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The Jellium Model and its Variants in Electronic Structure Calculations of Materials

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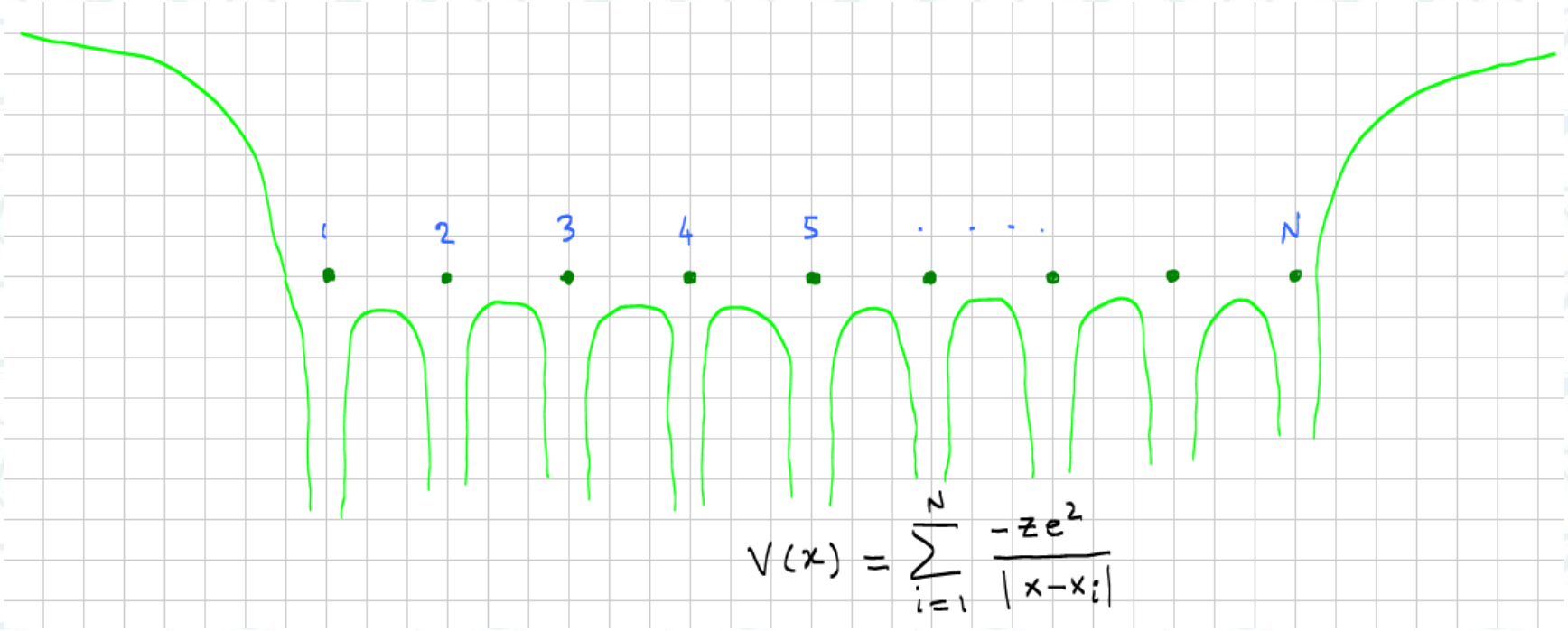
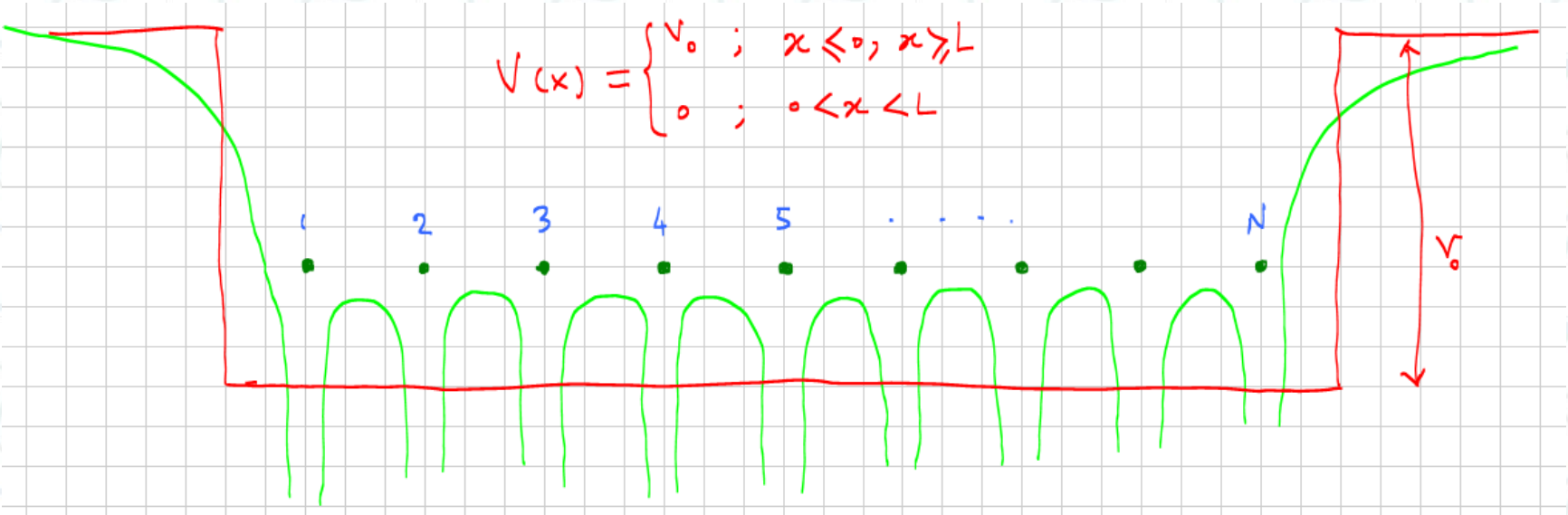
- Calculations based on simplified models
- Calculations based on first-principles methods


1
2
3
4
5
N
$V(x) = \sum_{i=1}^{N} \frac{-ze^2}{|x-x_i|}$

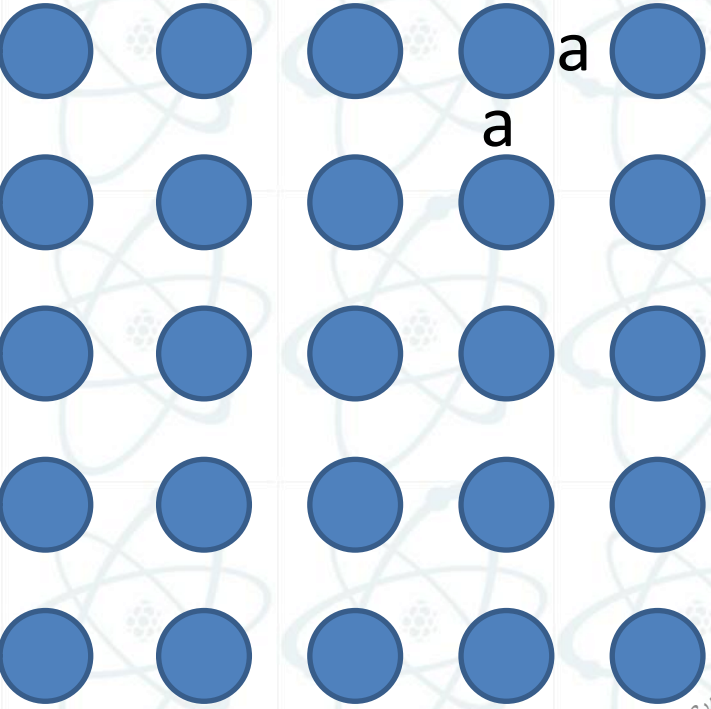

$V(x) = \begin{cases} V_0 ; & x \leq 0, x \geq L \\ 0 ; & 0 < x < L \end{cases}$
1
2
3
4
5
N
V_0

سؤال: این ساده سازی چه مواقعی امکان پذیر است؟

جواب : مواقعی که برهمکنش الکترونهای والانس با یونها ضعیف باشد و همچنین خواص الکترونی سیستم به مکان دقیق یونها حساس نباشد.

What is Jellium Model (JM)?

- In the simple JM, the discrete ions are replaced with a homogeneous positive background of density $\bar{n}$



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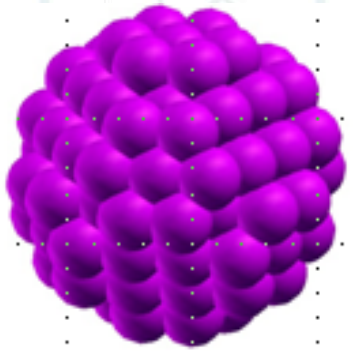
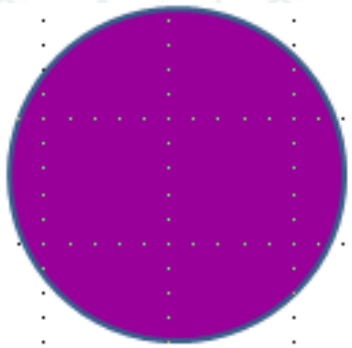




$$n_+(\vec{r}) = \sum_{\vec{R}} \delta(\vec{r} - \vec{R})$$

$$n_+(\vec{r}) = \bar{n}\theta(r_0 - |\vec{r}|)$$

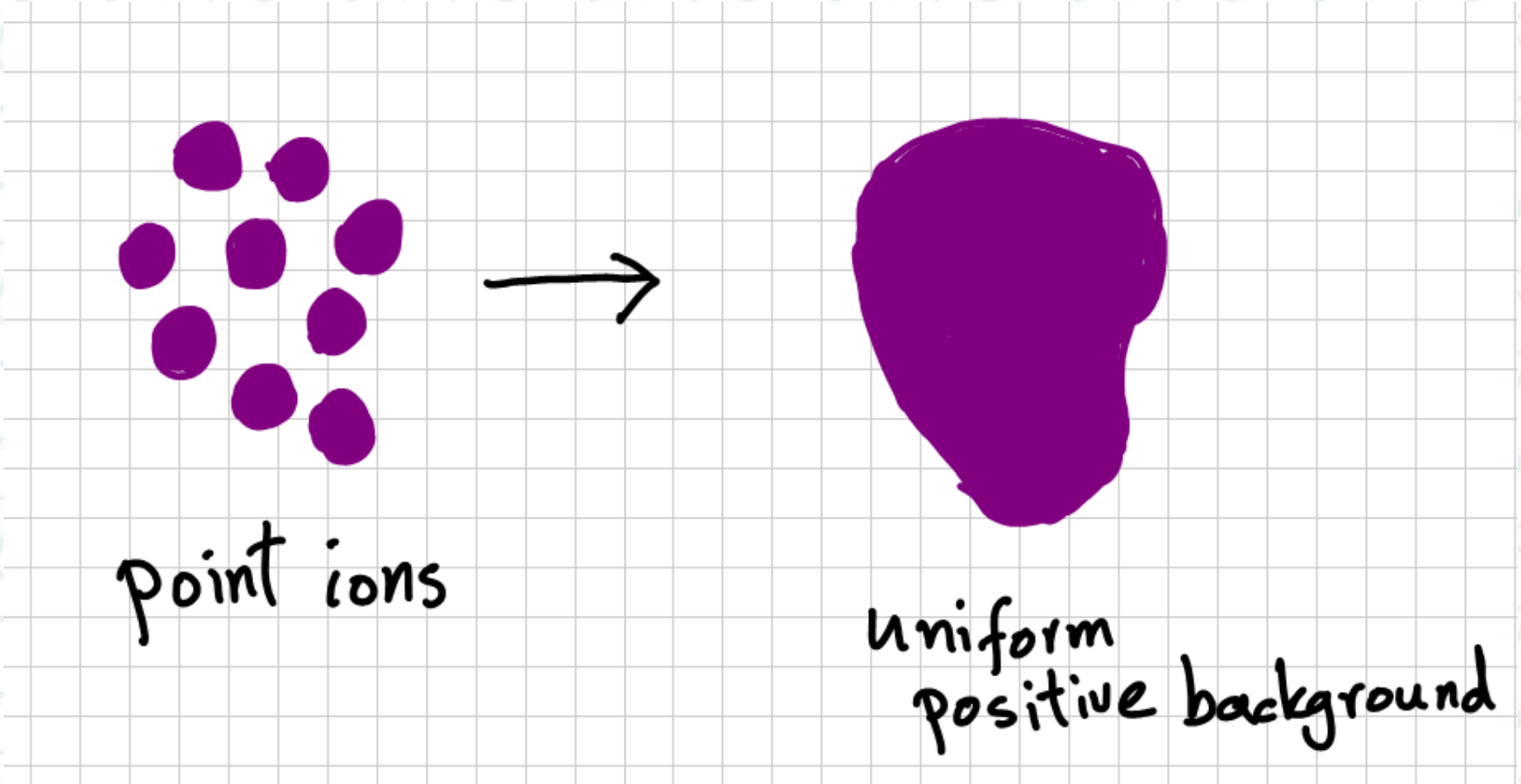
$$\bar{n} = 3/4\pi r_s^3$$

$$r_0 = z^{1/3} r_s$$

$$r_s = 3.99$$

r_s is constant

Jellium Model (JM)



