Investigando o mundo quântico: de átomos a líquidos

Parte 3

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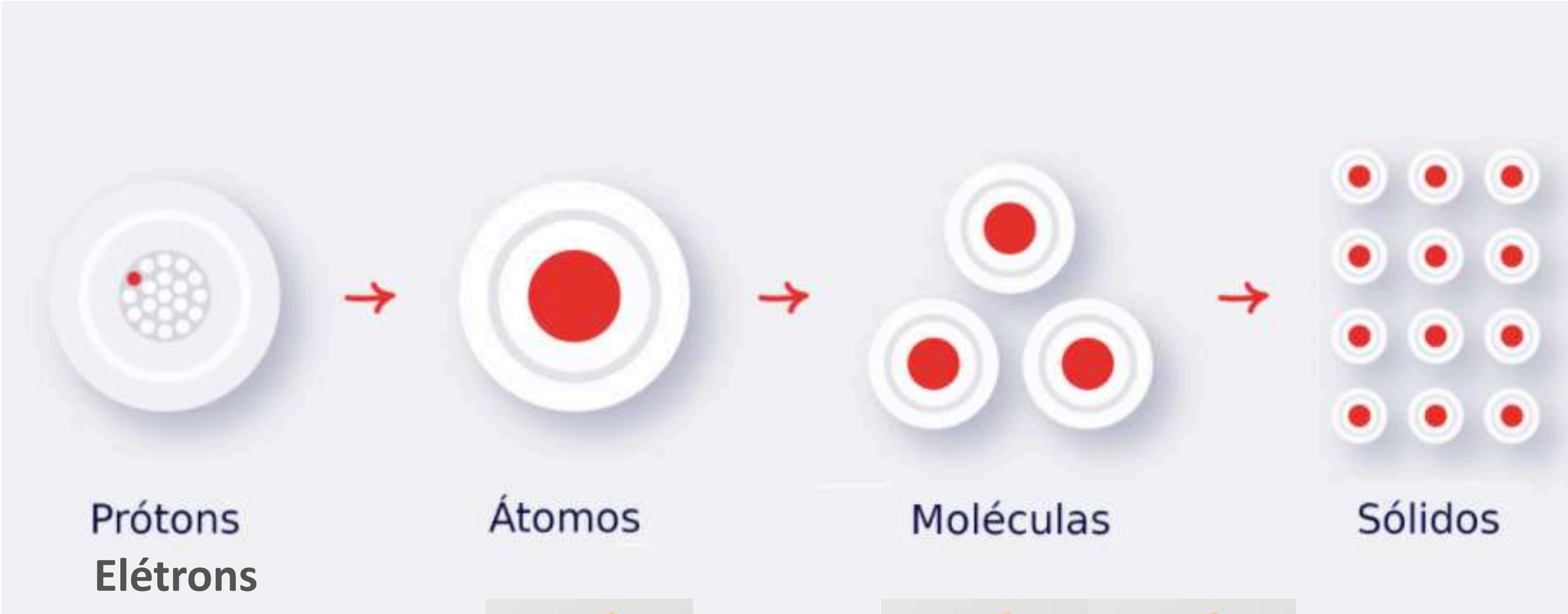
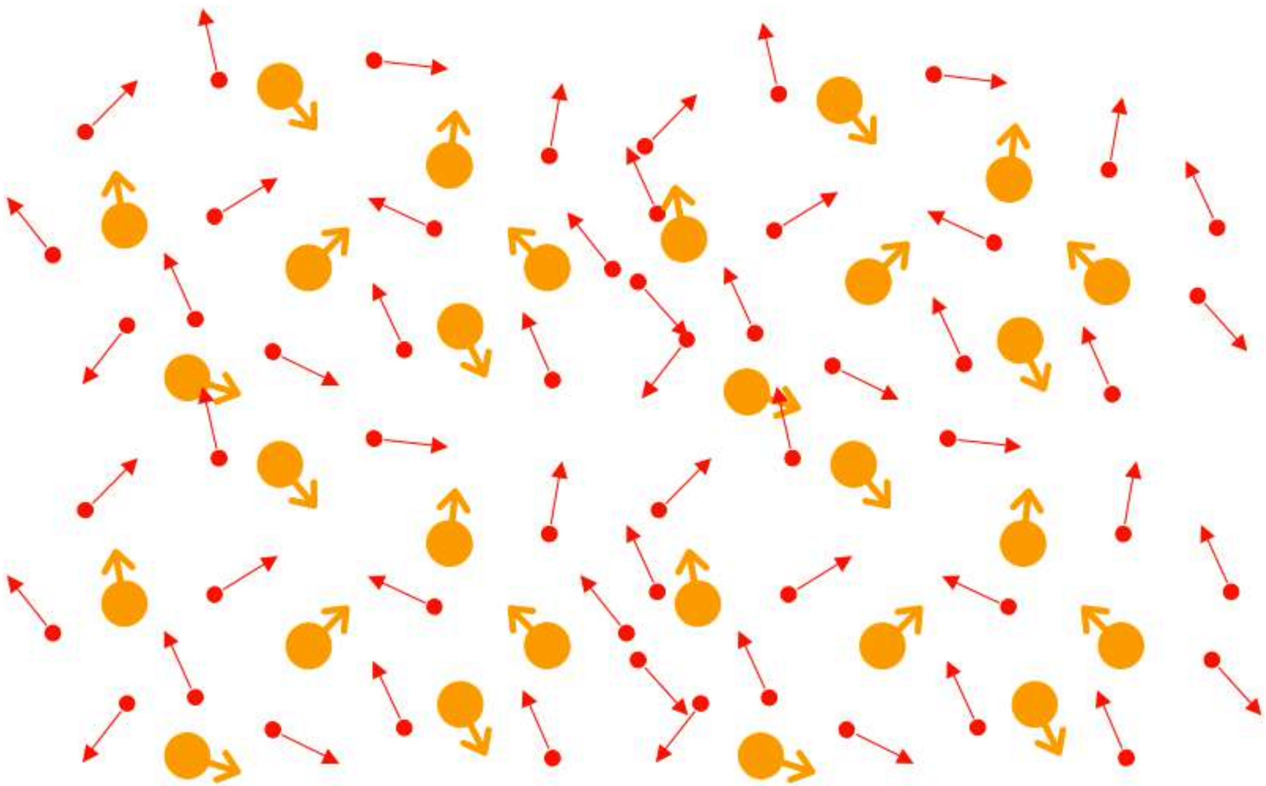
Objetivo



