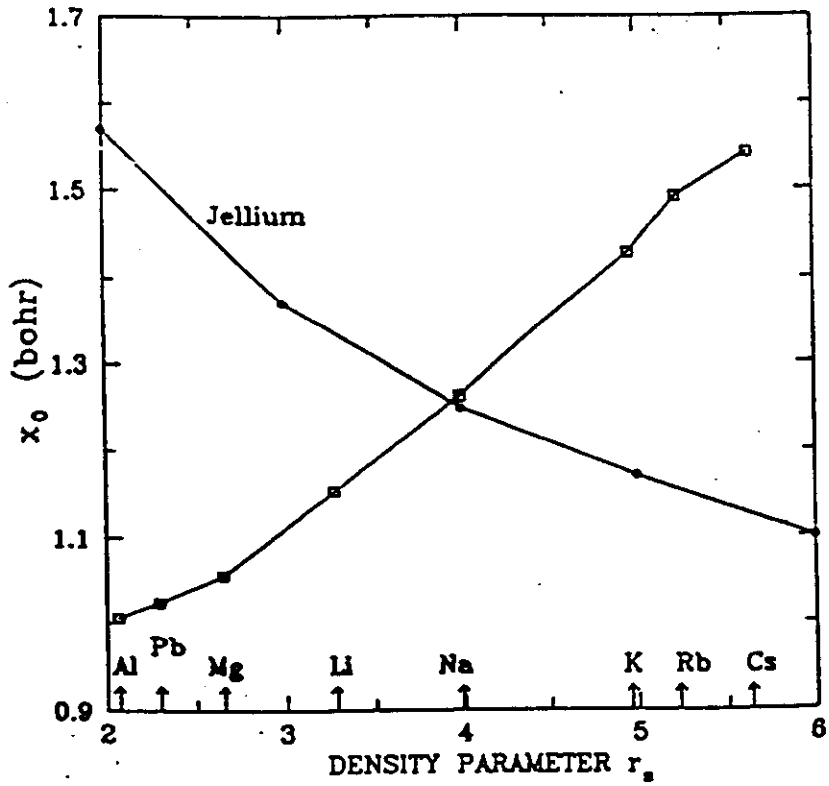

Image plane positions for jellium (LDA) and stabilized jellium model

For stabilized jellium, the larger screening length the closer to the background edge x_0 lies.