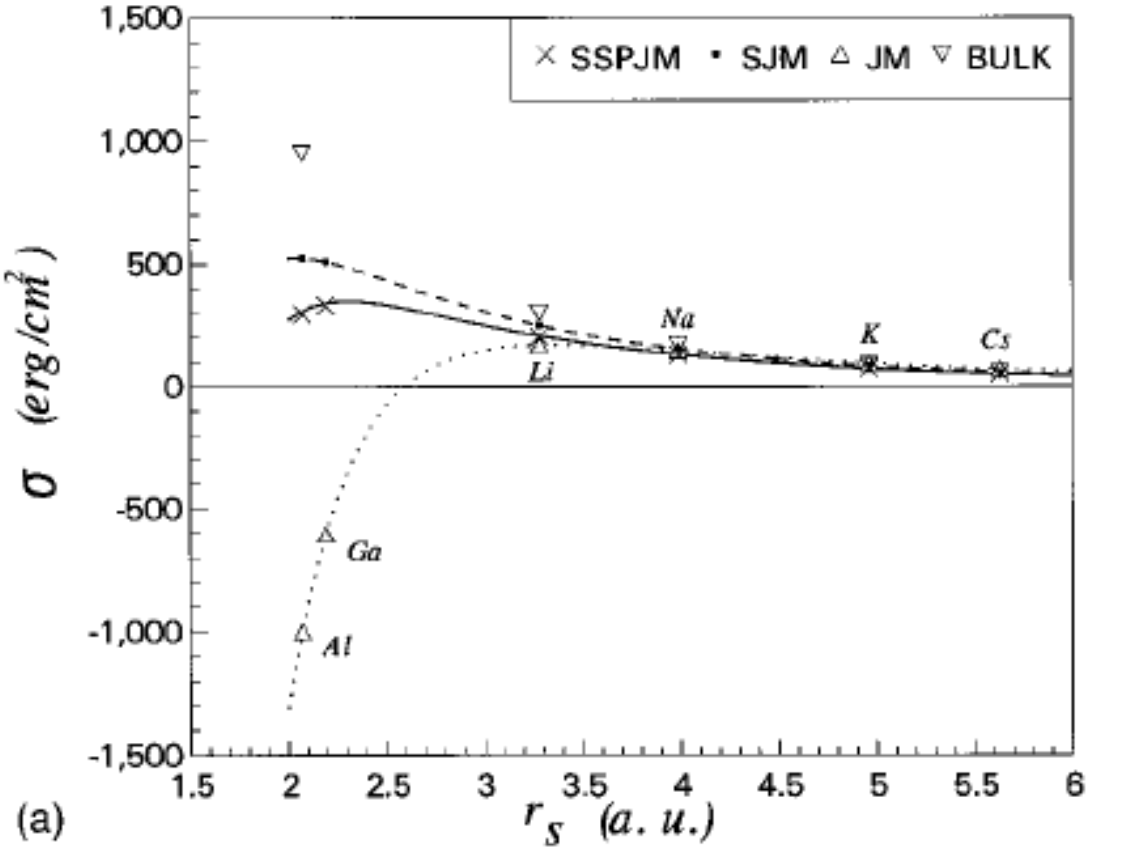
Density functional theory

$$E[n,n_+] = T_S[n] + E_{xc}[n] +$$

$$+ \frac{1}{2}\int d\underline{r}\ \phi([n,n_+];\underline{r})\left[n(\underline{r}) - n_+(\underline{r})\right]$$

$$\phi(\underline{r}) \equiv \int d\underline{r}'\ \frac{\left[n(\underline{r}') - n_+(\underline{r}')\right]}{|\underline{r} - \underline{r}'|}$$

Application of JM to metal surfaces



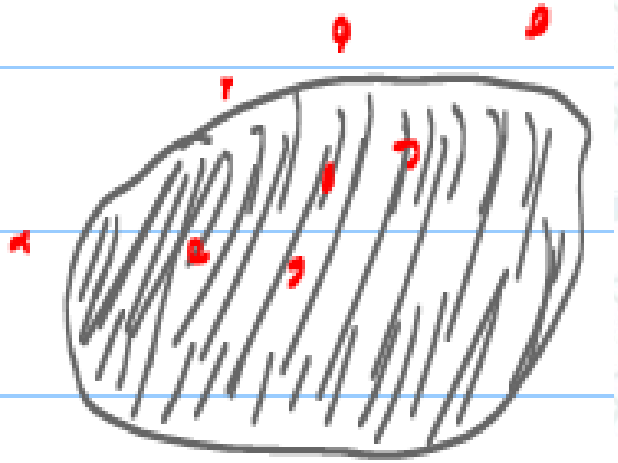
M. Payami and N. Nafari, *J. Chem. Phys.* **109**, 5730-40 (1998)

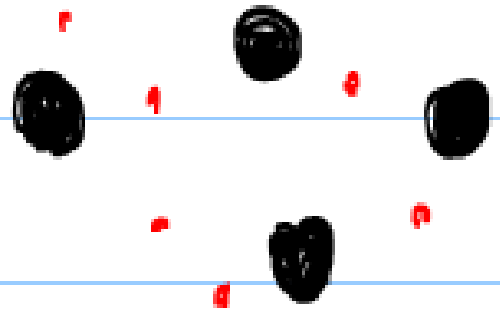
با استفاده از الگوی هسته‌ای برخی از خواص سیستم به خوبی و قابل مقایسه با نتایج تجربی به دست می‌آیند ولی در برخی موارد ($r_s \lesssim 2$) علامت انرژی سطحی را نادرست می‌دهند و به‌ازای $r_s \gtrsim 5$ مدول حجمی را منفی می‌دهند.

سؤال: چگونه الگوی ژله‌ای را اصلاح کنیم تا این مشکلات نسبتاً برطرف شود؟

ساده شده

واقعی





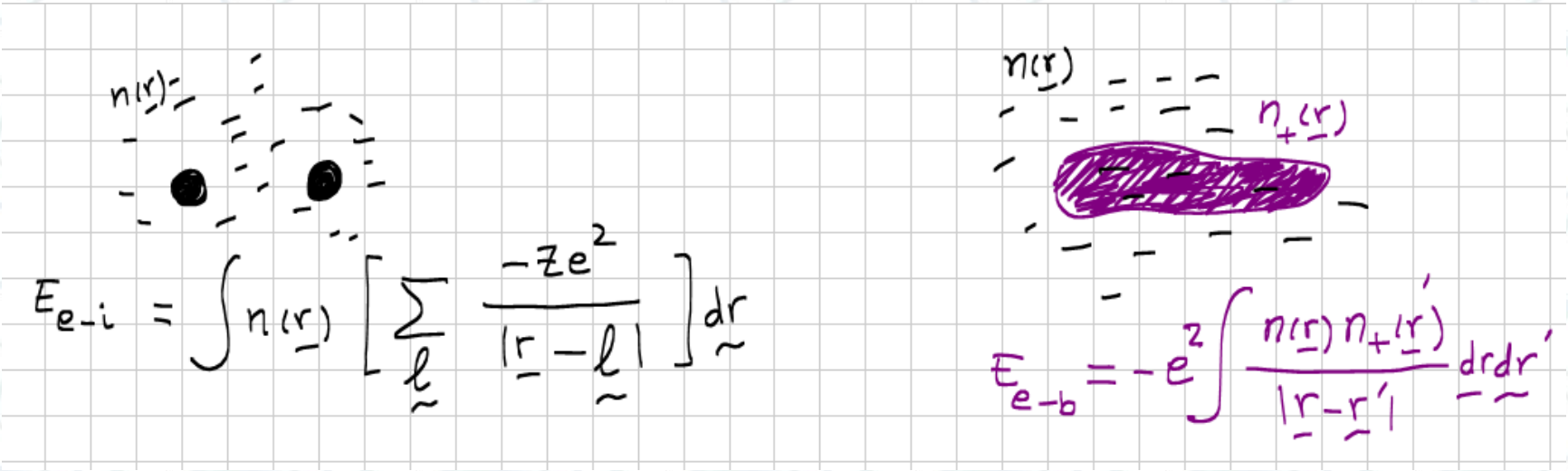
Corrections to JM

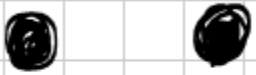
$$E_{pseudo}[n,\{\underline{l}\}] = E_{JM}[n,n_+]$$

$$+ \delta v$$

$$- \text{self-energy of jellium}$$

$$E_{pseudo}[n,\{\underline{\ell}\}] = E_{JM}[n,n_+]$$
$$+\left(\int d\underline{r}\sum_{\underline{\ell}} W(|\underline{r}-\underline{\ell}|)n(\underline{r}) - \frac{1}{2}\int d\underline{r}d\underline{r}'\frac{n_+(\underline{r}')n(\underline{r})}{|\underline{r}-\underline{r}'|}\right)$$
$$-\left(\frac{1}{2}\int\frac{n_+(\underline{r})n_+(\underline{r}')}{|\underline{r}-\underline{r}'|}d\underline{r}d\underline{r}' - \frac{1}{2}\sum_{\underline{\ell},\underline{\ell}'}{}'\frac{z^2}{|\underline{\ell}-\underline{\ell}'|}\right)$$


n(r)
$E_{e-i} = \int n(\underline{r}) \left[\sum_{\underline{\ell}} \frac{-Ze^2}{|\underline{r}-\underline{\ell}|} \right] d\underline{r}$
n(r)
$n_+(\underline{r})$
$E_{e-b} = -e^2 \int \frac{n(\underline{r})\, n_+(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r} d\underline{r}'$



$$E_{i-i} = \frac{1}{2} \sum_{\underset{\sim}{l} \neq \underset{\sim}{l}'} \frac{(Ze)^2}{|\underset{\sim}{l} - \underset{\sim}{l}'|}$$

JM

$$E_{b-b} = \frac{e^2}{2} \int \frac{n_+(\underset{\sim}{r}) n_+(\underset{\sim}{r}')}{|\underset{\sim}{r} - \underset{\sim}{r}'|}$$

$$W(r) = -\frac{Z}{r} + W_R(r)$$

$$W_R(r) = +\frac{Z}{r}\,\Theta(r_c - r)$$

core radius

Ashcroft empty-core Pseudo-pot.

Stabilized jellium model SJM

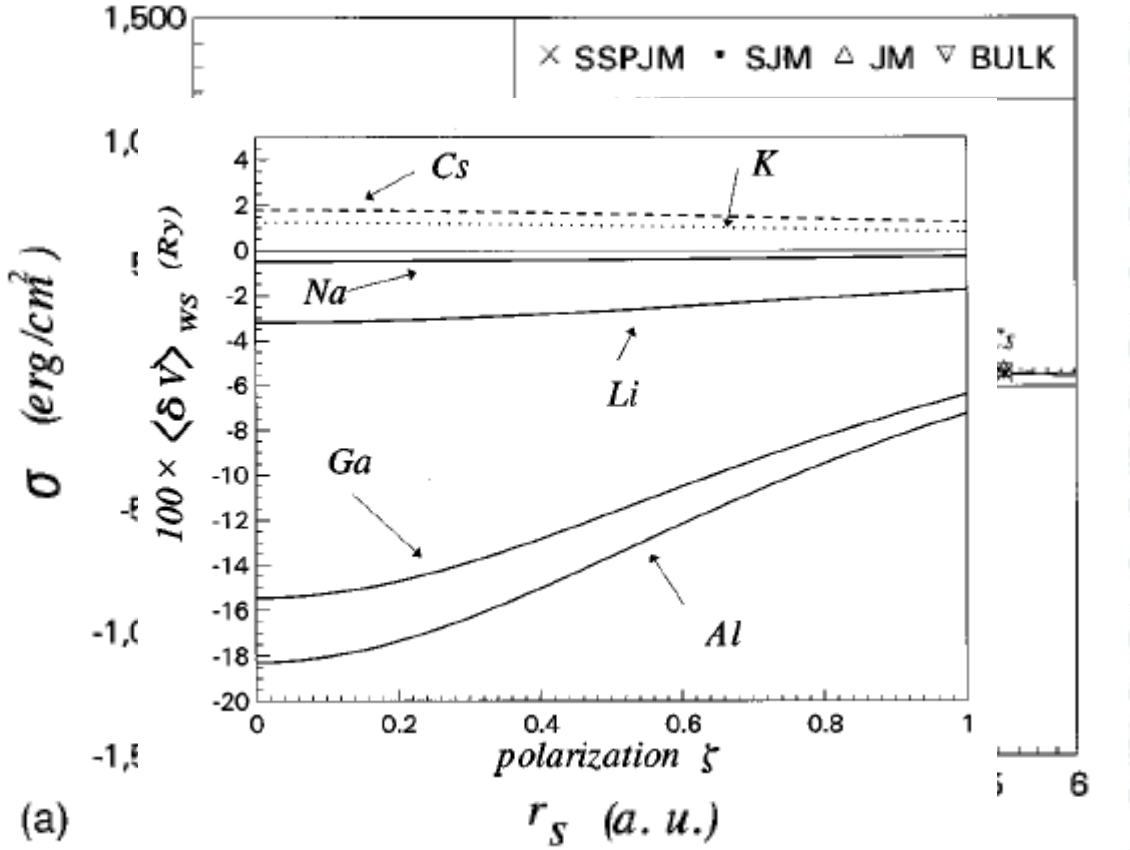
$$\text{SJM}: \begin{cases} \delta v \approx \langle \delta v \rangle_{WS} \oplus (\underset{\sim}{r}) \\ \text{self-energy} \approx N\tilde{\varepsilon} \quad ; \tilde{\varepsilon} \equiv \dfrac{3z}{5r_0} \end{cases}$$

