Métodos Computacionales

Dinámica Molecular

Octubre 23, 2024

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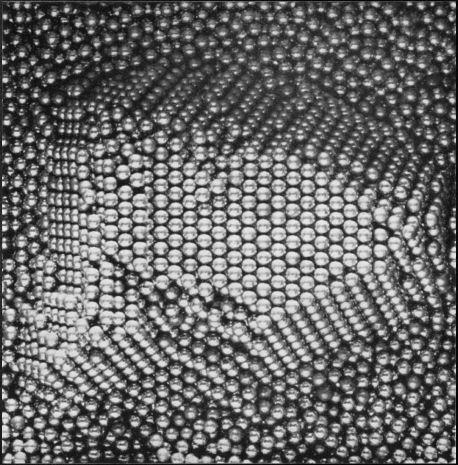


Bernal *et al.*, Proc. Roy. Soc. A 280(1964)16

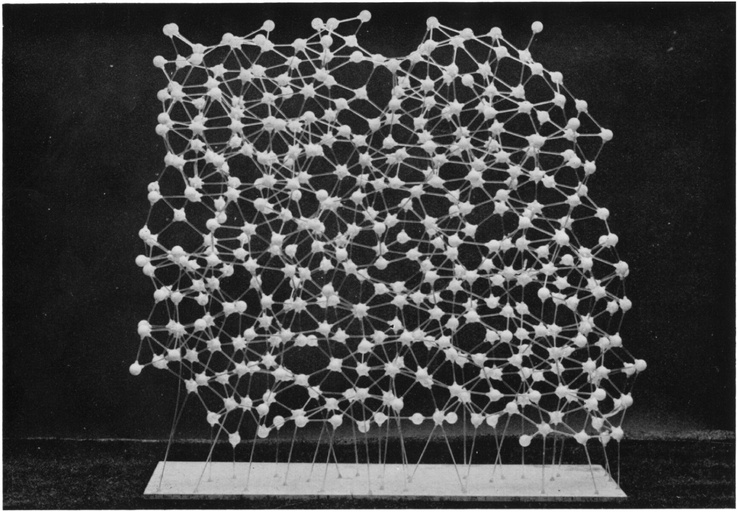
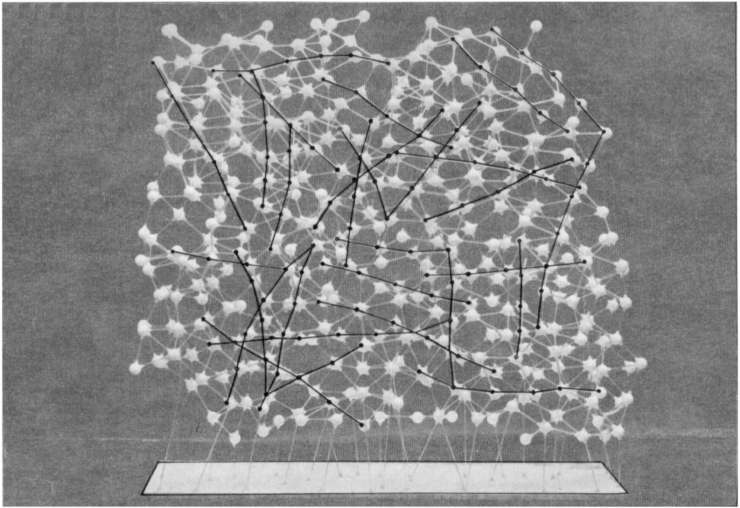


FIGURE 13. Ball and spoke model of random rigid sphere assembly. The transparency shows some of the collineations which occur in it.

Bernal *et al.*, Proc. Roy. Soc. A 280(1964)16



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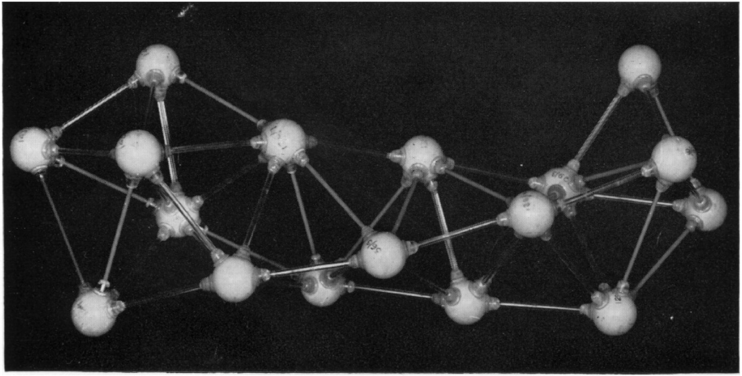


FIGURE 12. Triple helix of tetrahedra showing pseudonucleus from random rigid sphere assembly model.

Bernal *et al.*, Proc. Roy. Soc. A 280(1964)16

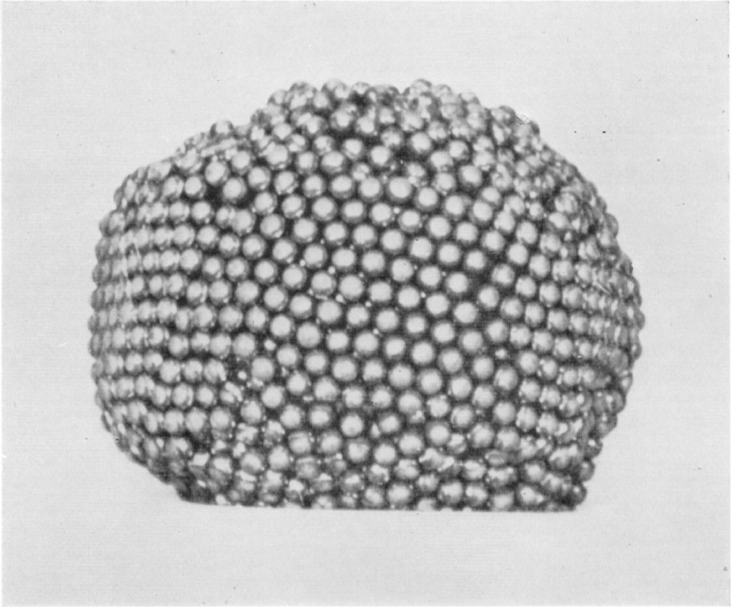


FIGURE 15. Regular crystalline patches induced on the sides of ball-bearing mass due to smoothness of balloon surface.

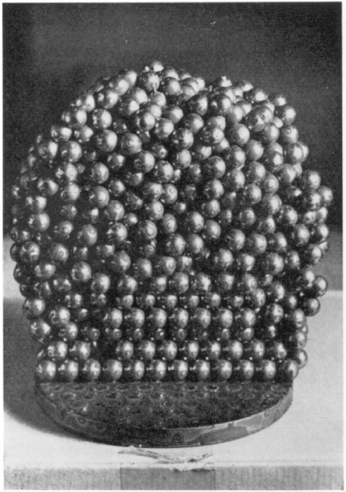


FIGURE 16. Ball-bearing assembly showing transition from random close-packing to regular crystalline array induced by inserting a flat plate.