Moléculas

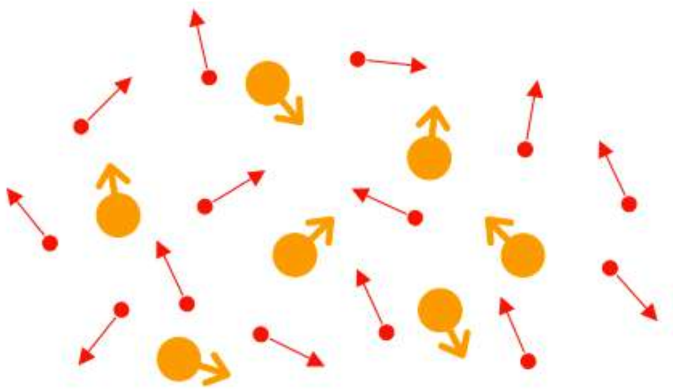
➢**Dinâmica dos núcleos e dos elétrons**

$$H\Psi = (T_e + T_n + V_{ee} + V_{nn} + V_{en})\Psi = E\Psi,$$



Moléculas

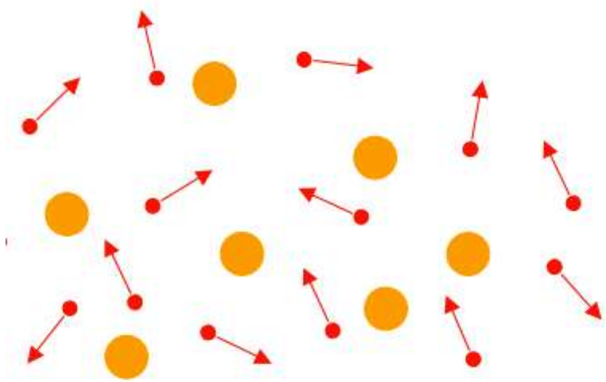
➢**Aproximação de Born-Oppenheimer**

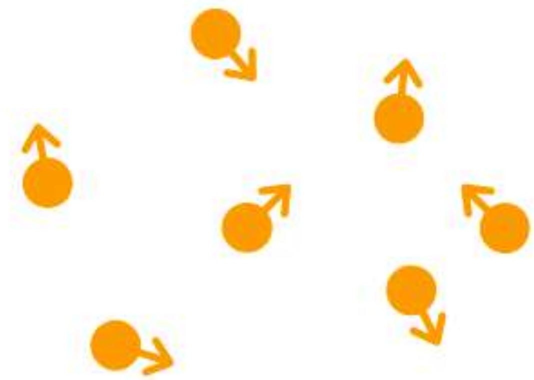


$$\frac{m_n}{m_e} >> 1$$

Dinâmica Molecular (DM) / Monte Carlo (MC)