SJM energy functional

$$E_{SJM}[n,n_+] = E_{JM}[n,n_+] + \langle \delta v \rangle_{WS} \int [n(\underline{r}) - n_+(\underline{r})]\, d\underline{r} + \left(\bar{W}_R(\bar{n}) + \varepsilon_M(\bar{n})\right) \int d\underline{r}\, n_+(\underline{r})$$

J. P. Perdew, H. Q. Tran, E. D. Smith, *Phys. Rev. B* **42**, 11627 (1990)

Application of SJM to metal surfaces



M. Payami and N. Nafari, *J. Chem. Phys.* **109**, 5730-40 (1998)

Spin-polarized EG

$$\varepsilon(r_s,\zeta)=t_s(r_s,\zeta)+\varepsilon_x(r_s,\zeta)+\varepsilon_c(r_s,\zeta)$$

به ازای قطبش مشخص، چه موقع سیستم متعادل است؟

Equilibrium condition for EG

$$0 = P(\bar{n},\zeta) = -\left(\frac{\partial E}{\partial V}\right)_{N,\zeta} = \bar{n}^2\left(\frac{\partial}{\partial \bar{n}}\right)_{\zeta} \varepsilon(\bar{n},\zeta)$$

$$= -\frac{1}{4\pi \bar{r}_s^2}\left(\frac{\partial}{\partial \bar{r}_s}\right)_{\zeta} \varepsilon(\bar{r}_s,\zeta).$$

$$0 = \frac{1}{4\pi r_s^2}\left\{\frac{2}{r_s} t_s(r_s,\zeta) + \frac{1}{r_s}\varepsilon_x(r_s,\zeta) - \left(\frac{\partial}{\partial r_s}\right)_{\zeta} \varepsilon_c(r_s,\zeta)\right\}$$

$$\bar{r}_s^{EG}(\zeta) = 4.18 + \Delta \bar{r}_s^{EG}$$

Generalization to any metal

$$\overline{r_s^X}(\zeta) = \overline{r_s^X}(0) + \Delta r_s^{EG}$$

X= Ga, Al, Li, Na, K, Cs

Stabilized spin-polarized JM

$$n_{\uparrow} = \tfrac{1}{2}(1+\zeta)n, \qquad n_{\downarrow} = \tfrac{1}{2}(1-\zeta)n$$

$$\varepsilon(n,\zeta) = t_s(n,\zeta) + \varepsilon_{\mathrm{xc}}(n,\zeta) + \overline{w}_R(n,r_c) + \varepsilon_M(n) + \varepsilon_{\mathrm{bs}},$$

where

$$t_s(n,\zeta) = \tfrac{1}{2}c_k[(1+\zeta)^{5/3} + (1-\zeta)^{5/3}]n^{2/3},$$

$$\varepsilon_{\mathrm{xc}}(n,\zeta) = \tfrac{1}{2}c_x[(1+\zeta)^{4/3} + (1-\zeta)^{4/3}]n^{1/3} + \varepsilon_c(n,\zeta),$$

$$c_k = \tfrac{3}{5}(3\pi^2)^{2/3}; \qquad c_x = \frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3}.$$

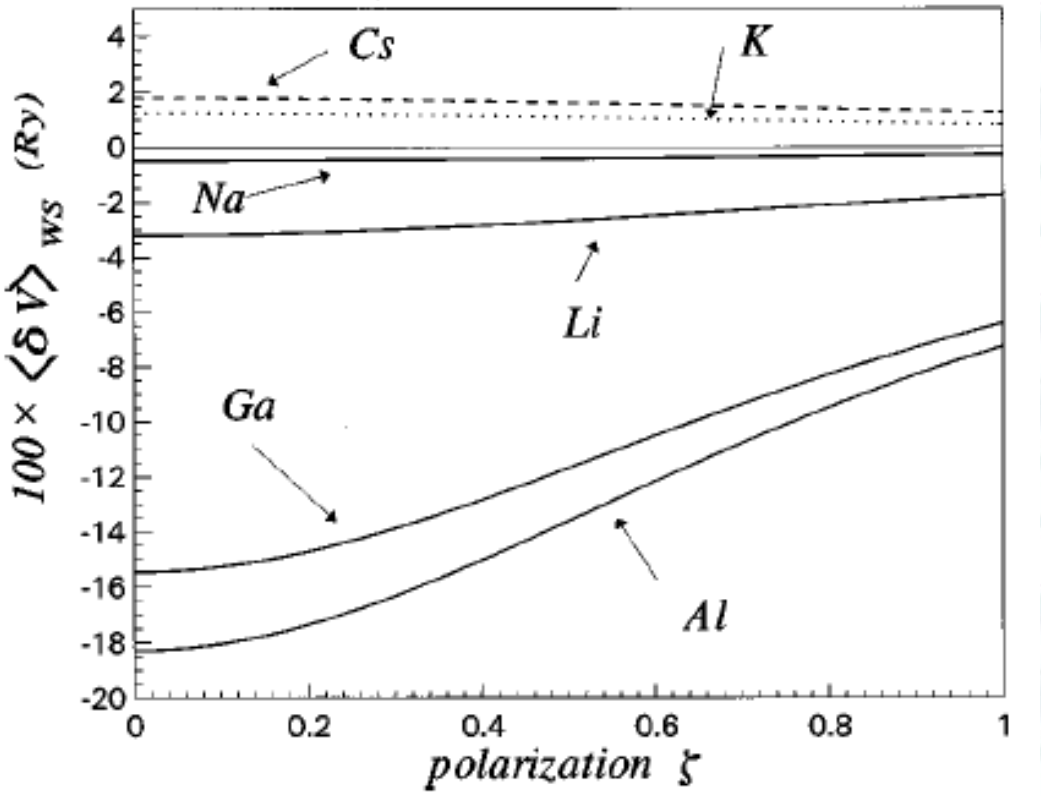
Equilibrium condition for SSPJM

$$2t_s(\overline{r_s},\zeta)+\varepsilon_x(\overline{r_s},\zeta)-\overline{r_s}\left(\frac{\partial}{\partial \overline{r_s}}\right)_{\zeta}\varepsilon_c(\overline{r_s},\zeta)$$

$$+\frac{9}{\overline{r_s}^3}r_c^2+\varepsilon_M(\overline{r_s})=0.$$

r_c as a function of r_s and zeta

Polarization dependence of <delta_v>



M. Payami and N. Nafari, *J. Chem. Phys.* **109**, 5730-40 (1998)

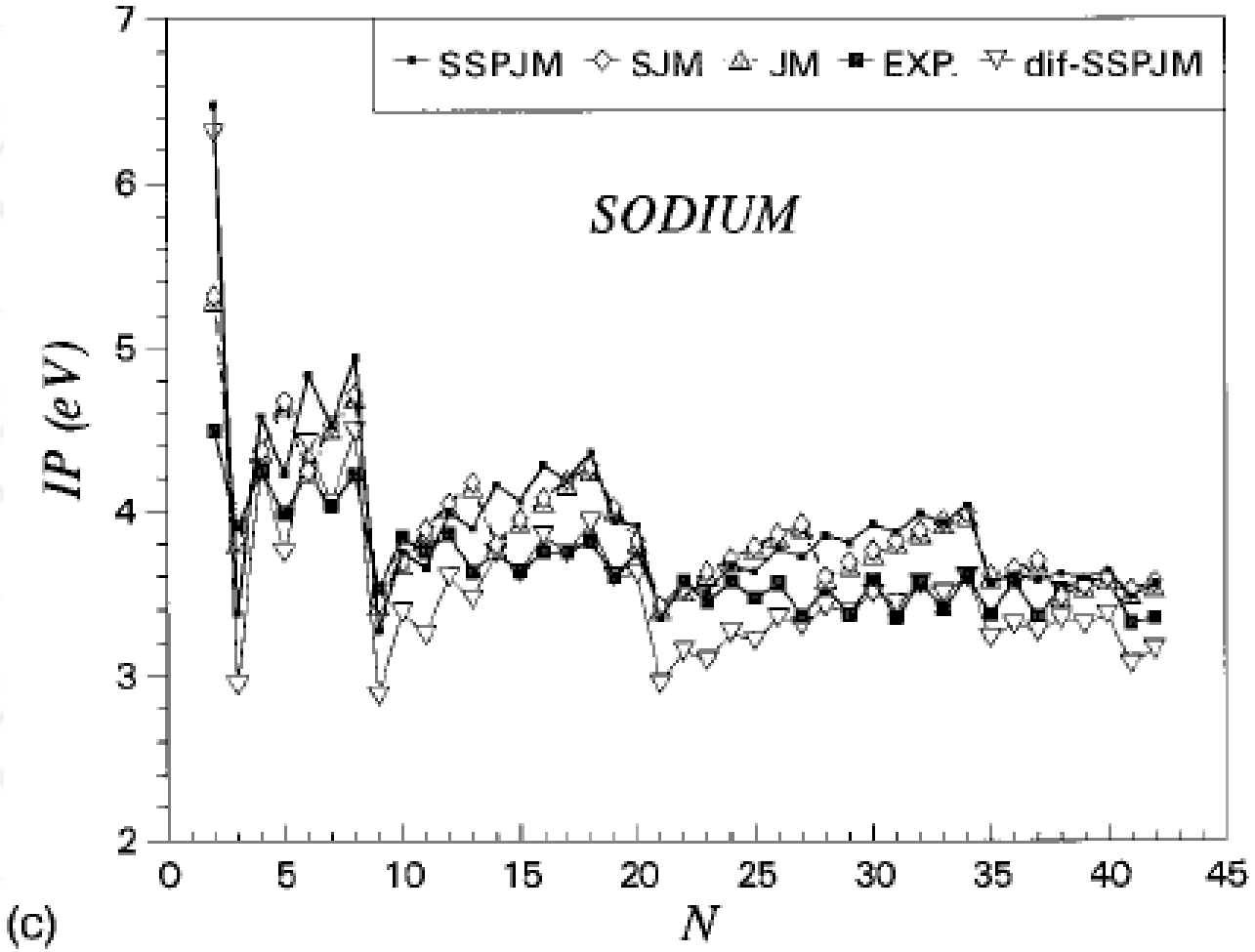
Energy functional in SSPJM

$$E_{\mathrm{SSPJM}}[n_{\uparrow}, n_{\downarrow}, n_{+}]$$

$$= E_{\mathrm{JM}}[n_{\uparrow}, n_{\downarrow}, n_{+}] + (\varepsilon_{M}(\overline{n}) + \overline{w}_{R}(\overline{n}, \zeta)) \int d\mathbf{r} n_{+}(\mathbf{r})$$

$$+ \langle \delta v \rangle_{\mathrm{WS}}(\overline{n}, \zeta) \int d\mathbf{r} \Theta(\mathbf{r}) [n(\mathbf{r}) - n_{+}(\mathbf{r})],$$

Application of SSPJM to metal clusters



SSPJM

- **Stabilized Spin-Polarized Jellium Model and Odd-Even Alternations in Jellium Metal Clusters**, M. Payami and N. Nafari, J. Chem Phys. 109, 5730 (1998)
- **Finite-size effects and the stabilized spin-polarized jellium model for metal clusters**, M. Payami, J. Chem. Phys. 111, 8344 (1999)
- **Volume change of bulk metals and metal clusters due to spin-polarization**, M. Payami, J. Phys.: Condens. Matter 13, 4129 (2001)
- **Equilibrium sizes of jellium metal clusters in the stabilized spin-polarized jellium model**, M. Payami, Phys. Stat. Sol. (b) 225, 77 (2001)