Bernal *et al.*, Proc. Roy. Soc. A 280(1964)16

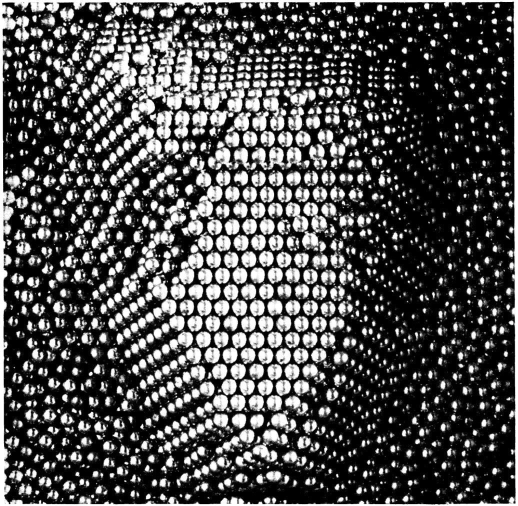


FIGURE 14. Face-centred cubic 'crystal' surrounded by 'liquid' caused by shearing ball-bearing mass. 111 face is shown at the top surface.

Bernal *et al.*, Proc. Roy. Soc. A 280(1964)16

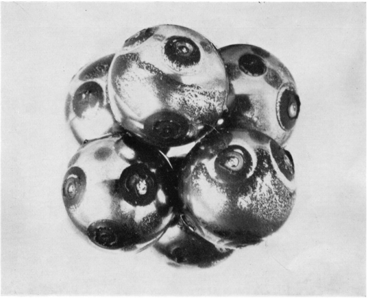


FIGURE 11. Portion of random close-packed ball assembly showing marks of further contacts.

Bernal *et al.*, Proc. Roy. Soc. A 280(1964)16

Dinámica

Estudia el movimiento en relación con las causas que lo producen.

Ecuaciones de movimiento, *por ejemplo...*:

Newton

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = -\nabla U(\mathbf{r})$$

Langevin $m\dfrac{\partial \mathbf{v}}{\partial t} = -\nabla U - \gamma\mathbf{v} + \sqrt{2\gamma k_B T}\boldsymbol{\eta}$

Browniano $\gamma\mathbf{v} = -\nabla U + \sqrt{2\gamma k_B T}\boldsymbol{\eta}$

Barostato de Andersen

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \frac{\mathbf{p}}{m} + \frac{\mathbf{r}}{3}\frac{\mathrm{d}\ln V}{\mathrm{d}t}$$

$$\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = -\nabla U - \frac{\mathbf{p}}{3}\frac{\mathrm{d}\ln V}{\mathrm{d}t}$$

$$\frac{\mathrm{d}^2 V}{\mathrm{d}t^2} = \frac{p_0}{M} + \frac{\left(\mathbf{p}^2/m - \nabla U\right)}{3MV}$$

DM acelerada por temperatura

$$\gamma\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = -\nabla U + \sqrt{2\gamma k_B T} - \kappa(\boldsymbol{\theta} - \mathbf{z})\nabla\boldsymbol{\theta}\boldsymbol{\eta}^x$$

$$\bar{\gamma}\frac{\mathrm{d}\mathbf{z}}{\mathrm{d}t} = \kappa(\boldsymbol{\theta} - \mathbf{z}) + \sqrt{2\bar{\gamma}k_B\bar{T}}\boldsymbol{\eta}^z$$

Distribución de equilibrio

¿Qué probabilidad de encontrar un estado del sistema generan?

Newton

$\rho(\mathbf{r}) = \Omega^{-1}, \ NVE$

Langevin $\rho(\mathbf{r}) = Z^{-1} e^{\beta U(\mathbf{r})}, \ NVT$

Browniano $\rho(\mathbf{r}) = Z^{-1} e^{\beta U(\mathbf{r})}, \ NVT$

Barostato de Andersen

$\rho(\mathbf{r}) = Z^{-1} e^{\beta U(\mathbf{r}) + \beta PV}$

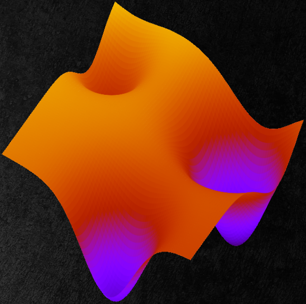
$NPH \rightarrow NPT$

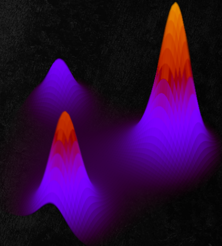
DM acelerada por temperatura

$\rho(\mathbf{r}) = Z^{-1} e^{\beta\left(U(\mathbf{r}) + \kappa(\boldsymbol{\theta} - \mathbf{z})^2/2\right)}$

$\rho(\mathbf{z}) \approx \bar{Z}^{-1} e^{\bar{\beta} F(\mathbf{z})}$

¡Pero la dinámica también muestrea fuera del equilibrio!

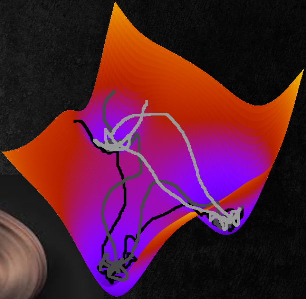


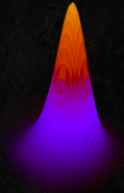


"Rush", Tomasz 'Darkshape' Kaluzny

"nude"
Shinichi Maruyama

Horton Plains

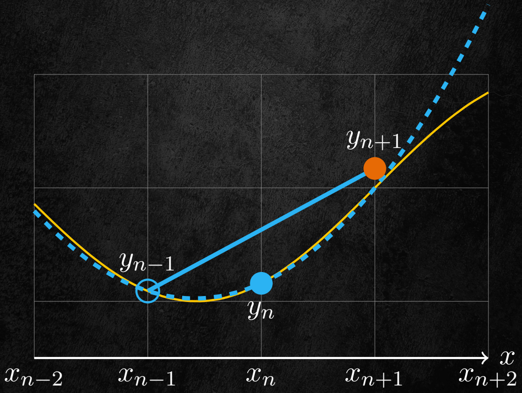




Lo vimos con esta notación $\frac{\mathrm{d}y}{\mathrm{d}x} = F(x, \vec{y})$

Verlet

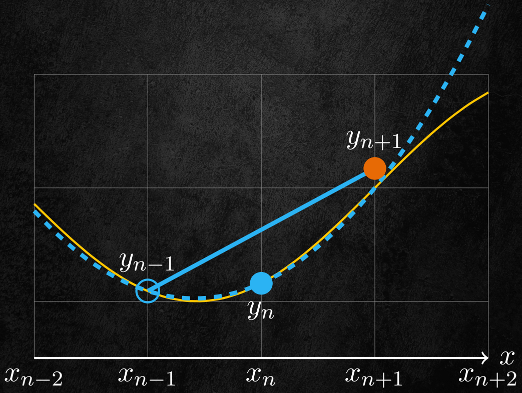
$$\mathbf{y}_{n+1} = 2\mathbf{y}_n - \mathbf{y}_{n-1} + h^2 \frac{\mathrm{d}^2\mathbf{y}}{\mathrm{d}x^2} + O\left(h^4\right)$$