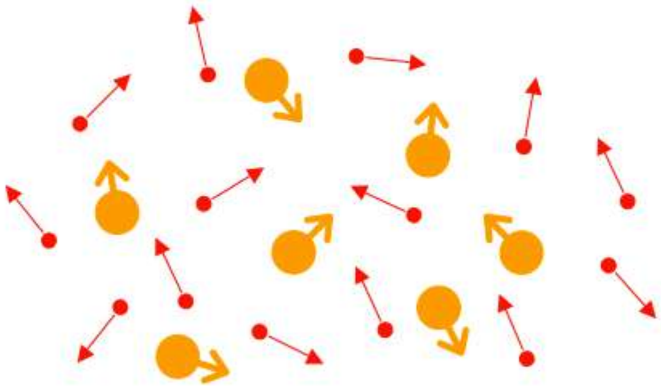
Núcleo fixo: problema eletrônico





Moléculas

➢**Aproximação de Born-Oppenheimer**



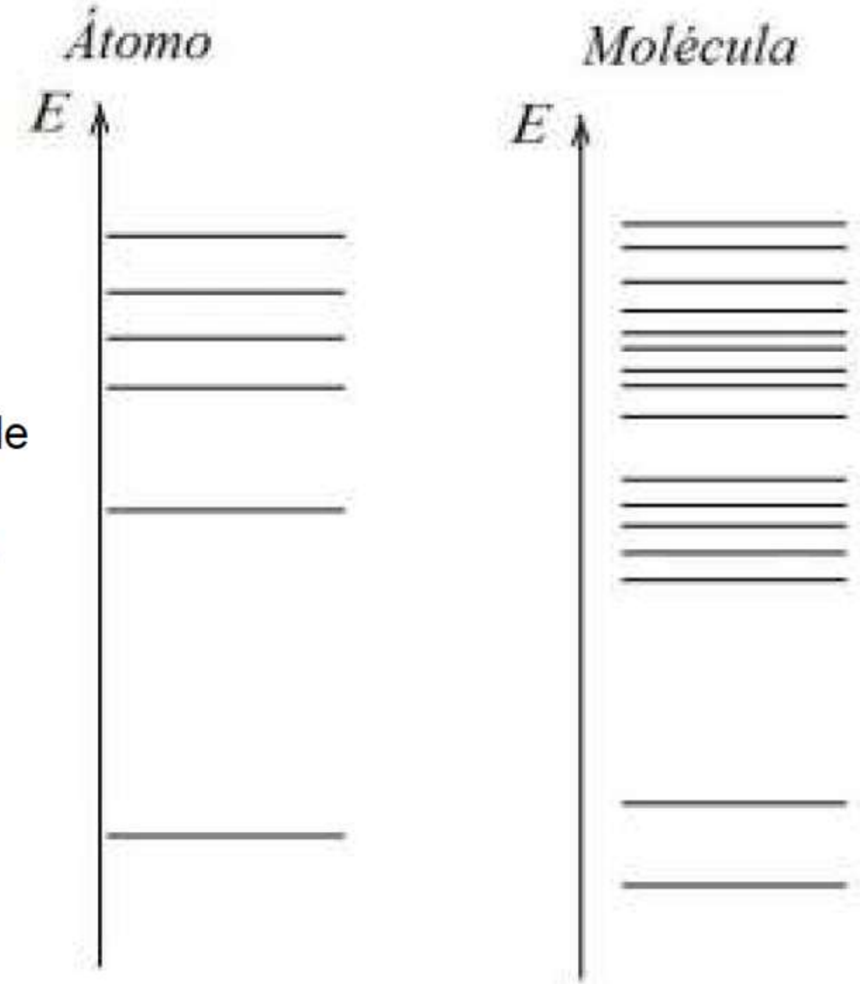
$$\frac{m_n}{m_e} >> 1$$

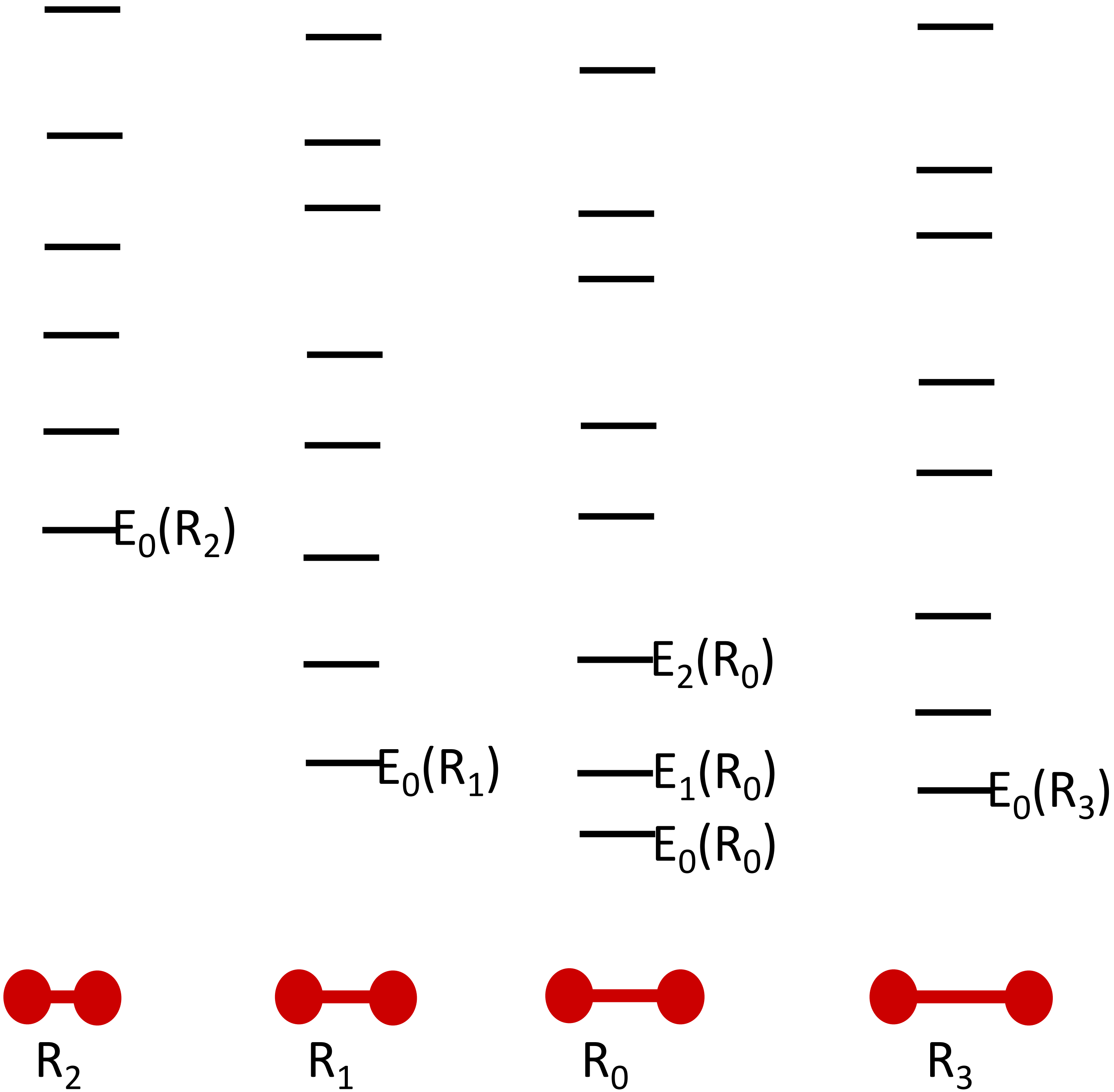