Self-compressed SJM

- Finite systems are not stable in SJM

J. P. Perdew, M. Brajczewska, and C. Fiolhais, Solid State Commun. 88, 795 (1993)

SC-SJM Energy functional

$$E_{SC\text{-}SJM}[n,\bar{n}] = E_{JM}[n,\bar{n}] + \langle \delta v \rangle_{WS} \int [n(\underline{r}) - n_+(\underline{r})]\, d\underline{r} + \left(\bar{w}_R(\bar{n}) + \varepsilon_M(\bar{n})\right) \int d\underline{r}\, n_+(\underline{r})$$

Let $\bar{n}$ change until the energy minimize

SC-SJM

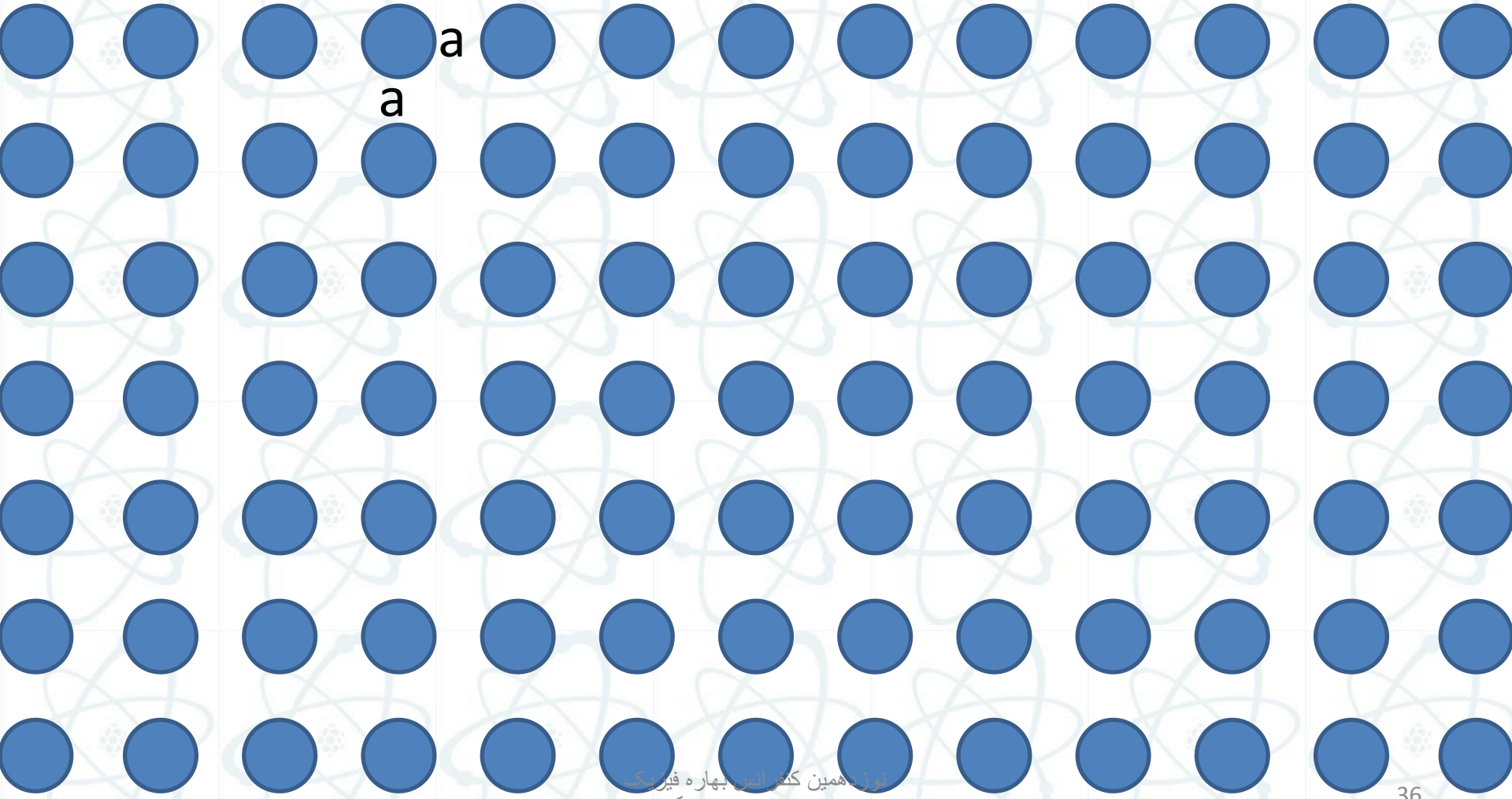
$$E_{SC-SJM} = E_{SJM}[n, \bar{n}t]$$

$$\left.\frac{\partial E[n, \bar{n}]}{\partial \bar{n}}\right|_{\bar{n}t} = 0$$

SC-SJM

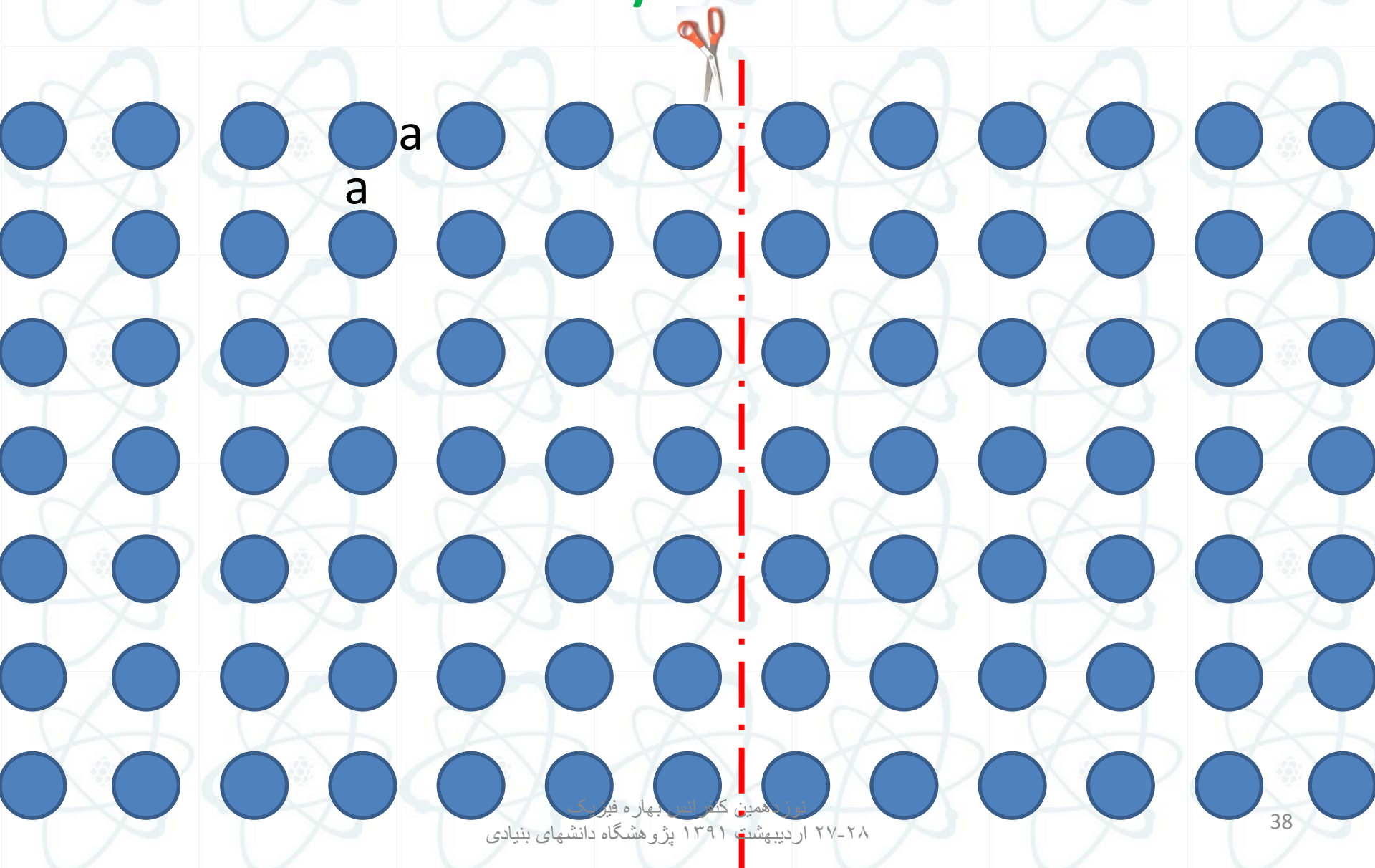
- **Fragmentation of positively charged metal clusters in stabilized jellium model with self-compression**, M. Payami, arXiv:physics/0112022
- **Study of interaction of high-power Ar$^+$ laser beam with Ag$^+$-doped glass**, A. Nahal, H. R. M. Khalesifard, M. Payami, arXiv:physics/0302073
- **Stabilized jellium model and structural relaxation effects on the fragmentation energies of ionized silver clusters**, M. Payami, Can. J. Phys. 82, 239 (2004)
- **Fragmentation of multiply charged simple metal clusters in liquid-drop stabilized jellium model**, M. Payami, Phys. Stat. Sol. (b) 241, 1838 (2004)
- **Self-consistent iterative solution of the exchange-only OEP equations for simple metal clusters in jellium model**, M. Payami, T. Mahmoodi, J. Phys.: Condens. Matter Vol 18, 75 (2006)
- **Exact exchange optimized effective potential and self-compression of stabilized jellium clusters**, M. Payami, Phys. Rev. B 73, 113106 (2006)
- **Equilibrium properties of simple metal thin films in the self-compressed stabilized jellium model**, T. Mahmoodi, M. Payami, J. Phys.: Condens. Matter 21, 265002 (2009)

Infinite Crystalline Solid



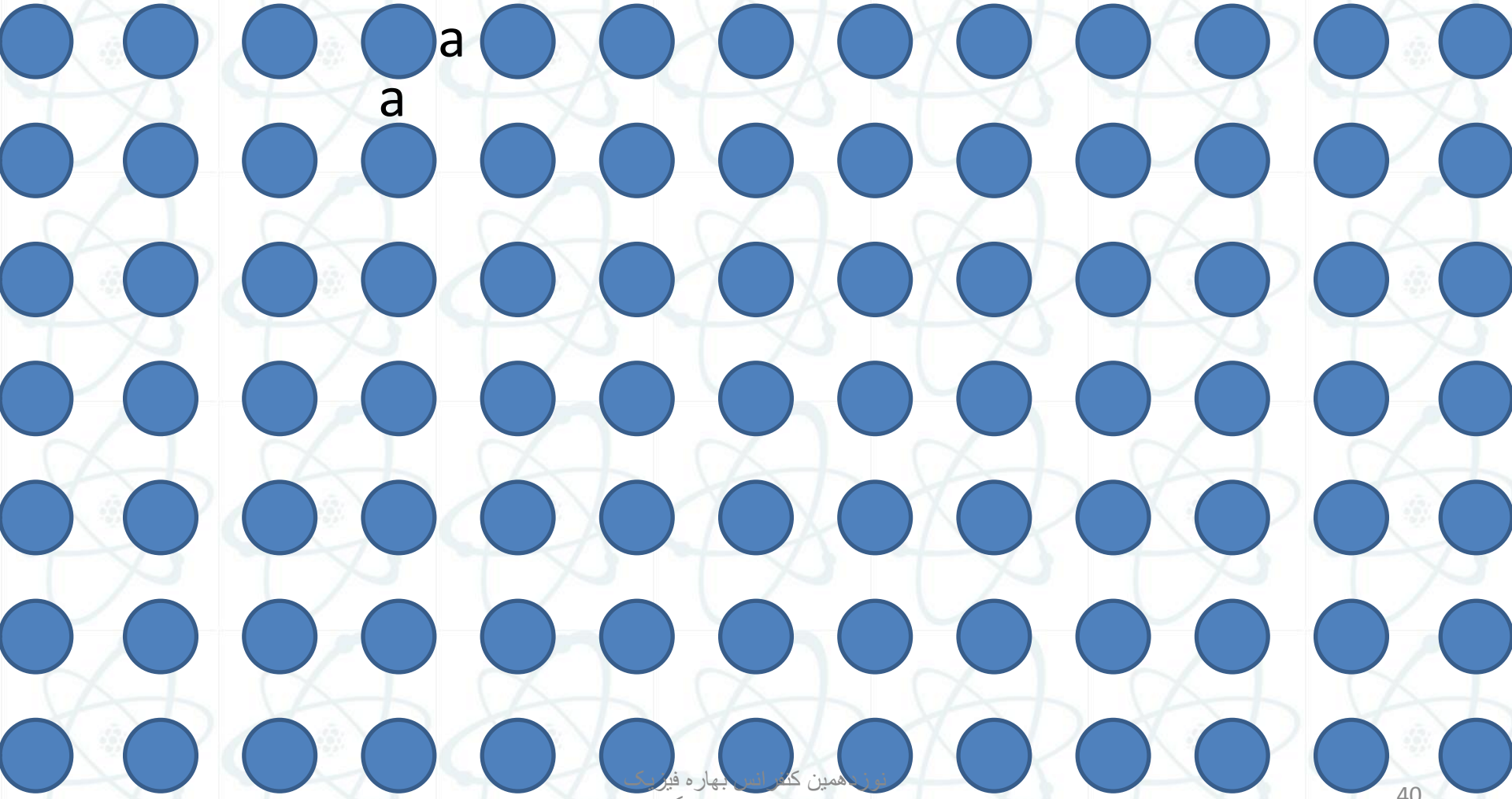
Cut into two pieces ...