Newton $\dfrac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \dfrac{F(\mathbf{r})}{m} = -\dfrac{\nabla U(\mathbf{r})}{m}$

Verlet

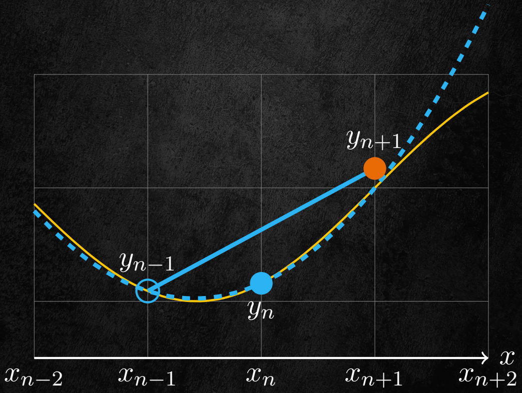
$$\mathbf{r}_{n+1} = 2\mathbf{r}_n - \mathbf{r}_{n-1} + \Delta t^2 \left.\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2}\right|_{\mathbf{r}_n} + O\left(h^4\right)$$



Newton $\frac{d^2\mathbf{r}}{dt^2} = \frac{F(\mathbf{r})}{m} = -\frac{\nabla U(\mathbf{r})}{m}$

Verlet

$$\mathbf{r}_{n+1} = 2\mathbf{r}_n - \mathbf{r}_{n-1} - \Delta t^2 \frac{F_n}{m} + O\left(h^4\right)$$



Velocity Verlet / Strömer-Verlet:

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{v}_n \Delta t + \frac{\mathbf{F}_n}{2m} \Delta t^2$$

$$\mathbf{v}_{n+1} = \mathbf{v}_n + \frac{\mathbf{F}_n + \mathbf{F}_{n+1}}{2m} \Delta t$$

Newton

Browniano Convencional:

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \frac{\Delta t}{m\gamma} F_n + \sigma_X \mathbf{X}_G \qquad \sigma_X = \sqrt{\frac{2k_B T \Delta t}{m\gamma}}$$

Browniano

Ermak:

Langevin

$$\mathbf{r}_{n+1} = \mathbf{r}_n + c_1 \Delta t \mathbf{v}_n + c_2 \Delta t^2 \frac{F_n}{m} + \sigma_X \mathbf{X}_G$$

$$\mathbf{v}_{n+1} = c_0 \mathbf{v}_n + c_1 \Delta t \frac{F_n}{m} + \frac{c_2 \Delta t}{m} (F_{n+1} - F_n) + \sigma_V \left(\sigma_{V,X} \mathbf{X}_G + \sigma_{V,V} \mathbf{V}_G \right)$$

Born-Oppenheimer:

$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2} - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{i>j} \frac{1}{r_{ij}} - \sum_A \frac{\nabla_A^2}{2M_A} + \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$

$$\hat{H} = \hat{H}_e(R,r) - \sum_A \frac{\nabla_A^2}{2M_A} + \sum_{B>A} \frac{Z_A Z_B}{R_{AB}} \qquad \Psi(R,r) = \psi(R,r)\phi(R)$$

Schrödinger: $\hat{H}\Psi(R,r) = E\Psi(R,r)$

$$\psi(R,r)\left[E_e(R) - \sum_A \frac{\nabla_A^2}{2M_A} + \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}\right]\phi(R) = \psi(R,r)E\phi(R)$$

$$\left[-\sum_A \frac{\nabla_A^2}{2M_A} + U(R)\right]\phi(R) = E\phi(R)$$

Potencial de a pares:

$$U(\mathbf{r}) = \sum_i U_1(\mathbf{x_i}) + \sum_{i<j} U_2(\mathbf{x_i}, \mathbf{x_j}) + \sum_{i<j<k} U_3(\mathbf{x_i}, \mathbf{x_j}, \mathbf{x_k}) + \cdots$$

$$U(\mathbf{r}) = \sum_{i<j} U_2(r_{ij}) + \sum_{i<j<k} U_3(\mathbf{r}_{ij}, \mathbf{r}_{jk}) + \cdots$$

Lennard-Jones

$$U_2(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

Morse

$$U_2(r_{ij}) = D_e(1 - e^{\alpha(r_{ij} - r_e)})^2 - D_e$$

Fuerza

$$\mathbf{F}_{r_i} = \nabla_{r_i} U_2(r_{ij})\Big|_{r1}$$

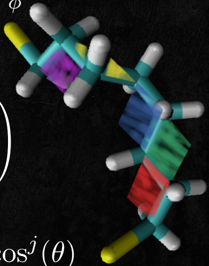
$$= \frac{\partial U_2(r_{ij})}{\partial r_{ij}} \nabla_{r_i} r_{ij}$$

$$= \frac{\partial U_2(r_{ij})}{\partial r_{ij}} \hat{\mathbf{r}}_{ij}$$

Campo de Fuerzas:

Hill (1942)

$$U\Big(\{r_{ij}\},\{d\},\{\phi\}\Big) = U_2^{\mathsf{LJ}}(r_{ij}) + \sum_d k_d\big(d - d_{eq}\big)^2 + \sum_\phi k_\phi\big(\phi - \phi_{eq}\big)^2$$



OPLS (1984)

$$U\Big(\{r_{ij}\},\{d\},\{\phi\},\{\theta\}\Big) = \sum_{i<j} f_{ij}\left(\frac{q_i q_j e_0^2}{r_{ij}} + U_2^{\mathsf{LJ}}(r_{ij})\right)$$

$$+\sum_d k_d\left(d - d_{eq}\right)^2 + \sum_\phi k_\phi\left(\phi - \phi_{eq}\right)^2 + \sum_\theta \sum_{j=0}^{5} C_j \cos^j(\theta)$$

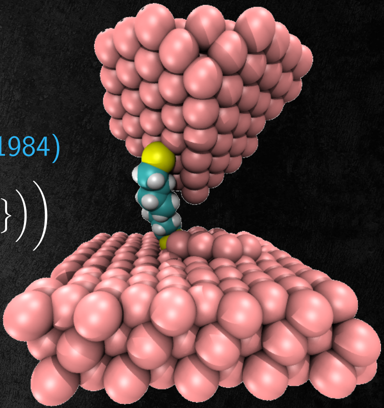
CHARMM, GROMOS, AMBER, Tersoff, ReaxFF, . . .