Desacopla problema eletrônico e nuclear

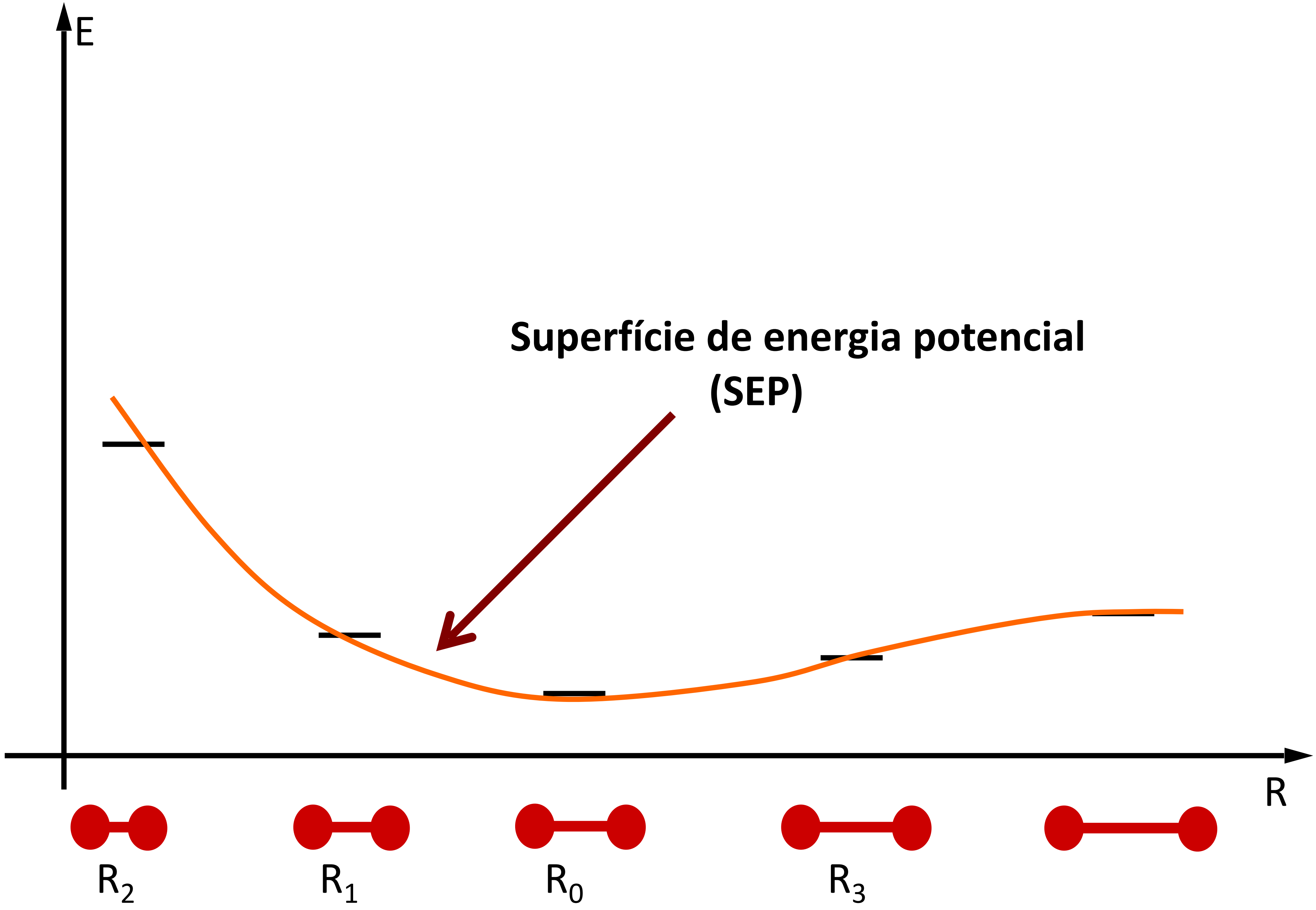
$$\Psi(r_i,R_\alpha) = \psi(r_i;R_\alpha)\Phi(R_\alpha)$$

Átomos e Moléculas

Níveis discretos de Energia Eletrônica.