Infinite Crystalline Solid

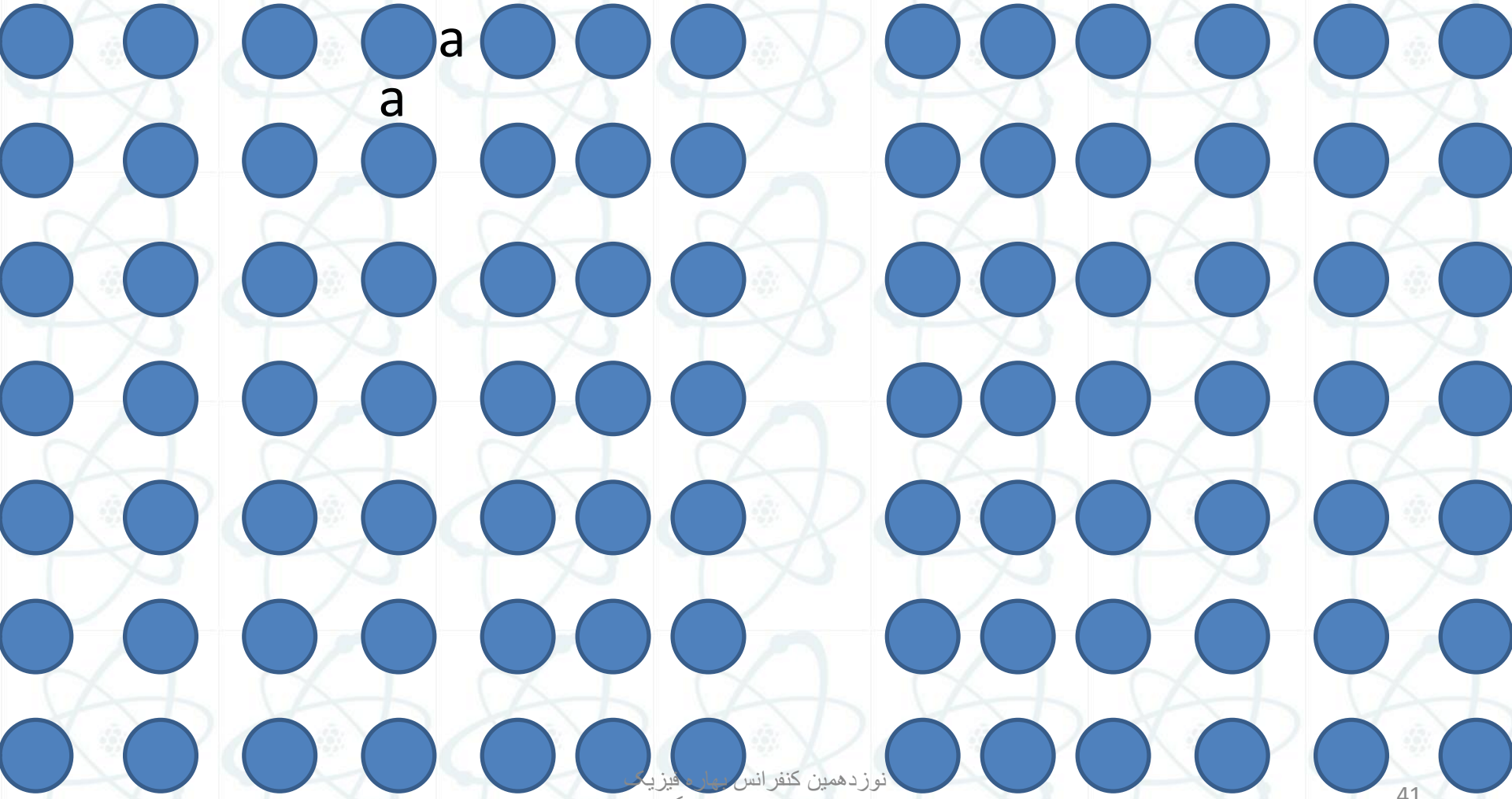


What happens ...?

Infinite Crystalline Solid

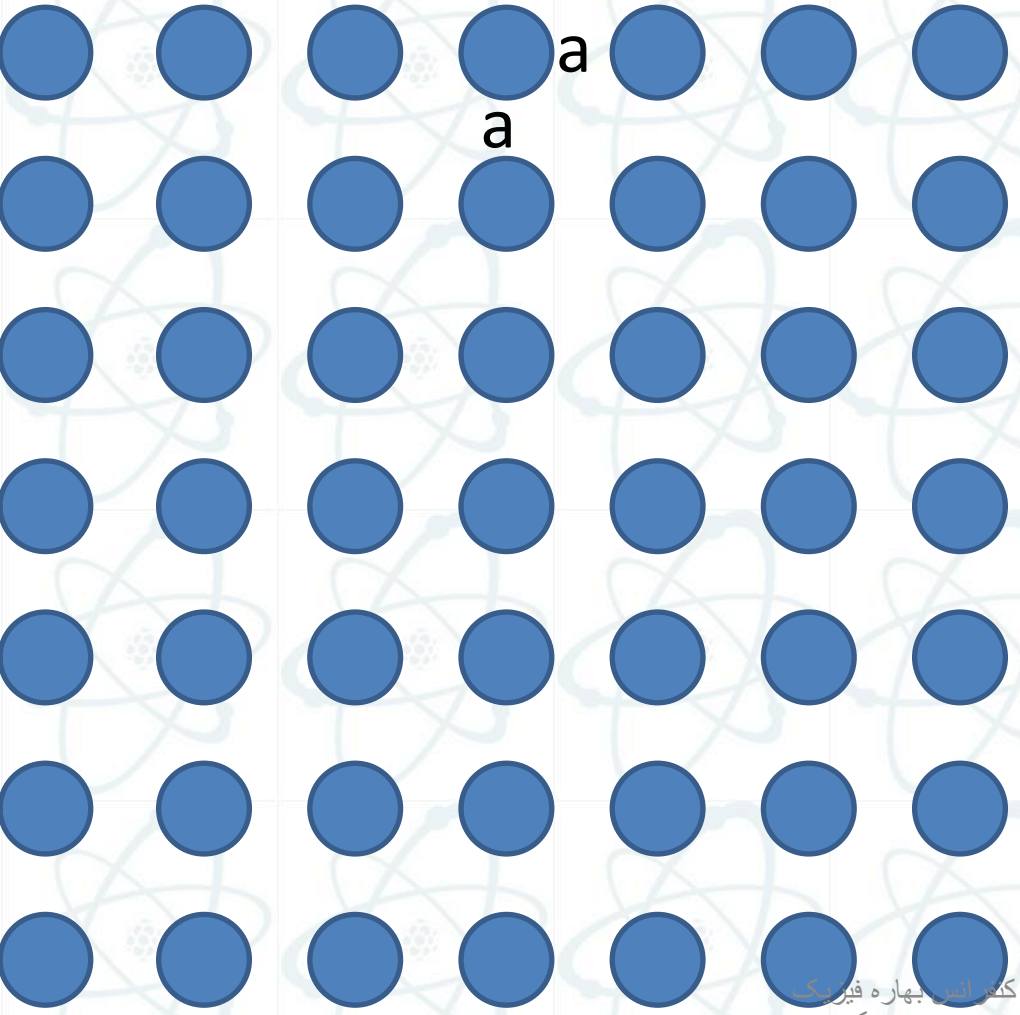


Two Semi-Infinite Crystalline Solid

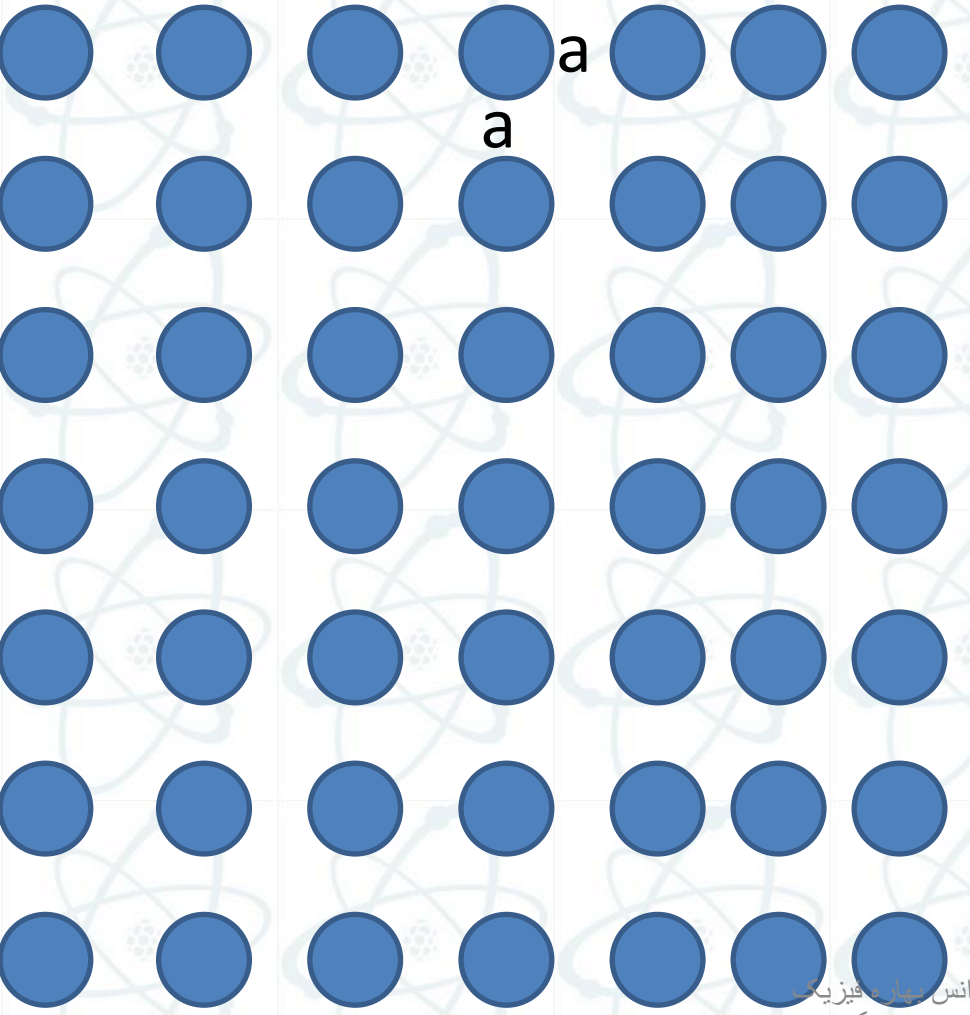


The surface atoms redistribute themselves...