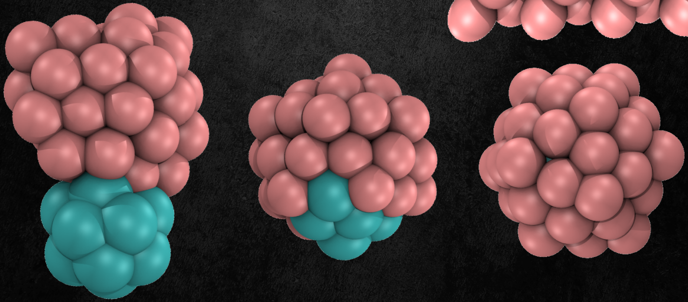
Muchos Cuerpos:

El método del átomo embebido, EAM (1984)

$$U(\mathbf{r}) = \frac{1}{2}\sum_{i<j} U_2(r_{ij}) + \sum_i E_i\Big(\rho_i\big(\{r_{ij}\}\big)\Big)$$

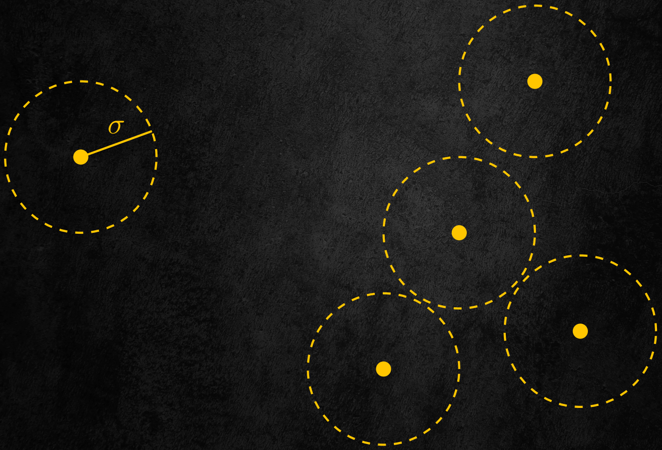
$$\rho_i = \textstyle\sum_{j\neq i} \psi_j(r_{ij})$$





Lista de Vecinos

Escalea con N^2



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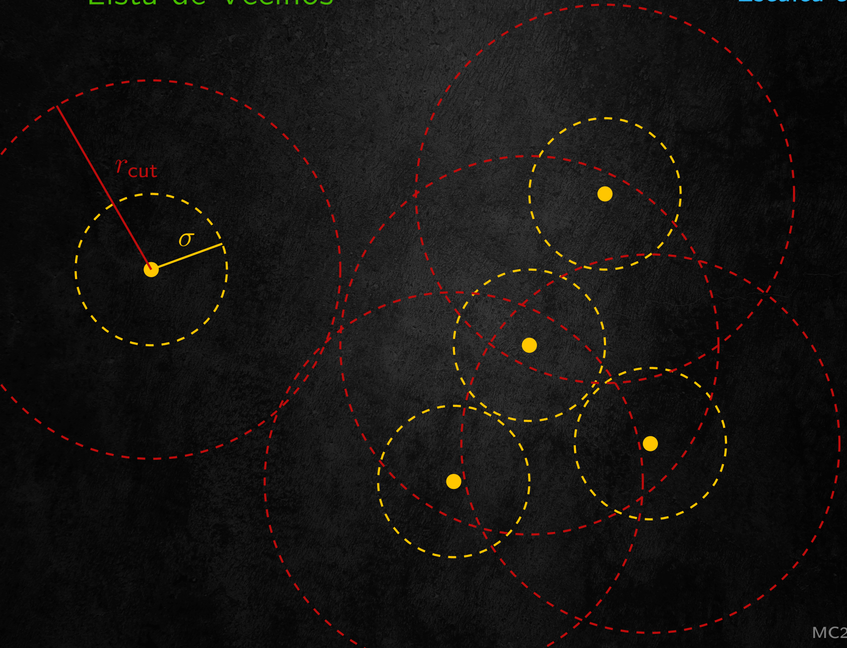
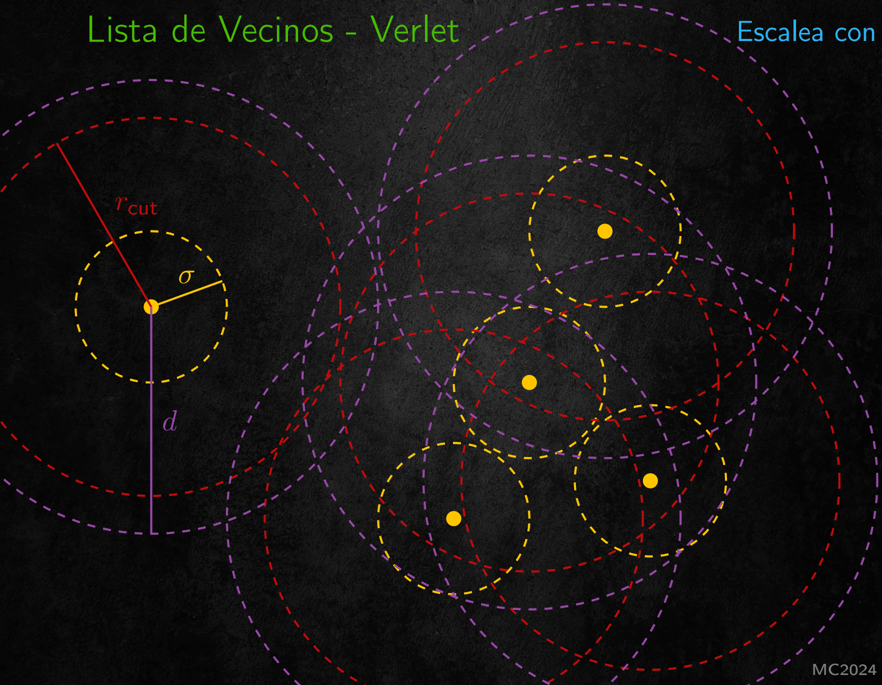