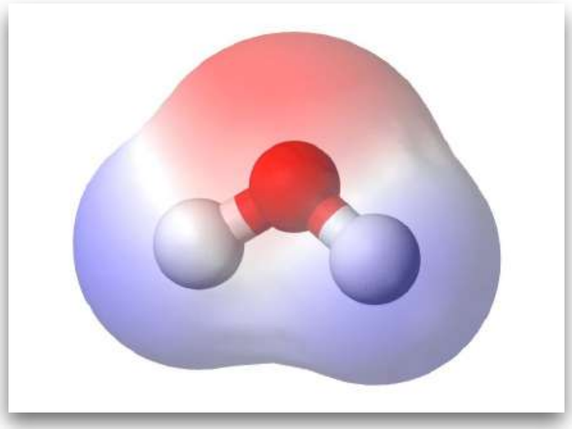

E0(R2)
E0(R1)
E2(R0)
E1(R0)
E0(R0)
E0(R3)
R2
R1
R0
R3

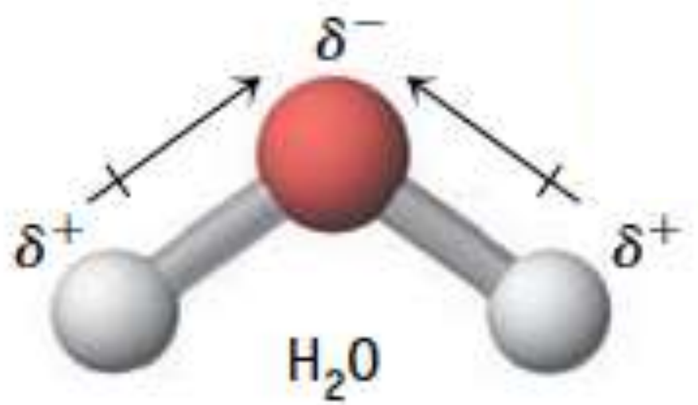

E
Superfície de energia potencial
(SEP)
R
R_2
R_1
R_0
R_3

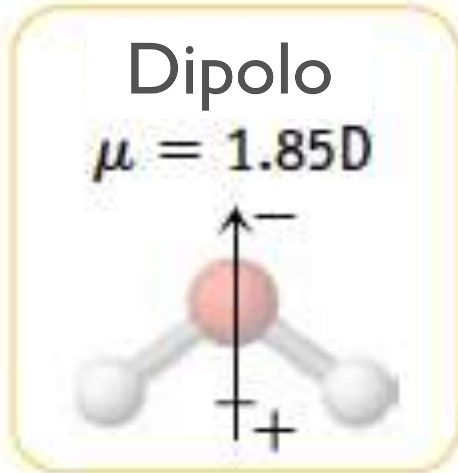
ESTRUTURA DA (MOLÉCULA DE) ÁGUA

Mecânica Quântica

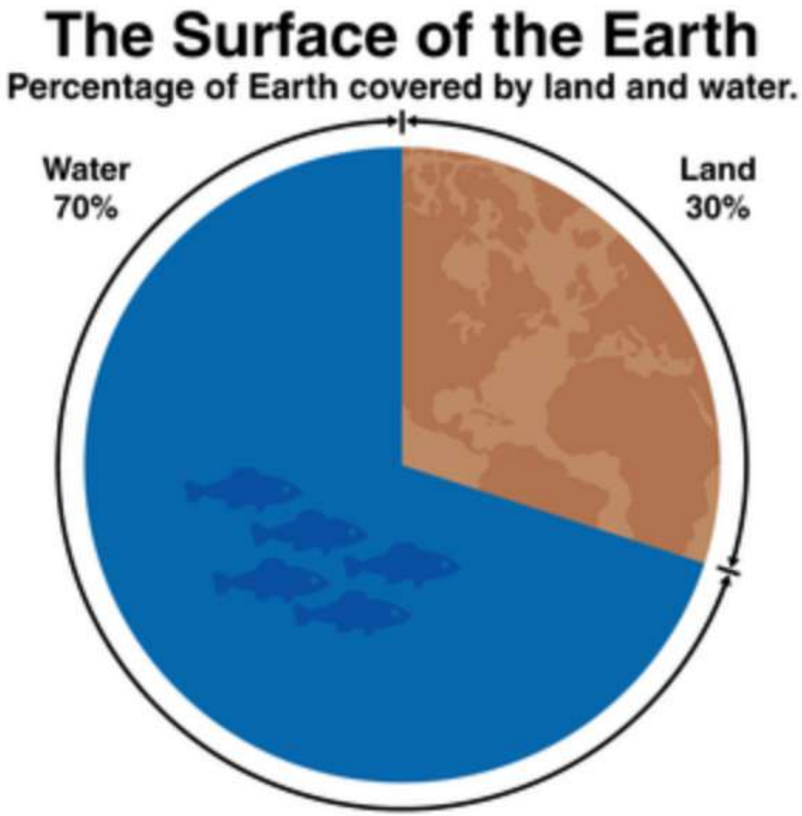
$$\left[\sum_{i}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m}+v(\mathbf{r}_i)\right)+\sum_{i<j}U(\mathbf{r}_i,\mathbf{r}_j)\right]\Psi(\mathbf{r}_1,\mathbf{r}_2\ldots,\mathbf{r}_N)=E\Psi(\mathbf{r}_1,\mathbf{r}_2\ldots,\mathbf{r}_N)$$







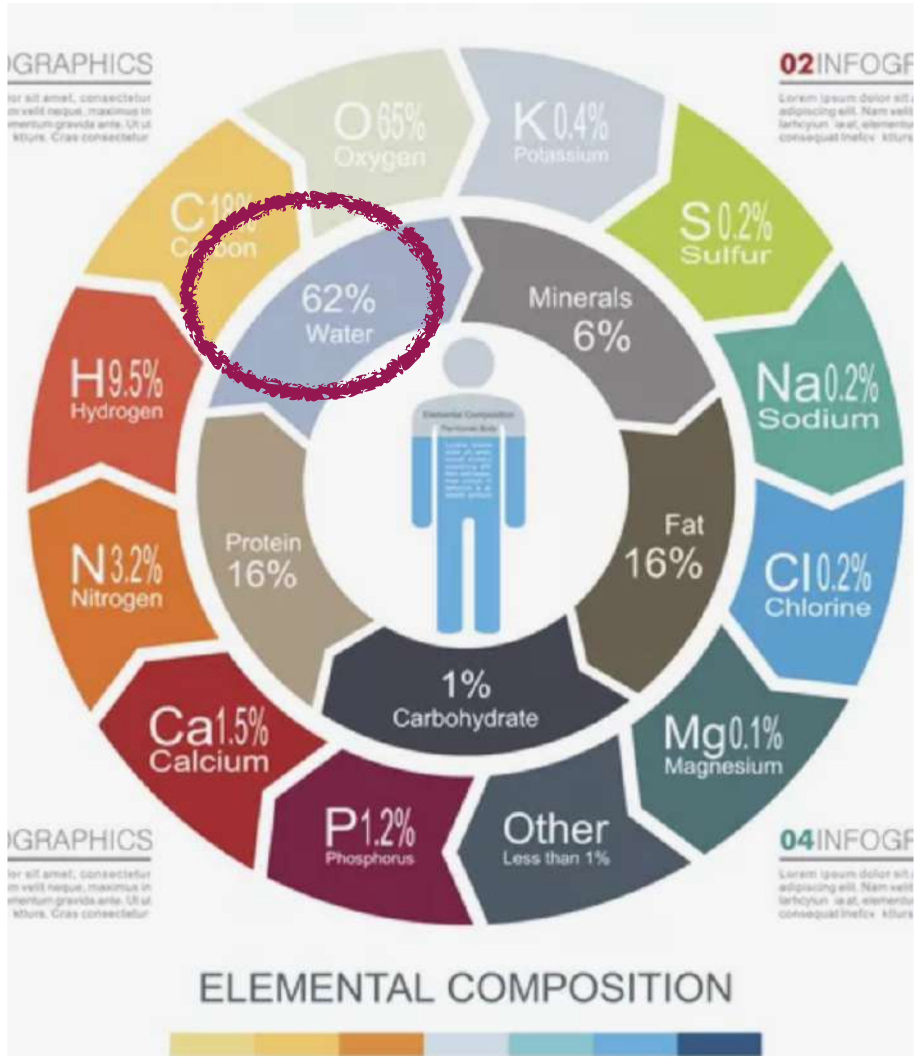
PLANETA ÁGUA ?