Semi-Infinite Crystalline Solid



Semi-Infinite Crystalline Solid

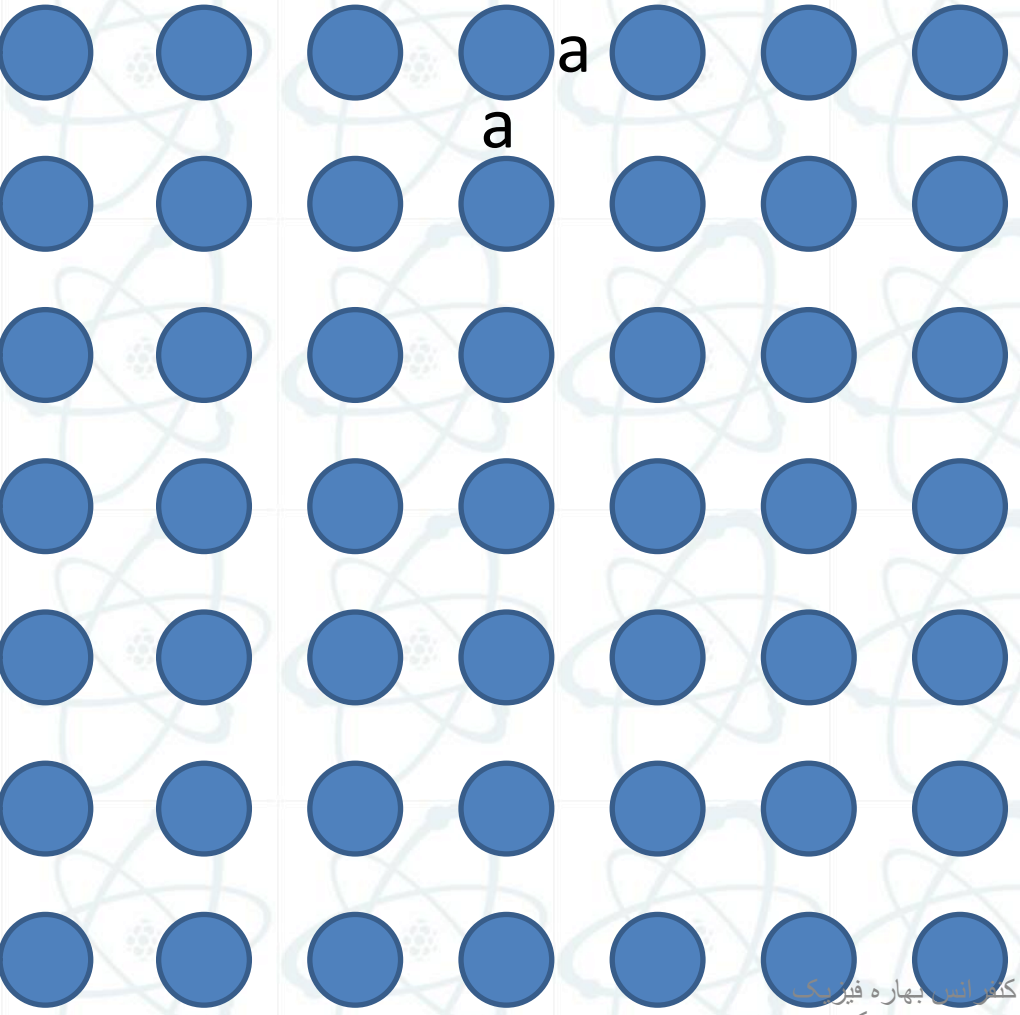


- Near the surface of a semi-infinite crystal, the interatomic distances are different from those in the bulk.
- That is: the ionic density in surface region is different from that in the bulk region.

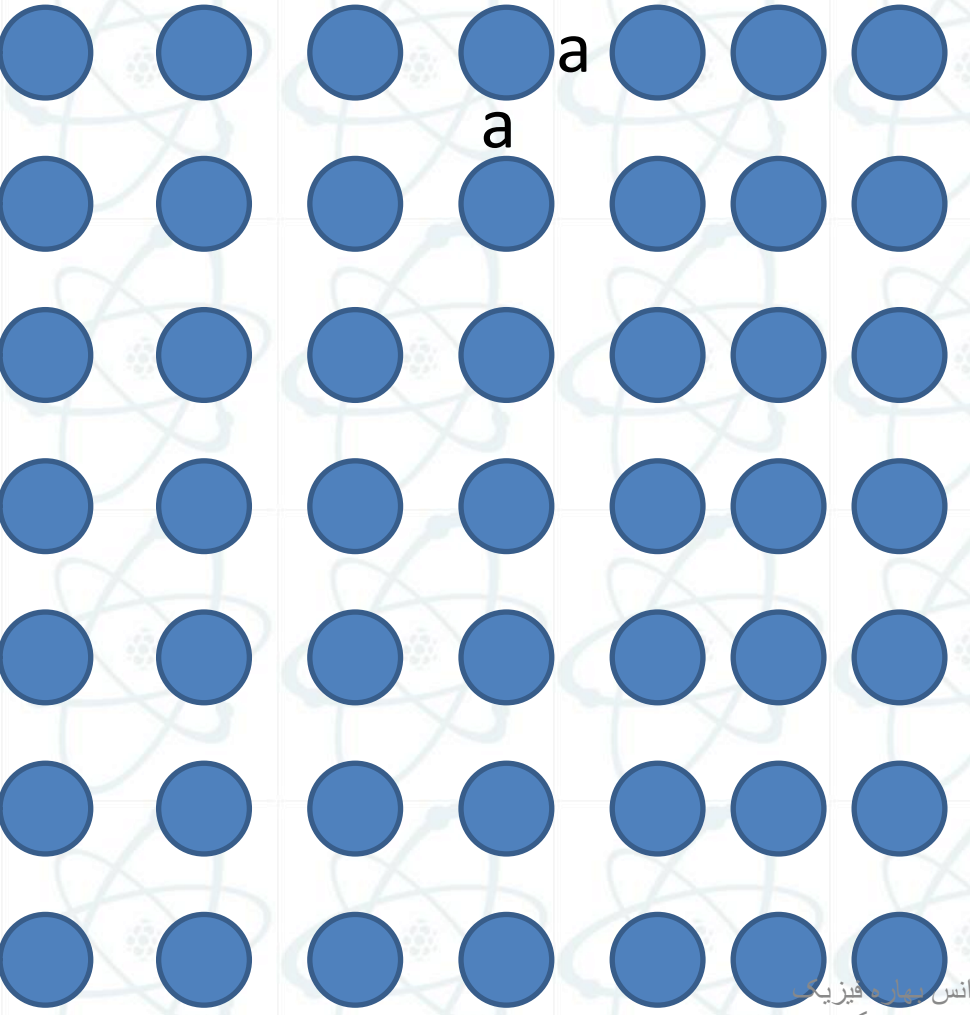

I LIKE A MANAGER WHO ASKS QUESTIONS.
WHO?


I LIKE A MANAGER WHO ASKS QUESTIONS.
WHO?

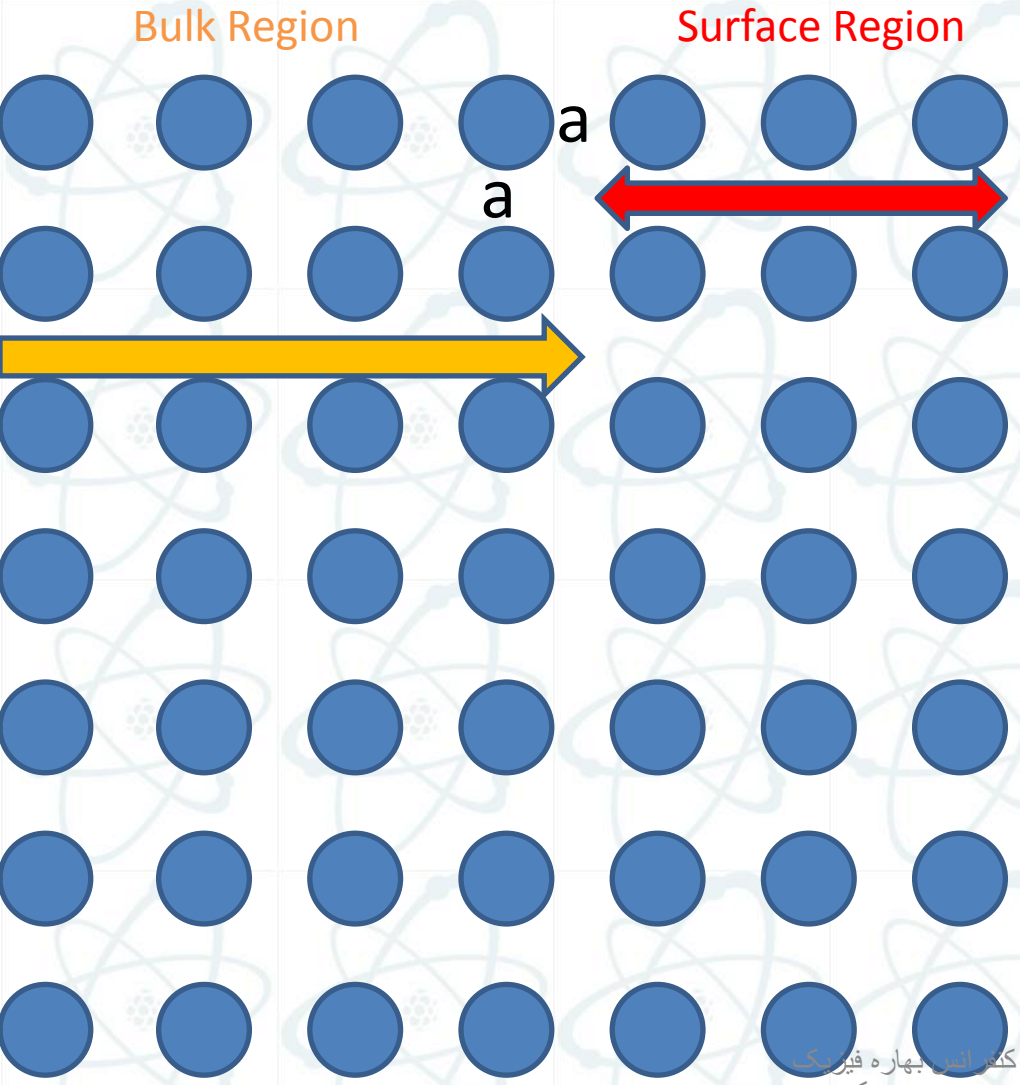
Semi-Infinite Crystalline Solid



Semi-Infinite Crystalline Solid



Semi-Infinite Crystalline Solid



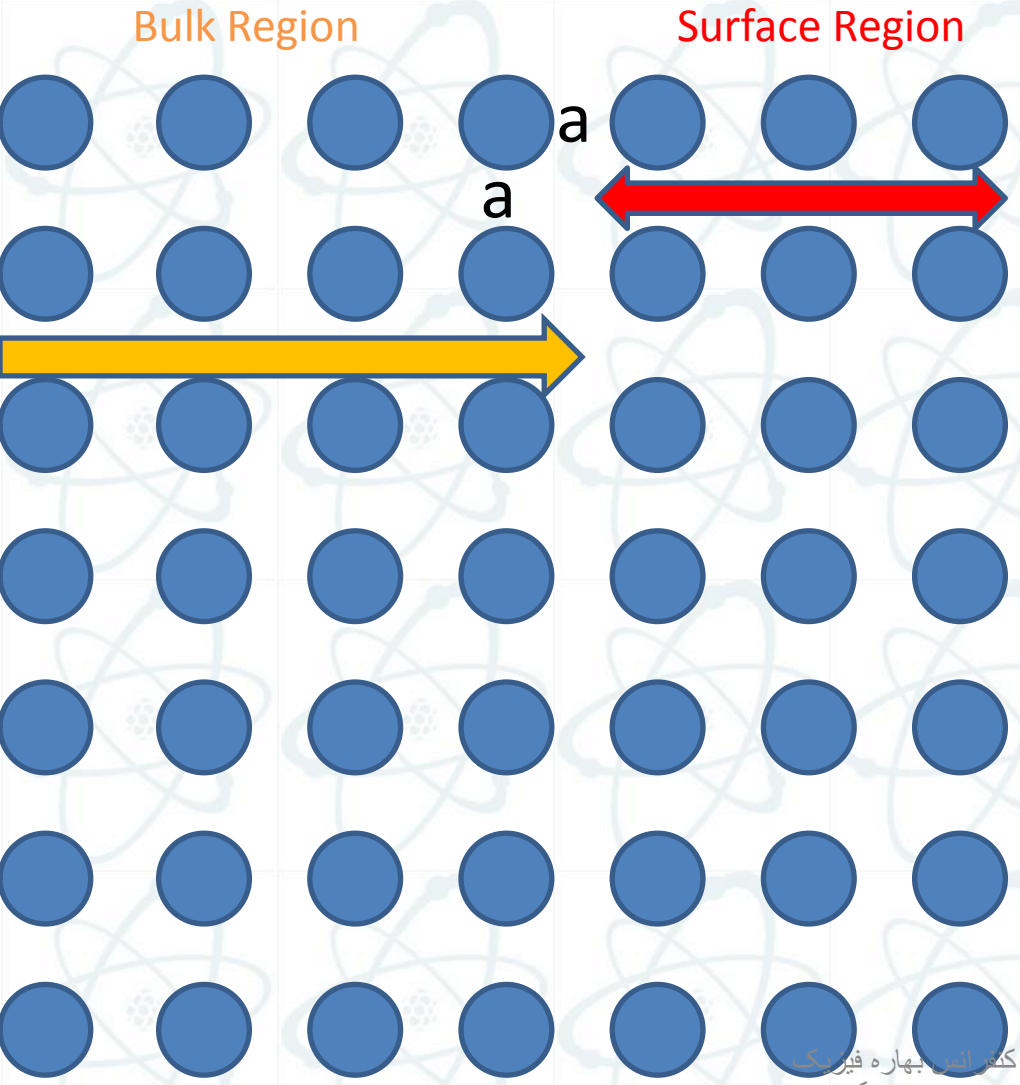
- How many atomic layers in the surface region?
- Surface Region: Expansion or Contraction?