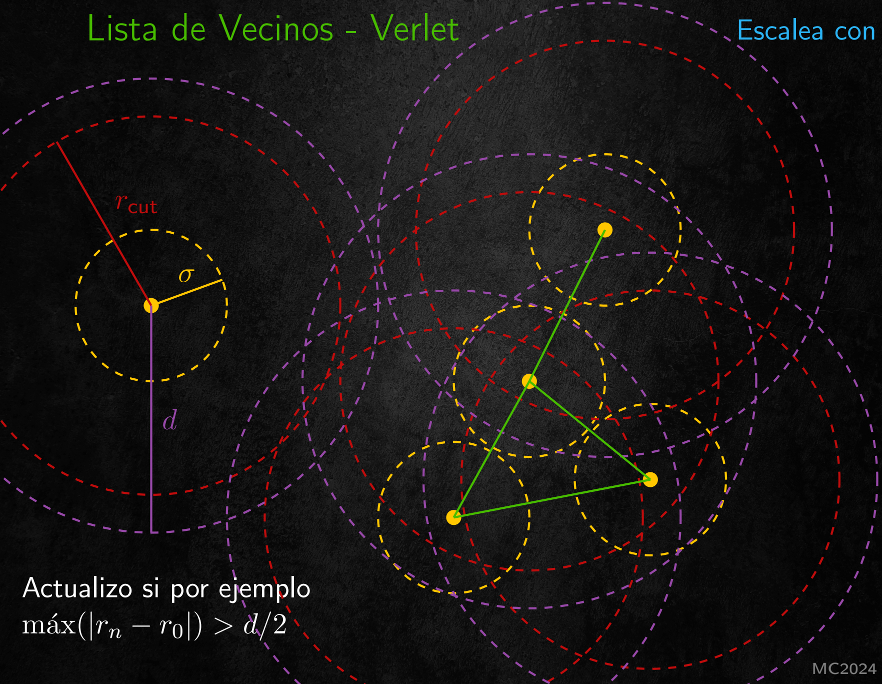
Lista de Vecinos - Verlet

Escalea con $N^{5/3}$



Lista de Vecinos - Verlet

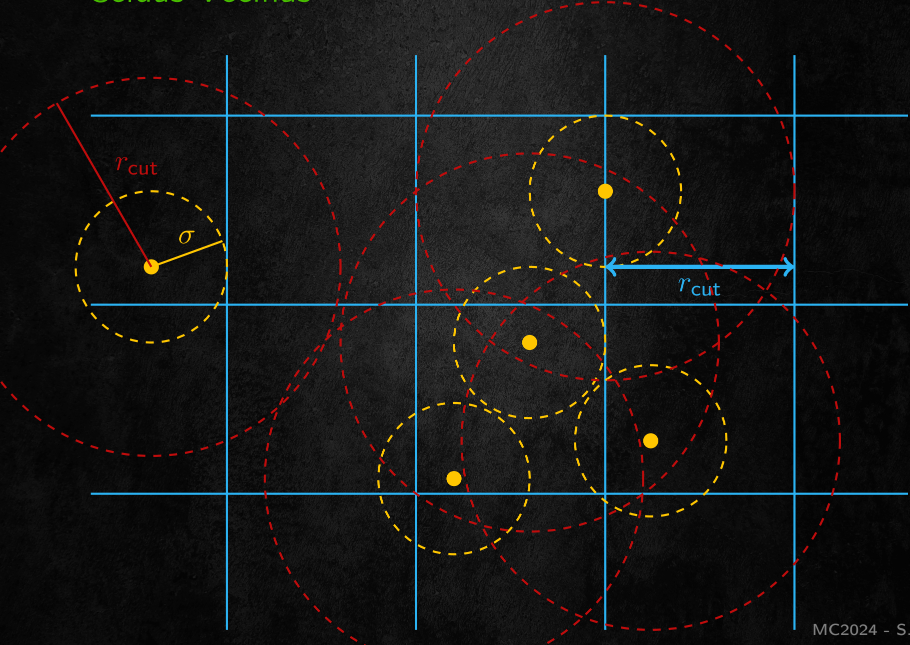
Escalea con $N^{5/3}$



Actualizo si por ejemplo
$\max(|r_n - r_0|) > d/2$

Celdas Vecinas

Escalea con N



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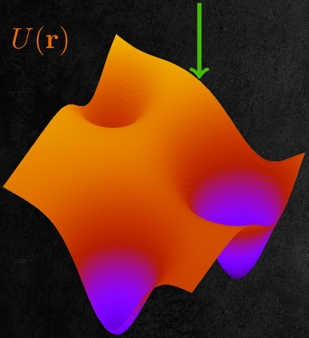

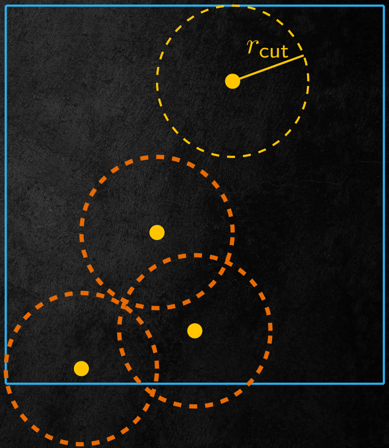

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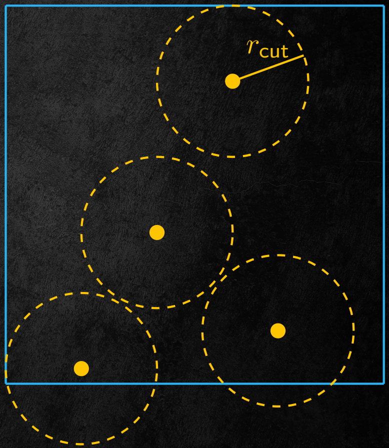

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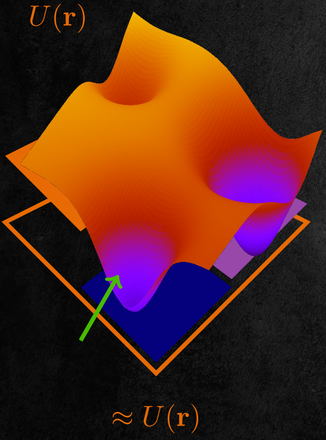

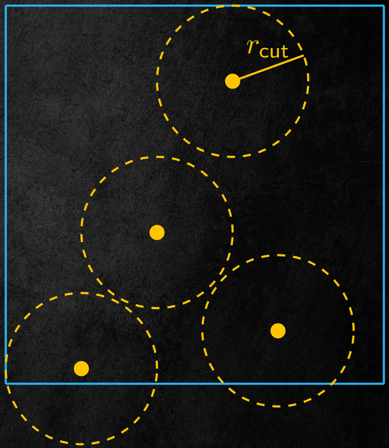

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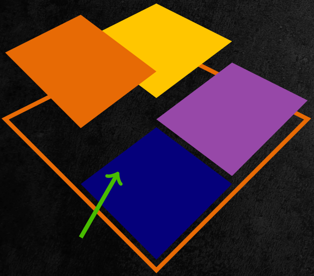
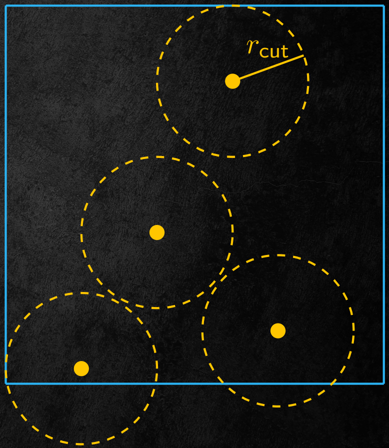
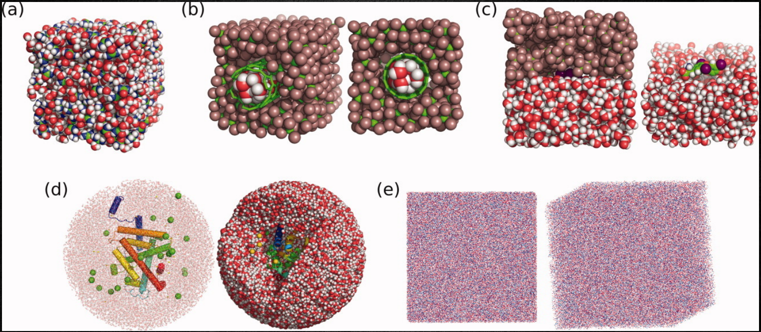


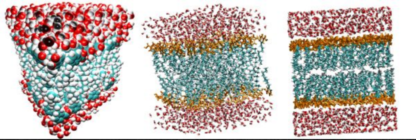
$\approx U(\mathbf{r})$

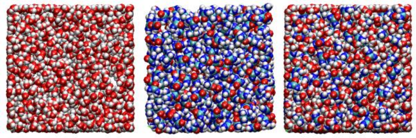


PACKMOL

Initial configurations for Molecular Dynamics Simulations by packing optimization







Martinez *et al.*, J. Comp. Chem. 24(2003)819
Martinez *et al.*, J. Comp. Chem. 30(2009)2157