Superfície da Terra
70% água

CORPO HUMANO

62% água



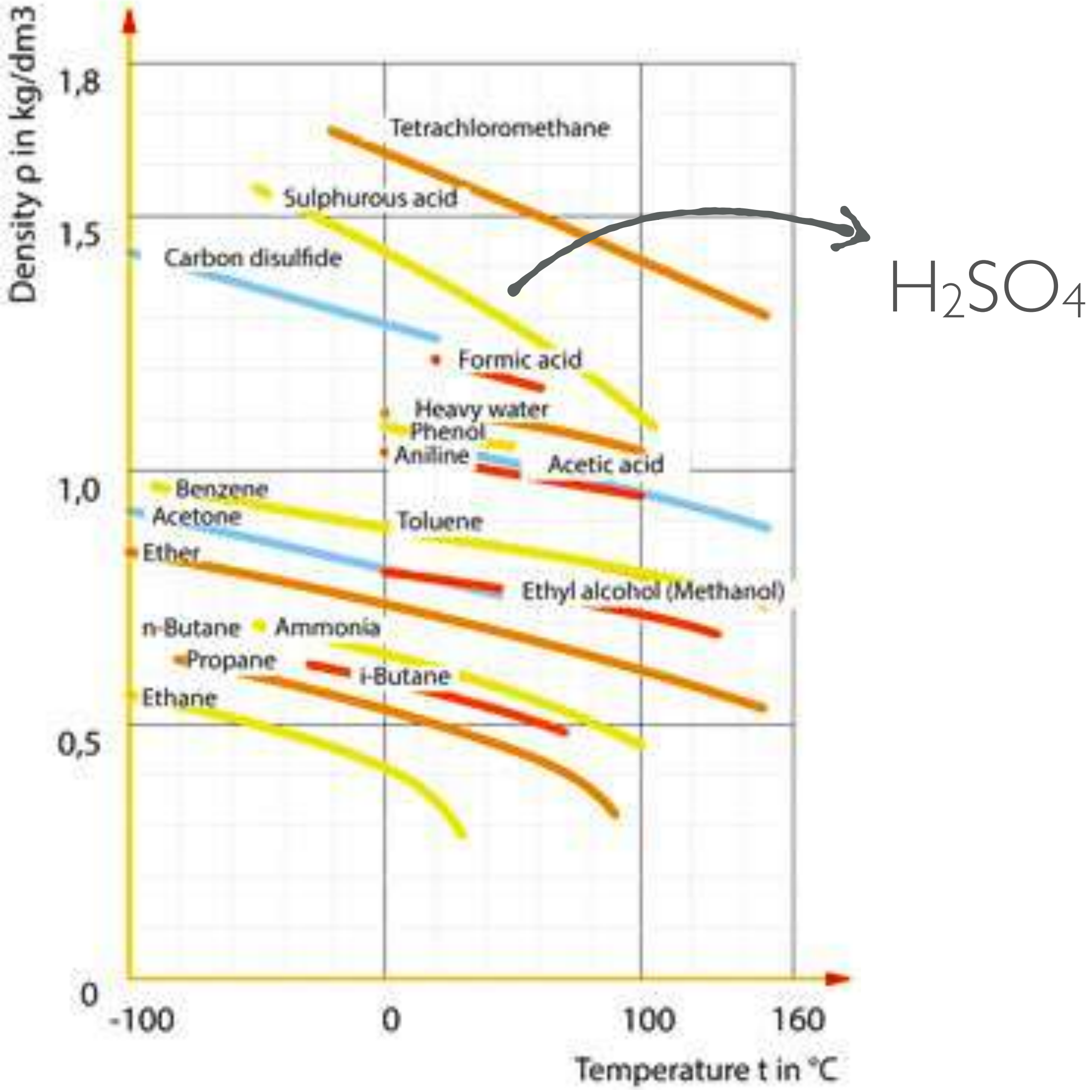
LÍQUIDO SIMPLES...

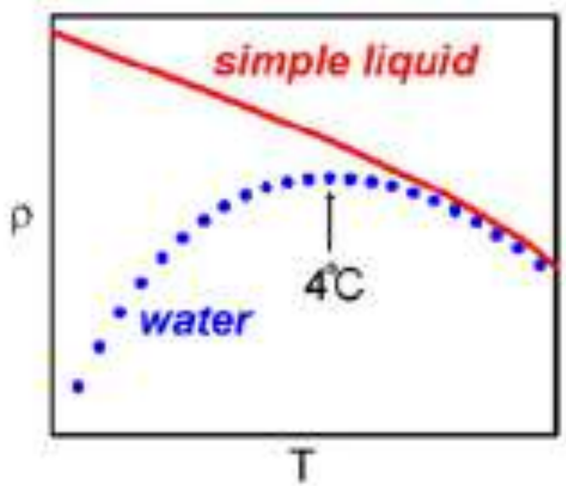
ESSENCIAL PARA A VIDA

MAS NEM TANTO!

ANOMALIAS DA ÁGUA

- Densidade em função da temperatura





ANOMALIAS DA ÁGUA

Water phase anomalies [d]

1. Water has an unusually high melting point. [Explanation]
2. Water has an unusually high boiling point. [Explanation]
3. Water has an unusually high critical point. [Explanation]
4. Solid water exists in a wider variety of stable (and metastable) cryst materials. [Explanation]
5. The thermal conductivity, shear modulus and transverse sound velo [Explanation]
6. The structure of liquid water changes at high pressure. [Explanation
7. Supercooled water has two phases and a second critical point at ab
8. Liquid water is easily supercooled but glassified with difficulty. [Expl
9. Liquid water exists at very low temperatures and freezes on heating
10. Liquid water may be easily superheated.
11. Hot water may freeze faster than cold w
12. Warm water vibrates longer than cold w
13. Water molecules shrink as the te

Water material anomalies

1. No aqueous solution is ideal. [Explanation]
2. D_2O and T_2O differ significantly from H_2O in their physical properties. [Explanation]
3. Liquid H_2O and D_2O differ significantly in their phase behavior. [Explanation]
4. H_2O and D_2O ices differ significantly in their quantum behavior. [Explanation]
5. The mean kinetic energy of water's hydrogen atoms increases at low temperature (disputed). [Explanation]
6. Solutes have varying effects on properties such as density and viscosity. [Explanation]
7. The solubilities of non-polar gases in water decrease with temperature to a minimum and then rise. [Explanation]
8. The dielectric constant of water and ice are high. [Explanation]
9. The relative permittivity shows a temperature maximum. [Explanation]
10. The relative permittivity shows a 'kink' in its behavior with the temperature at 60 °C. [Explanation]
11. The imaginary part of the dielectric constant shows a minimum near 20 K. [Explanation]
12. Proton and hydroxide ion mobilities are anomalously fast in an electric field. [Explanation]
13. The electrical conductivity of water rises to a maximum at about 230 °C. [Explanation]

Water thermodynamic anomalies

…sity-
…7 °C. [Explanation]
…ation]
…ation]
… [Explanation]
…planation]

Water density anomalies

1. The density of ice increases o
2. Water shrinks on melting. [Ex
3. Pressure reduces ice's meltin
4. Liquid water has a high-dens
5. The surface of water is dense
6. Pressure red
7. There is a r
8. Water has a
9. Water's the
10. Water's the
11. The numbe
12. The numbe
13. Water has u
14. The compre
15. There is a r
16. The speed o
17. The speed o
18. 'Fast sound'
19. NMR spin-la
20. The NMR sh
21. The refracti
22. The change