To answer these questions, we have formulated:

Self-compressed inhomogeneous stabilized jellium model (SC-ISJM)

M. Payami, T. Mahmoodi, *Can. J. Phys.* ***89***, 967 (2011).

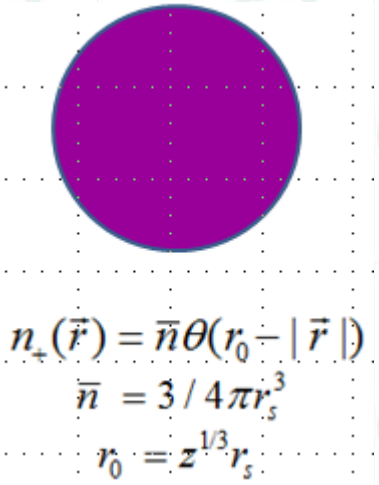
Semi-Infinite Crystalline Solid



- How many atomic layers in the surface region?
- Surface Region: Expansion or Contraction?

SC-SJM

- In Self-Compressed Stabilized Jellium Model (SC-SJM) :



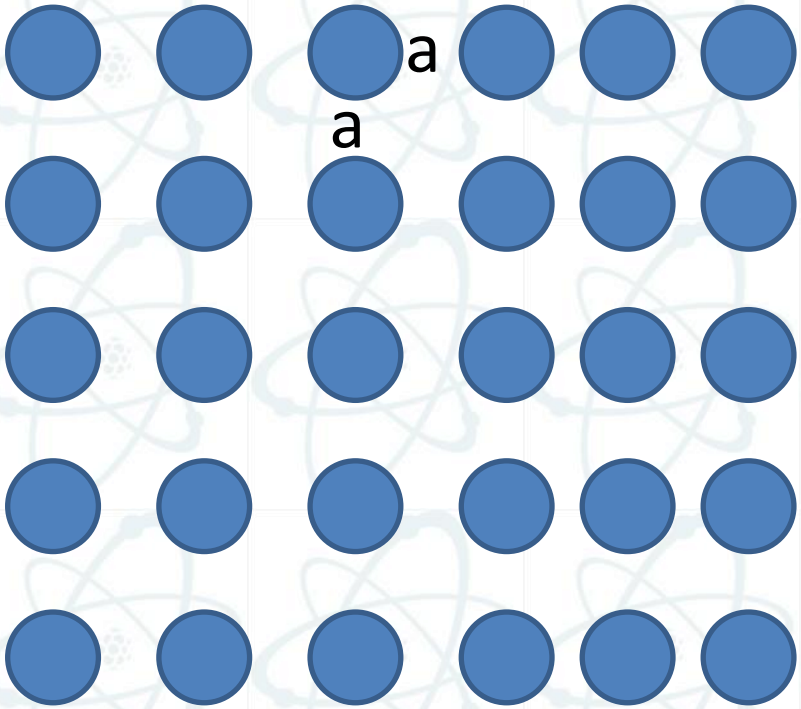
Energy minimization determines r_s :

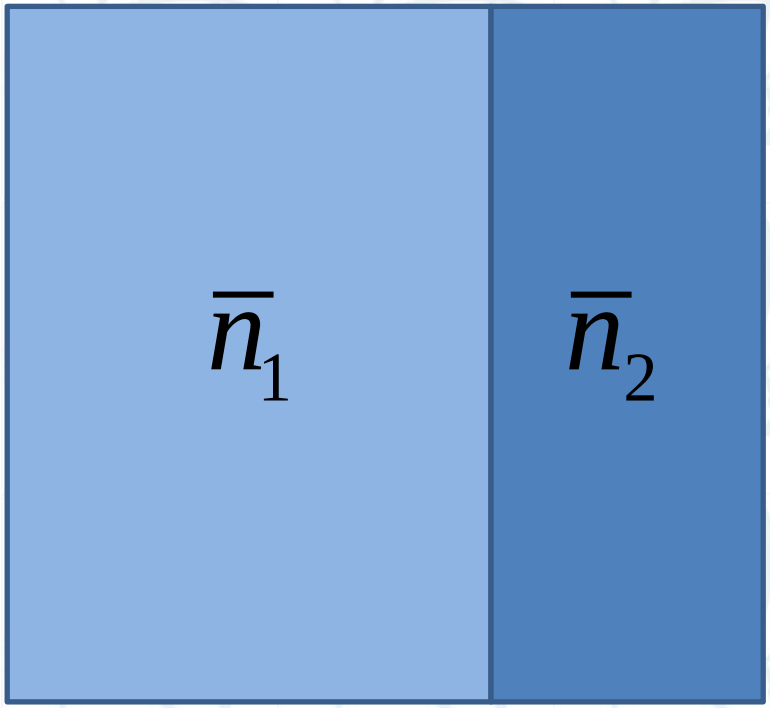
$$\partial E / \partial r_s \big|_{r_s \dagger} = 0$$

$r_s \dagger$ determines the equilibrium density

r_s is variable

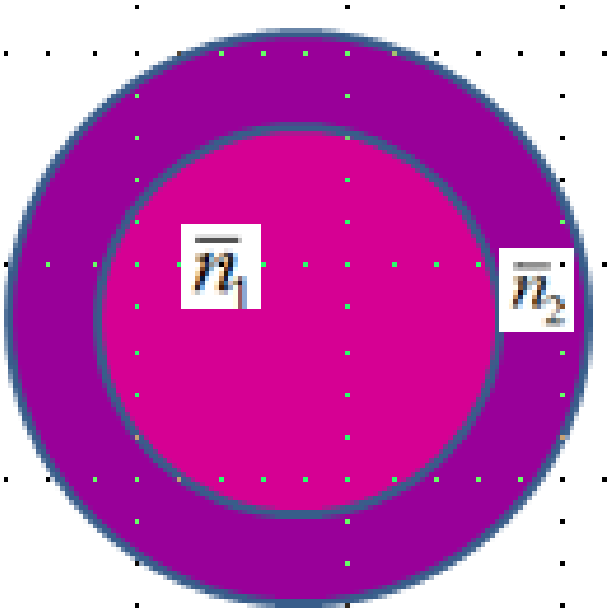
Inhomogeneous Jellium Model





SC-ISJM

- In Self-Compressed Inhomogeneous Stabilized Jellium Model:



$\bar{n}_1$ and $\bar{n}_2$ are variables

$$\partial E / \partial \bar{n}_1 \big|_{\bar{n}_1 \dagger} = 0$$

$$\partial E / \partial \bar{n}_2 \big|_{\bar{n}_2 \dagger} = 0$$

ISJM

$$E_{ISJM}[n,\{n_+^{(\alpha)}\}] = E_{JM}[n,\{n_+^{(\alpha)}\}] + \sum_\alpha < \delta v >_{WS} (\bar{n}_\alpha) \int d\vec{r}\,\Theta^{(\alpha)}(\vec{r})[n(\vec{r}) - n_+^{(\alpha)}(\vec{r})]$$

$$+ \sum_\alpha [\bar{w}_R(\bar{n}_\alpha) + \varepsilon_M(\bar{n}_\alpha)] \int d\vec{r}\; n_+^{(\alpha)}(\vec{r})$$

α enumerates different regions

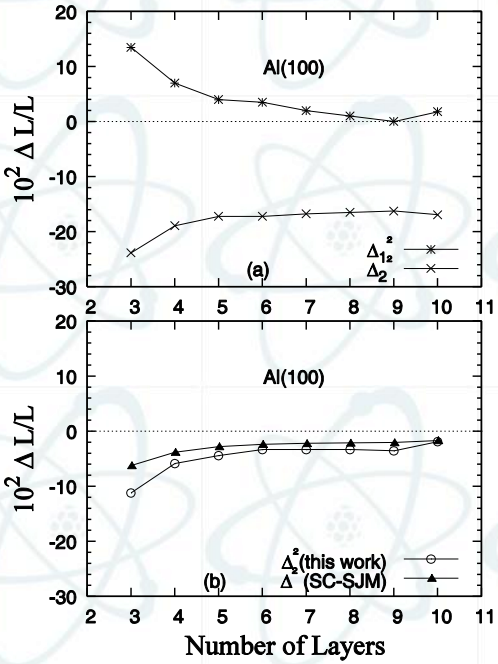
M. Payami, T. Mahmoodi, *Can. J. Phys.* ***89***, 967 (2011)

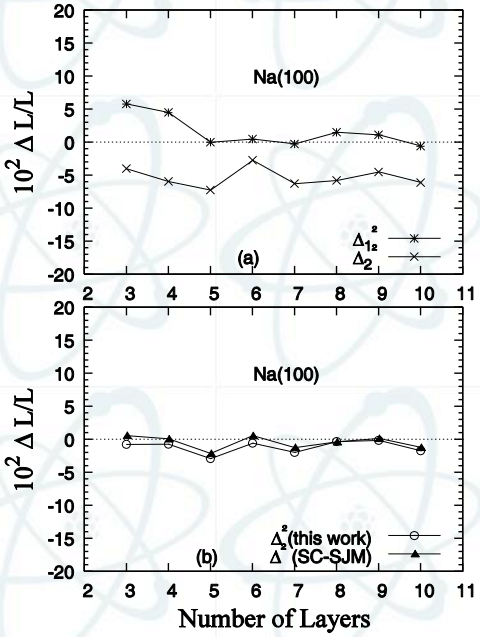
Calculation Method

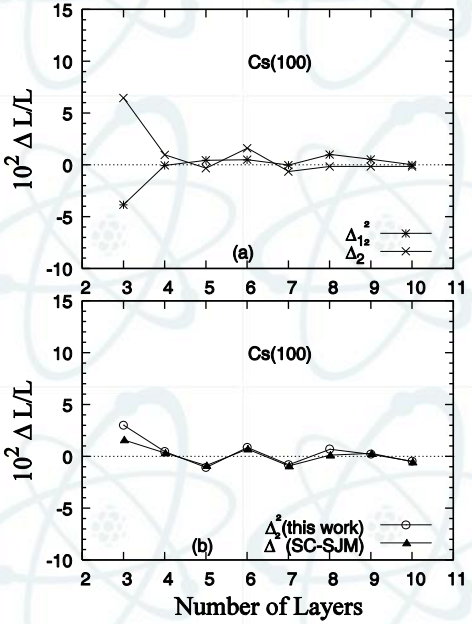
Equilibrium State:

$$E_0 / N \equiv E(\{\bar{n}_\alpha^\dagger\}) / N = \min_{\{\bar{n}_\alpha\}} E(\{\bar{n}_\alpha\}) / N$$