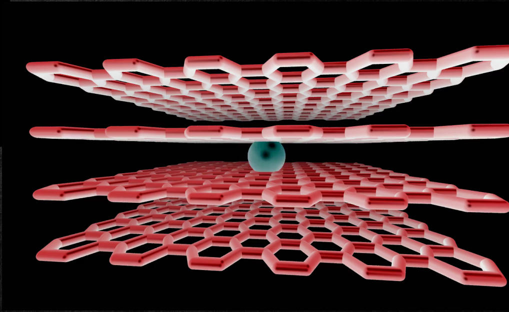
Integracion de los momentos (NVT):

Distribución de Maxwell-Boltzmann / Espacio de configuraciones

$$
\begin{aligned}
\rho(\mathbf{p},\mathbf{r}) &= Z^{-1} e^{-\beta E(\mathbf{p},\mathbf{r})} \\
&= \frac{e^{-\beta \mathbf{p}^2/2m}}{\int_{\mathbf{p}} e^{-\beta \mathbf{p}^2/2m}\,\mathrm{d}\mathbf{p}} \frac{e^{-\beta U(\mathbf{r})}}{\int_{\mathbf{r}} e^{-\beta U(\mathbf{r})}\,\mathrm{d}\mathbf{r}} \\
&= \left(\frac{\beta}{2m\pi}\right)^{\frac{3}{2}} e^{-\beta \mathbf{p}^2/2m} \frac{e^{-\beta U(\mathbf{r})}}{Q} \\
&= \tilde{f}(\mathbf{p}) q(\mathbf{r}) \qquad\qquad \tilde{f}(\mathbf{p}) = f_1(p_x) f_1(p_y) f_1(p_z)
\end{aligned}
$$

$$
f(v) = \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} 4\pi v^2 e^{-\beta m v^2/2} \qquad \langle A \rangle = \int A(\mathbf{r}) q(\mathbf{r})\,\mathrm{d}\mathbf{r}
$$

Condiciones de Contorno Periódicas



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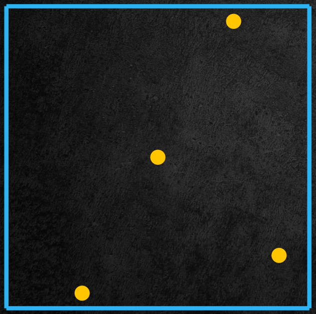

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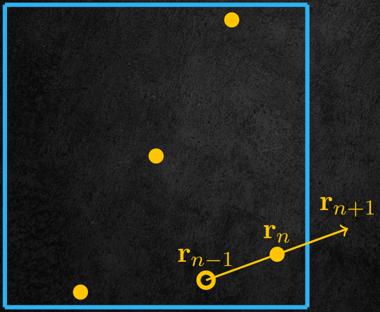

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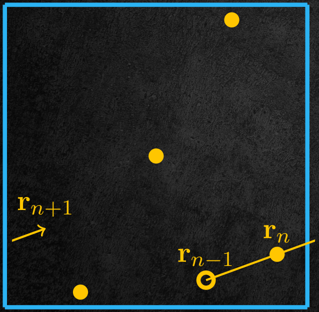

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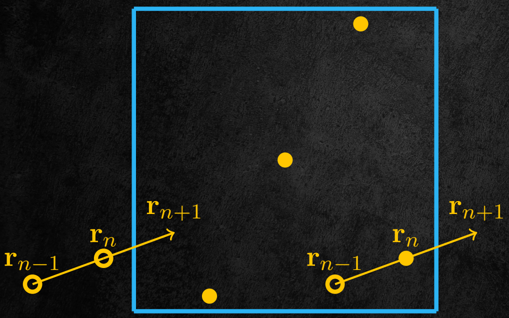

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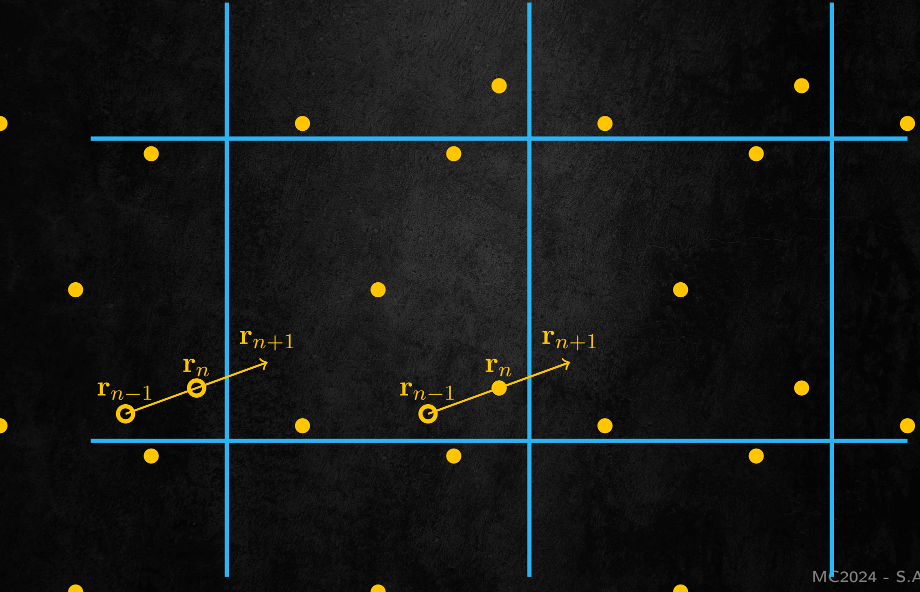

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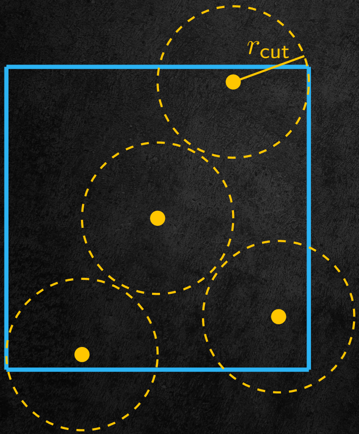

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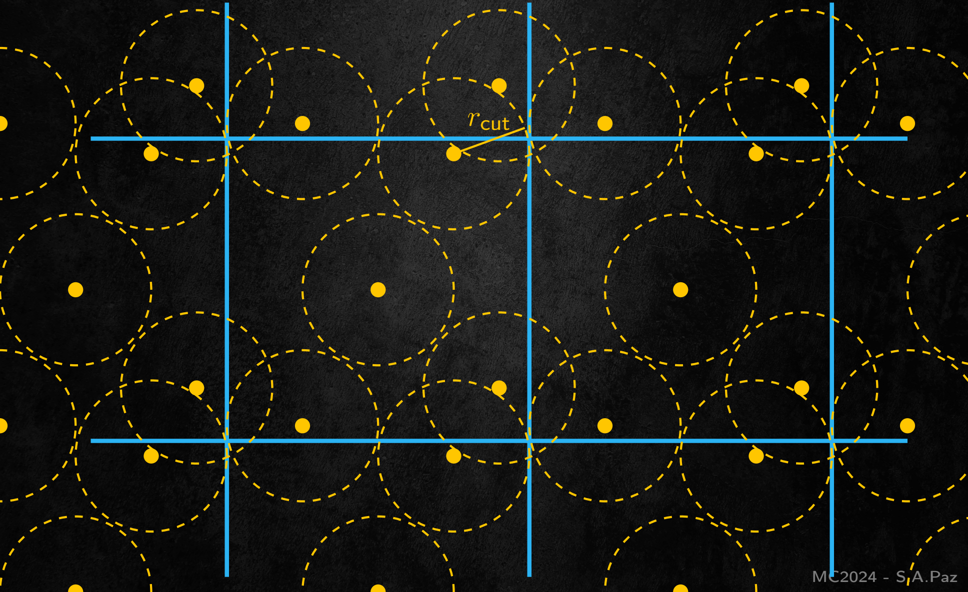