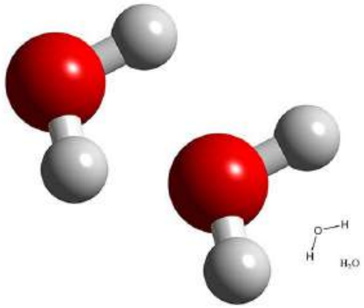
75 ANOMALIAS

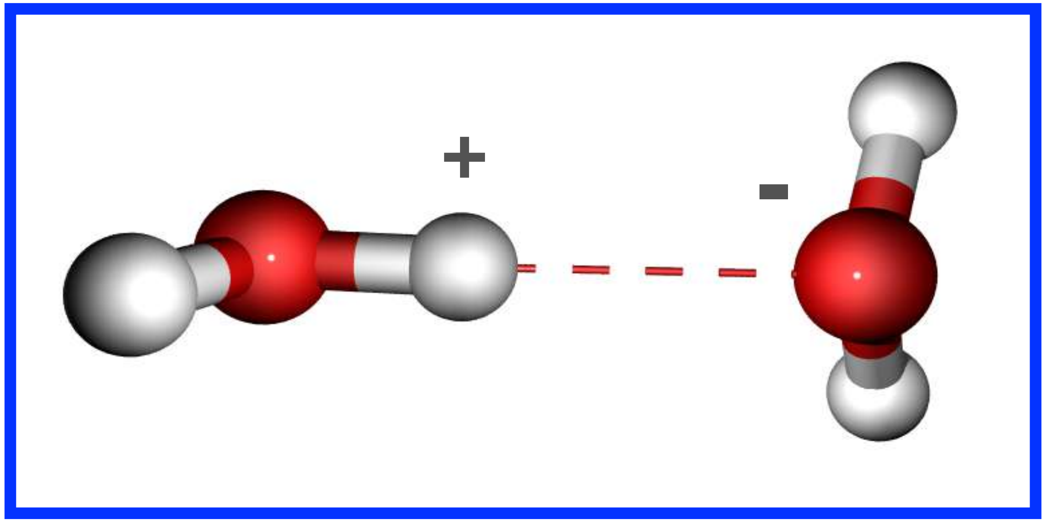
Water physical anomalies

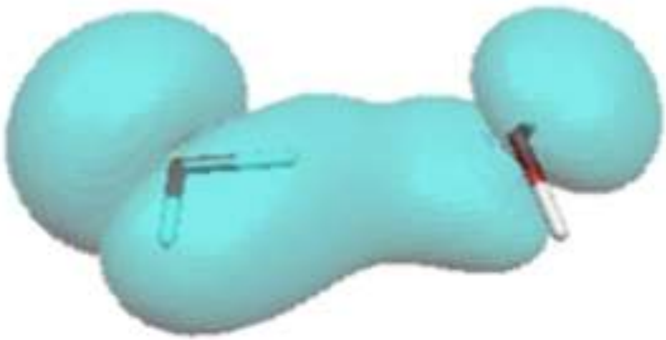
1. Water has unusually high viscosity. [Explanation]
2. Large viscosity and Prandtl number increase as the temperature is lowered. [Explanation]
3. Water's viscosity decreases with pressure below 33 °C. [Explanation]
4. Large diffusion decrease as the temperature is lowered. [Explanation]
5. At low temperatures, the self-diffusion of water increases as the density and pressure increase. [
6. The thermal diffusivity rises to a maximum at about 0.8 GPa. [Explanation]
7. Water has unusually high surface tension. [Explanation]
8. Some salts give a surface tension-concentration minimum; the Jones-Ray effect. [Explanation]
9. Some salts prevent the co
10. The molar ionic volumes o

http://www1.lsbu.ac.uk/water/water_anomalies.html#bi

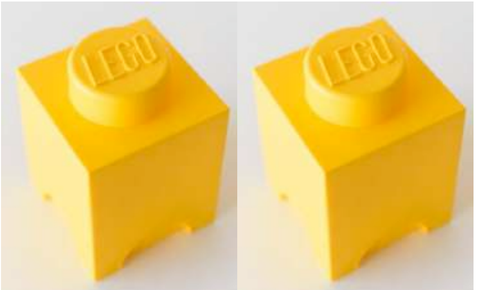
ESTRUTURA DA ÁGUA: LIGAÇÃO DE HIDROGÊNIO