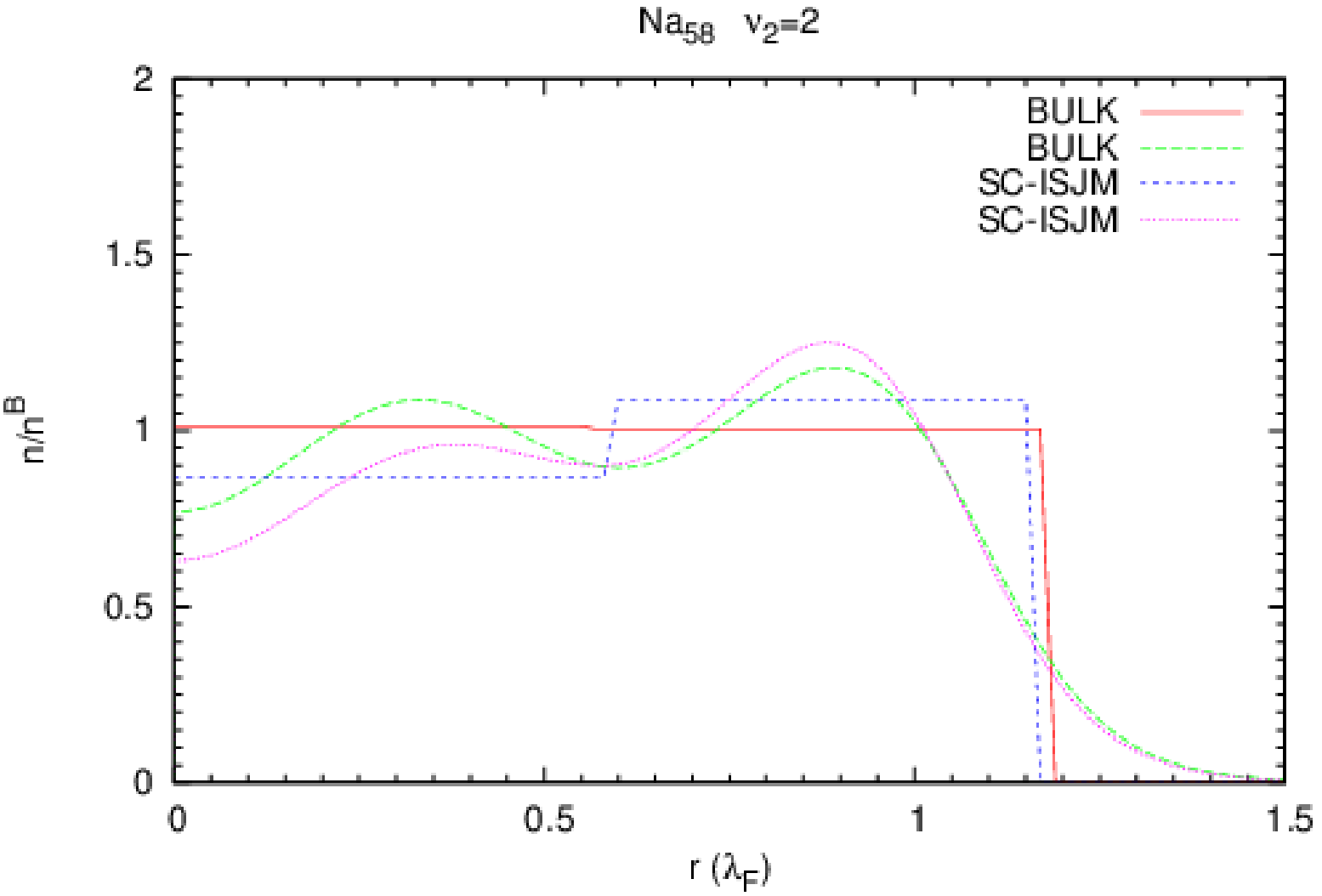
SC-ISJM Results for Thin films



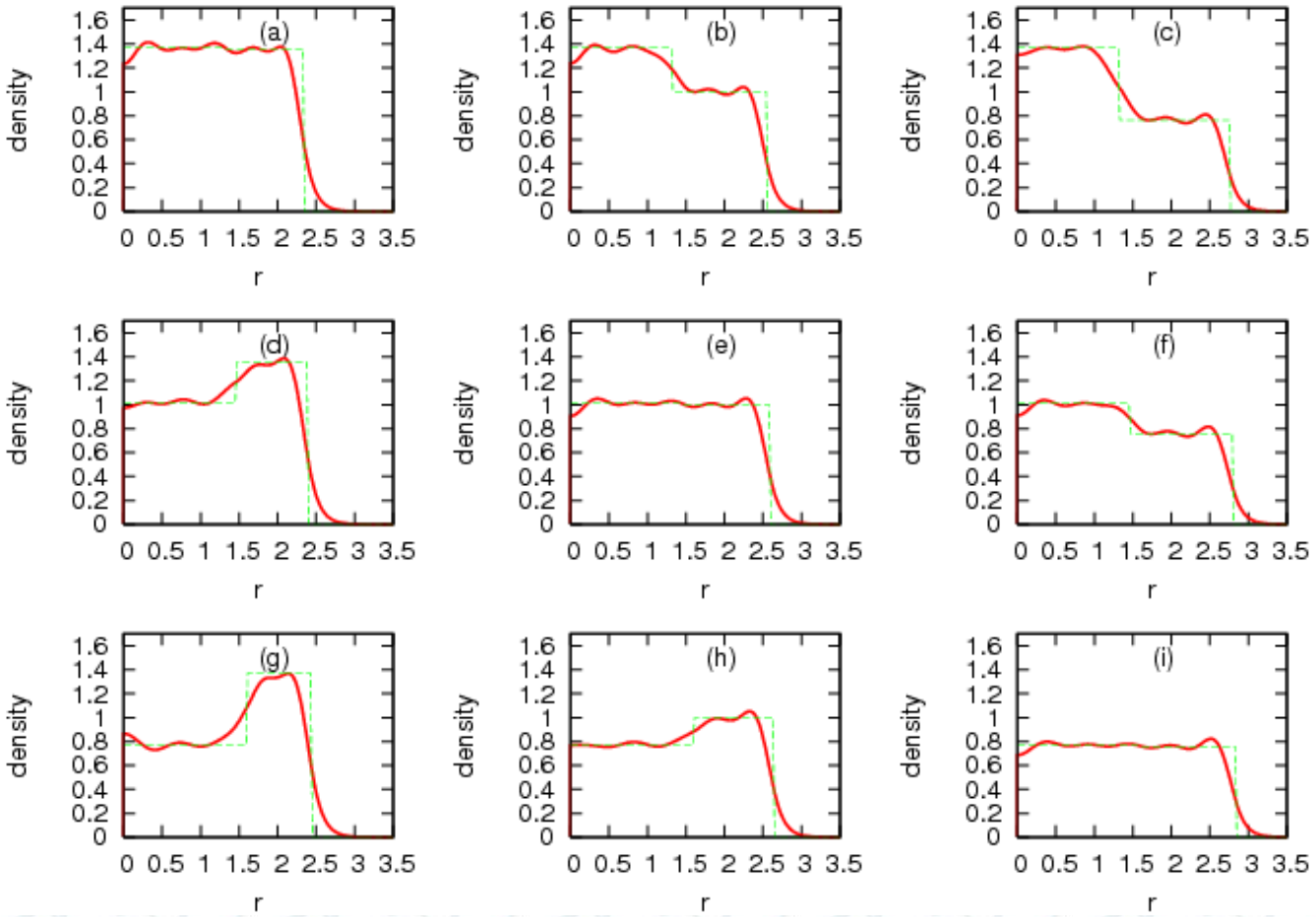




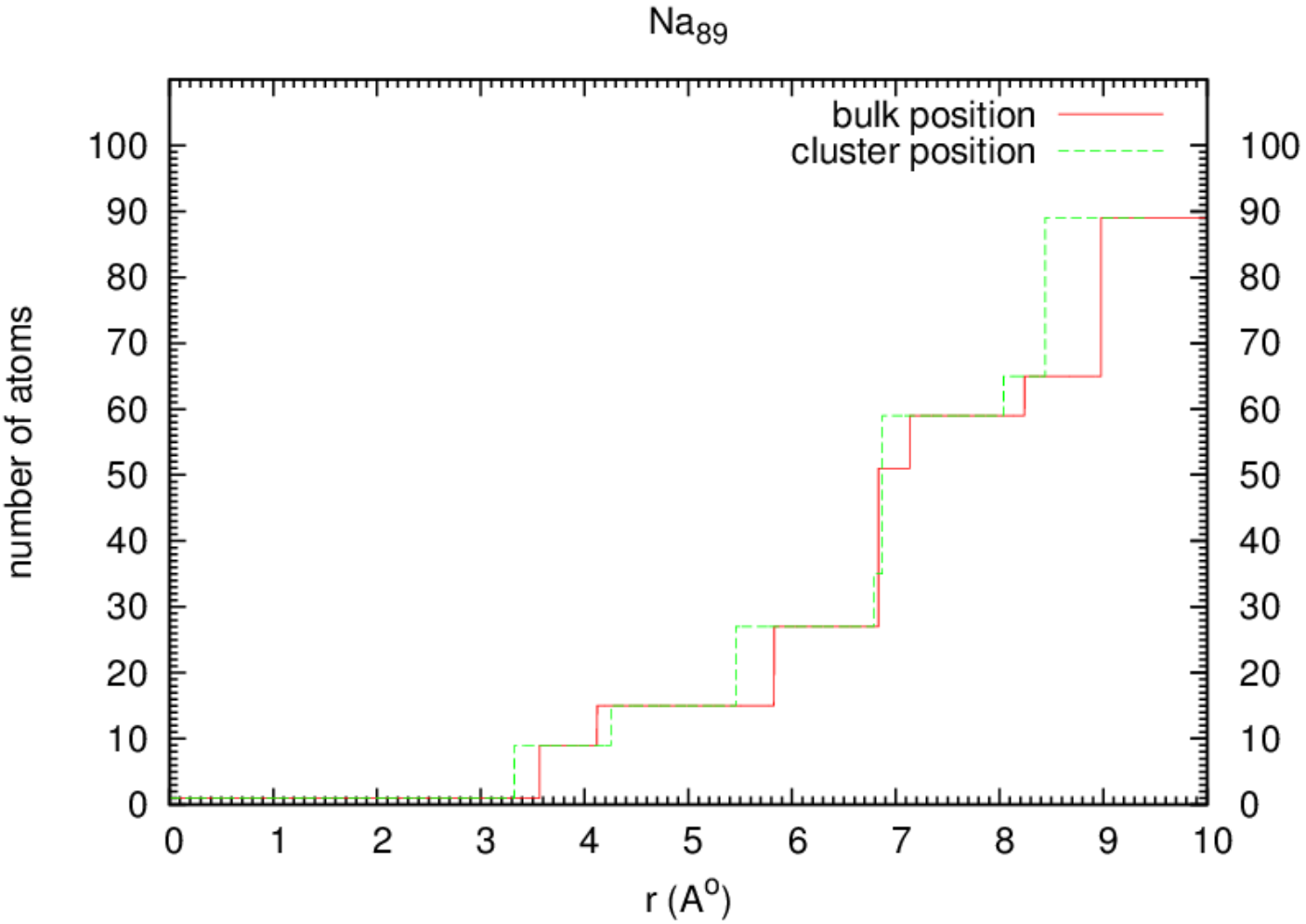
SC-ISJM results fo metal clusters



Al204,n2=2



Results: First-Principles



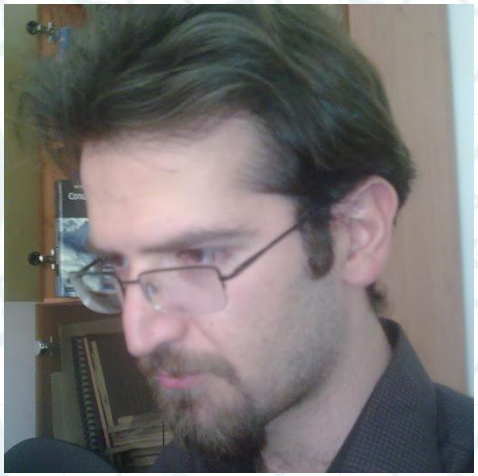
از توجه شما بینهایت سپاسگزارم

Our Group

M. Payami

Dr. T. Mahmoodi

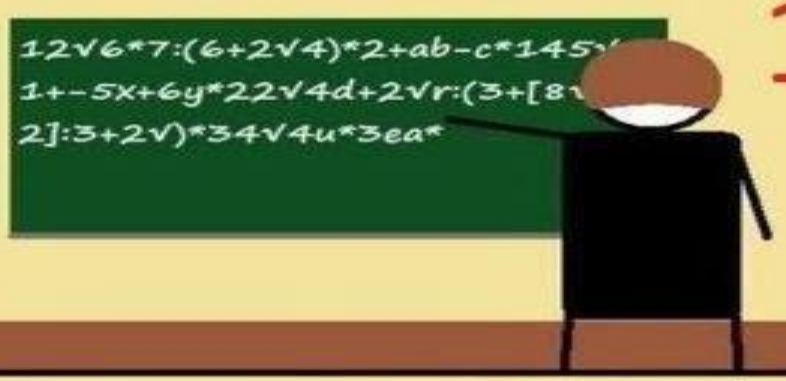
Dr. N. Zare



Y. Taghipour Azar
PhD Student

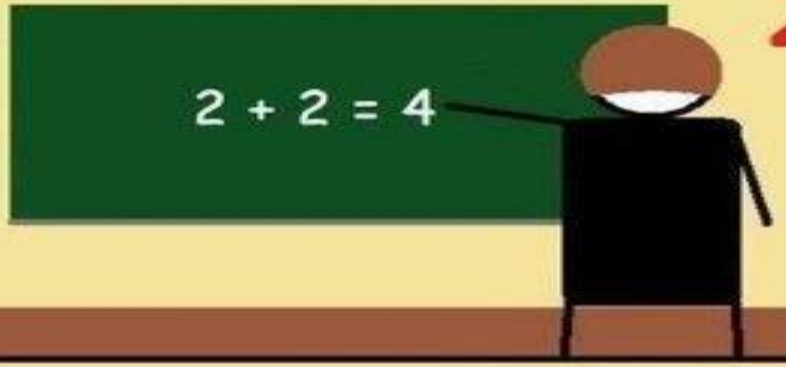
1

نوشته های روی تخته !



2

توضیح استاد ؟!

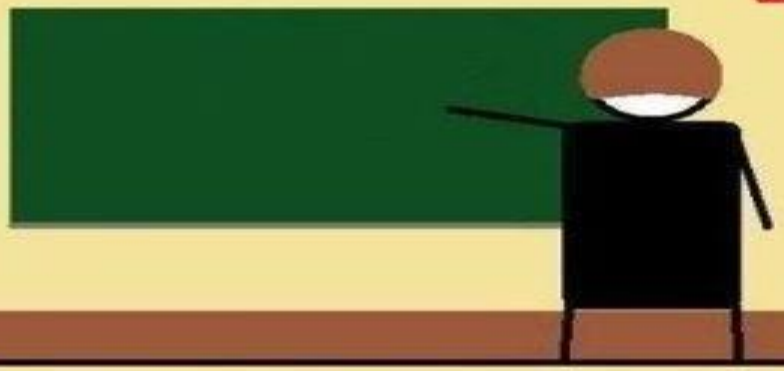


3

چیزی که دانشجو میبینه :دی

4

چیزی که دانشجو یادش میمونه



5

چیزی که تو امتحان میاد ؟!

6

مشاهدات نظافتکار !