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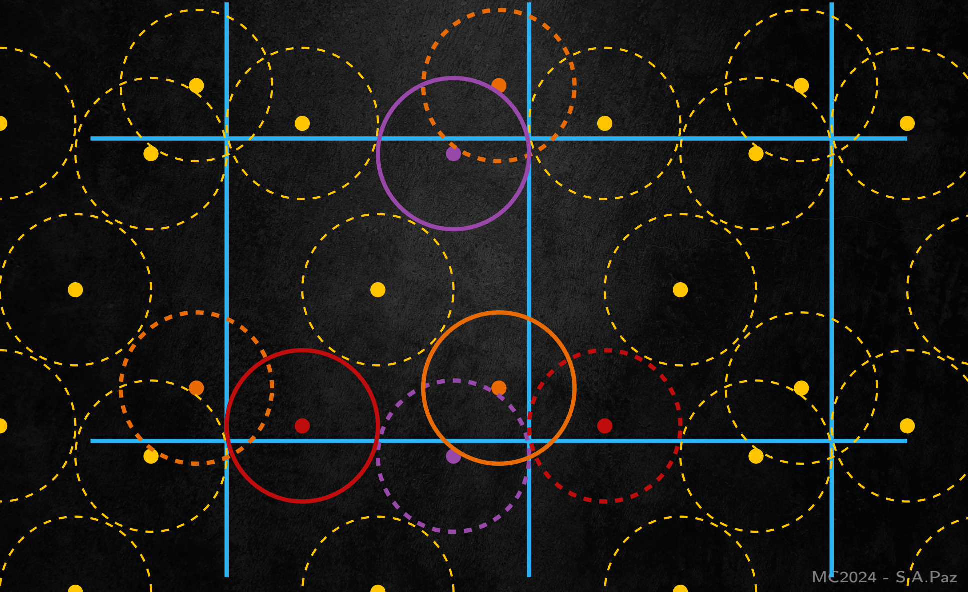

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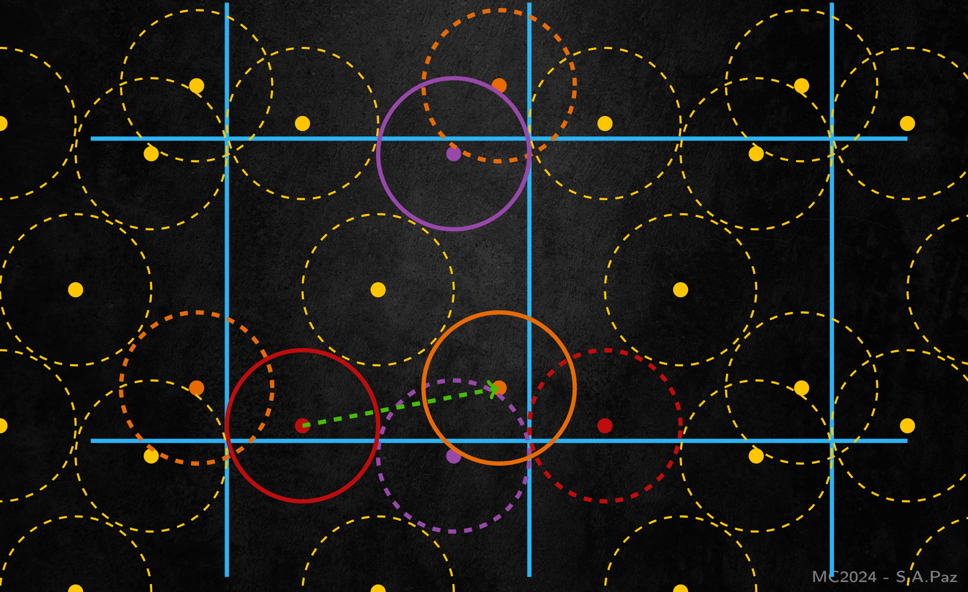
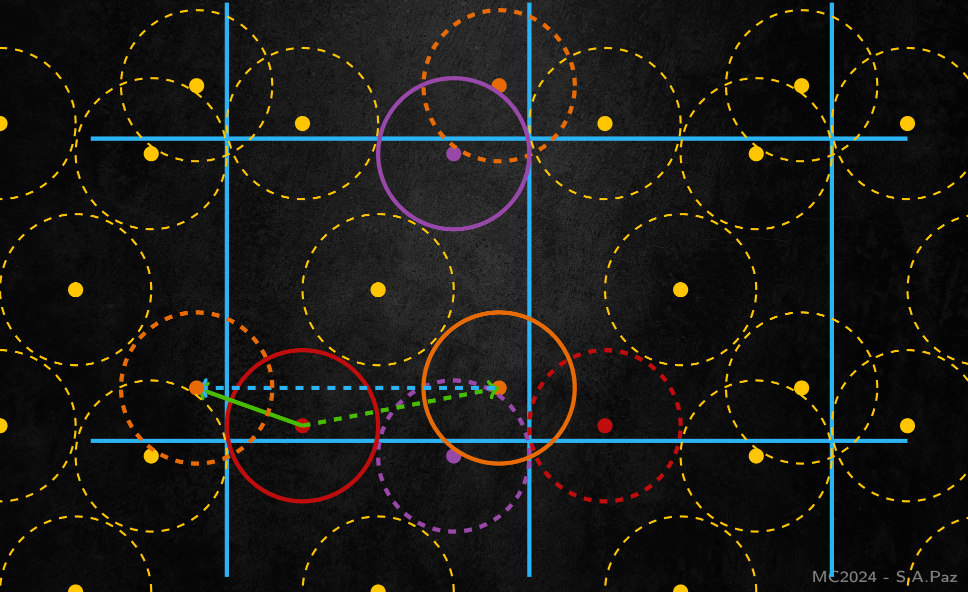


Condiciones de Contorno Periódicas



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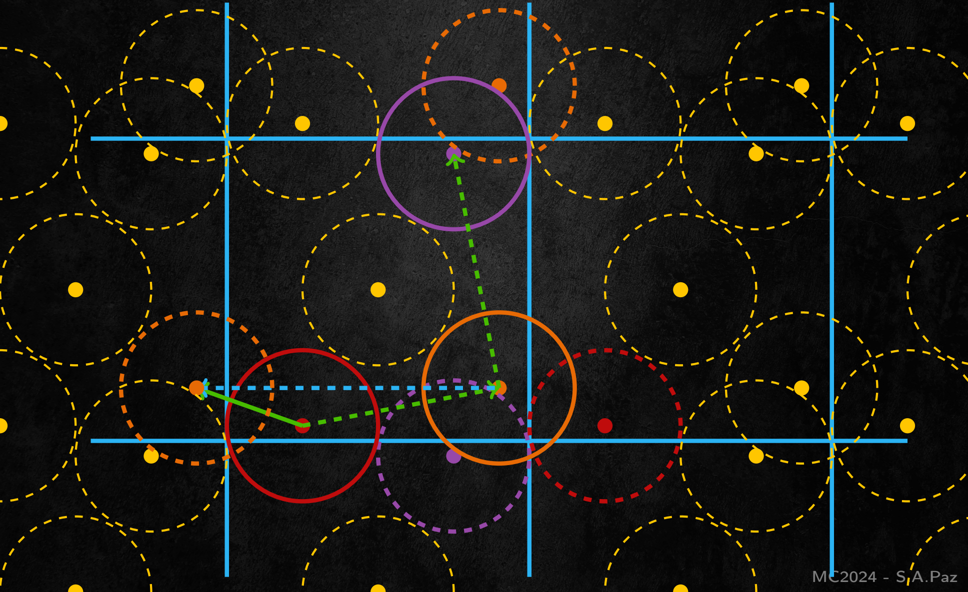

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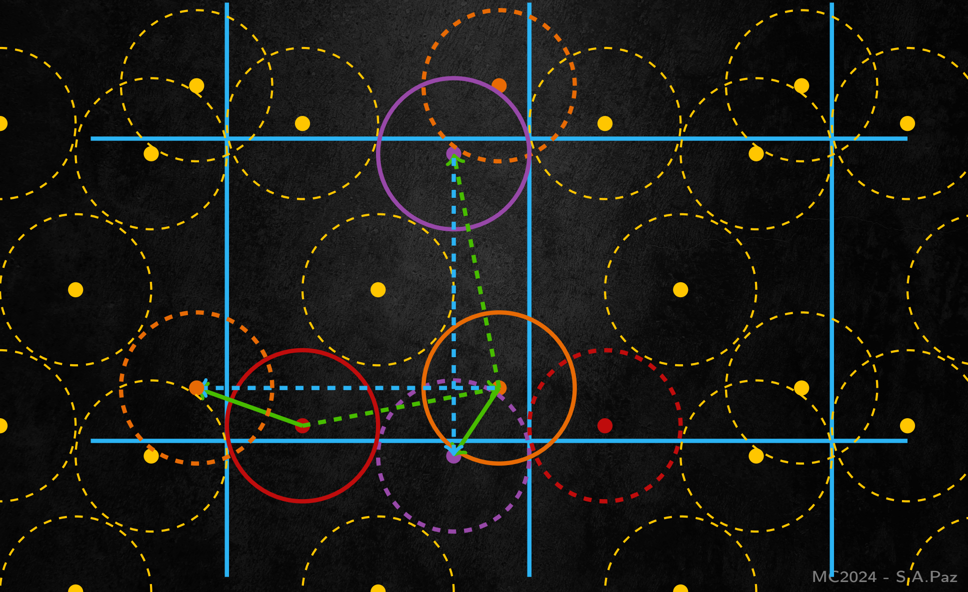
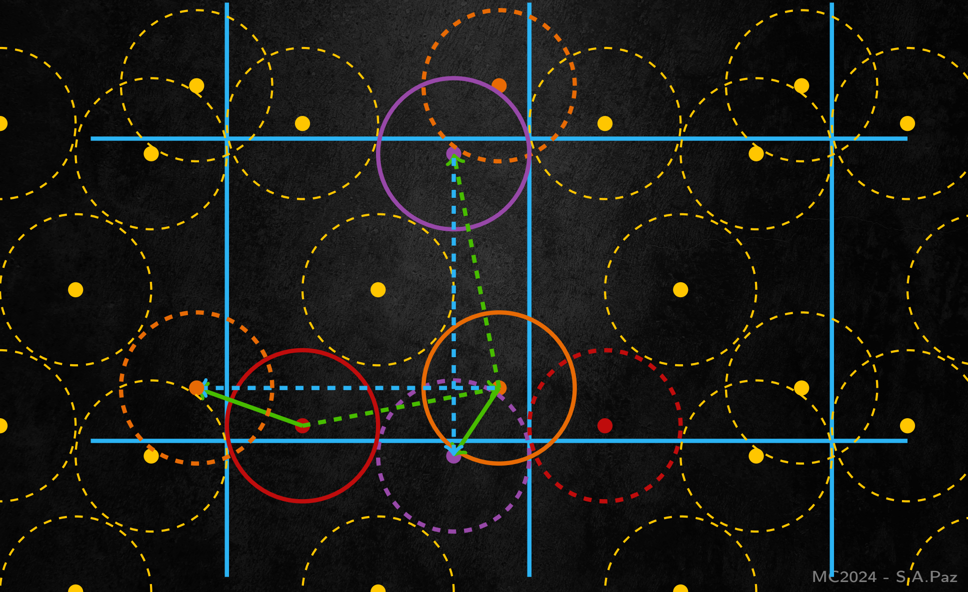
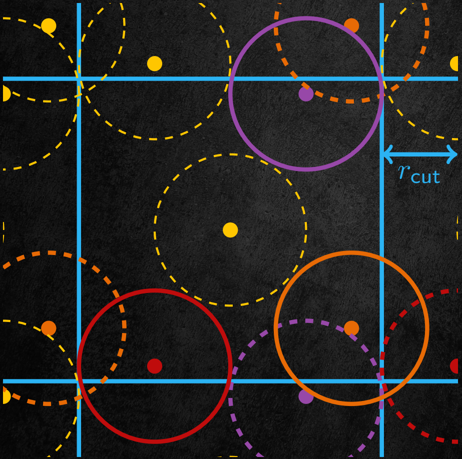


Conveción de Imagen Mínima

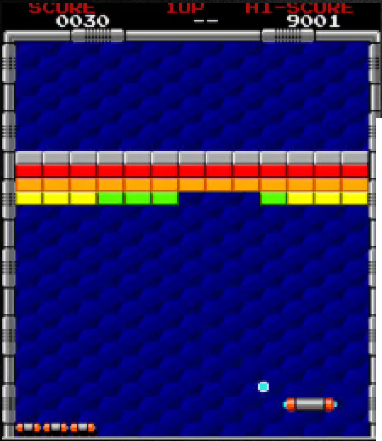


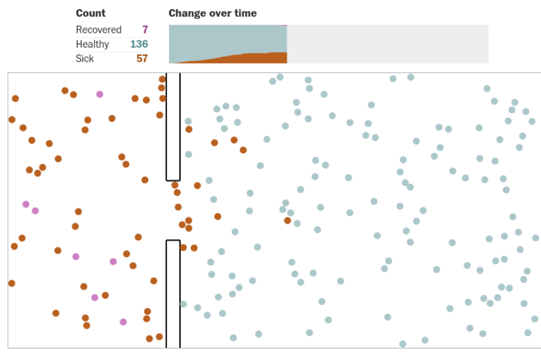
Partículas Fantasma

¡Paralelización!



Condiciones de Contorno Paredes Duras





Stevens, The Washington Post, March 14, 2020

Condiciones de Contorno Reservorios