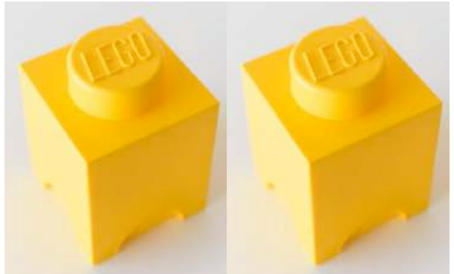


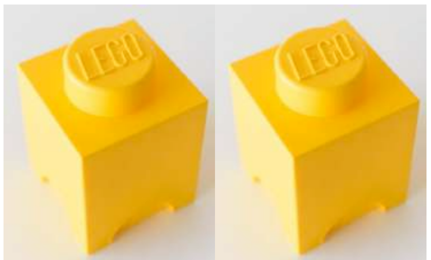




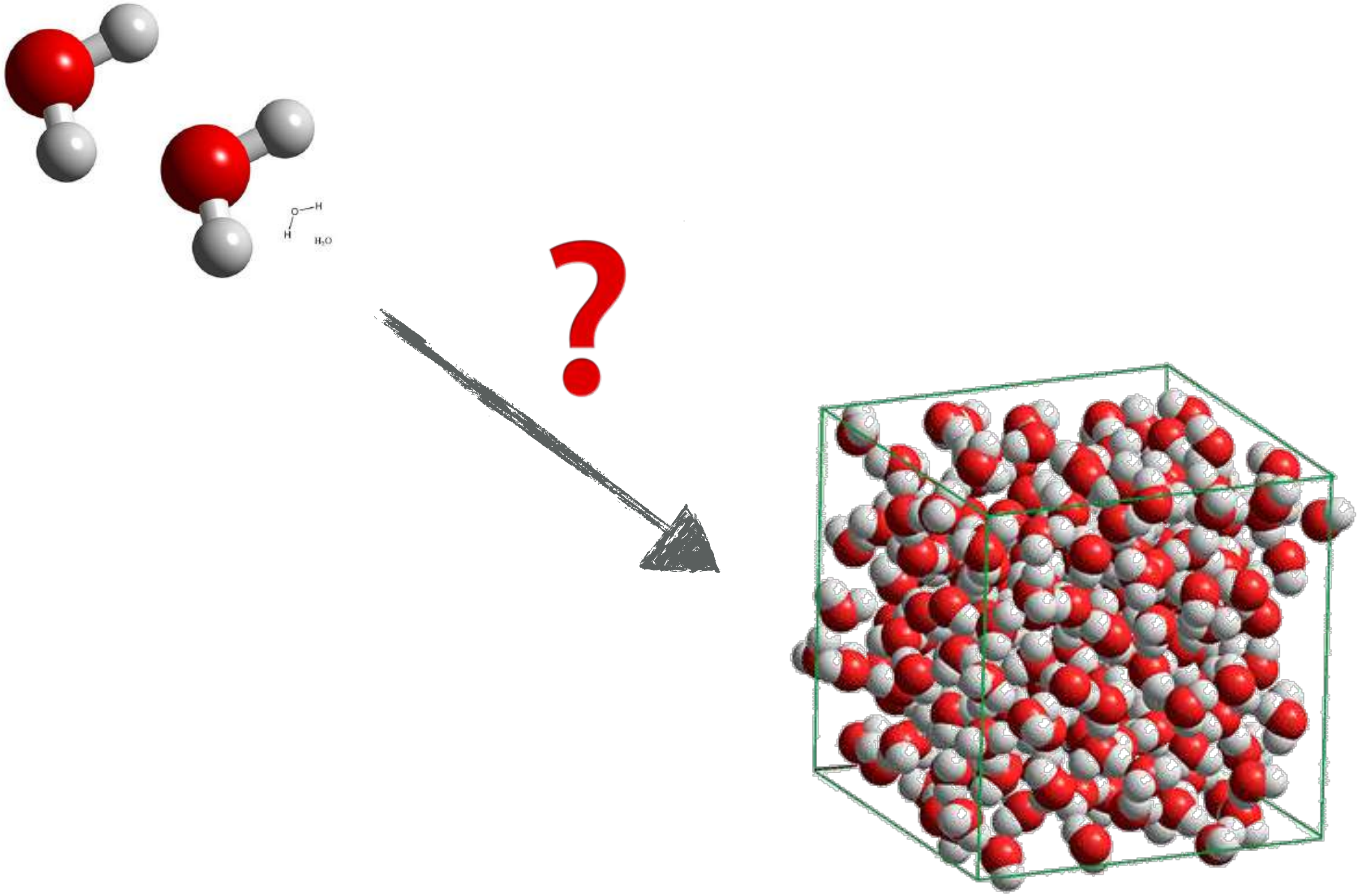
Interação entre moléculas







ESTRUTURA DA ÁGUA



ESTRUTURA DA ÁGUA

Science

www.sciencemag.org

Science 1 July 2005:

Vol. 309 no. 5731 pp. 78-102

DOI: 10.1126/science.309.5731.78b

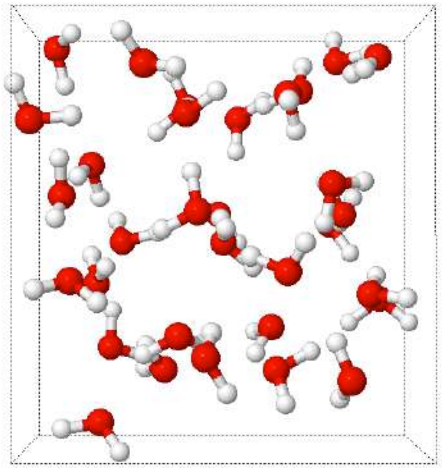
- NEWS

So Much More to Know ...

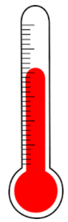
What is the structure of water?

Researchers continue to tussle over how many bonds each H_2O molecule makes with its nearest neighbors.

SIMULAÇÕES COMPUTACIONAIS



$$\left[\sum_{i}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m}+v(\mathbf{r}_i)\right)+\sum_{i<j}U(\mathbf{r}_i,\mathbf{r}_j)\right]\Psi(\mathbf{r}_1,\mathbf{r}_2\ldots,\mathbf{r}_N)=E\Psi(\mathbf{r}_1,\mathbf{r}_2\ldots,\mathbf{r}_N).$$



SIMULAÇÕES COMPUTACIONAIS

# Step	T (K)	E_KS (eV)	E_tot (eV)	Vol (A^3)	P (kBar)
1	297.14	-94257.47542	-94234.46992	5984.582	-7.988
2	294.57	-94257.27702	-94234.47054	5984.582	-8.012
3	290.96	-94256.99312	-94234.46574	5984.582	-7.823
4	287.12	-94256.69088	-94234.46106	5984.582	-7.460
5	283.97	-94256.44299	-94234.45725	5984.582	-6.964
6	282.28	-94256.31038	-94234.45540	5984.582	-6.374
7	282.43	-94256.32294	-94234.45634	5984.582	-5.723
8	284.27	-94256.46846	-94234.45946	5984.582	-5.050
9	287.17	-94256.69809	-94234.46392	5984.582	-4.387
10	290.27	-94256.94217	-94234.46834	5984.582	-3.740
11	292.68	-94257.13155	-94234.47145	5984.582	-3.117
12	293.77	-94257.21728	-94234.47248	5984.582	-2.540
13	293.34	-94257.18293	-94234.47134	5984.582	-2.034
14	291.58	-94257.04442	-94234.46905	5984.582	-1.641
15	288.94	-94256.83763	-94234.46648	5984.582	-1.366
16	285.94	-94256.60311	-94234.46453	5984.582	-1.238
17	283.01	-94256.37439	-94234.46302	5984.582	-1.267
18	280.46	-94256.17665	-94234.46212	5984.582	-1.465
19	278.54	-94256.02665	-94234.46130	5984.582	-1.816
20	277.38	-94255.93653	-94234.46074	5984.582	-2.326
21	277.08	-94255.91308	-94234.46067	5984.582	-2.933
22	277.62	-94255.95557	-94234.46136	5984.582	-3.602
23	278.85	-94256.05268	-94234.46291	5984.582	-4.290
24	280.46	-94256.17910	-94234.46516	5984.582	-4.942
25	281.94	-94256.29675	-94234.46766	5984.582	-5.504
26	282.78	-94256.36316	-94234.46951	5984.582	-5.924

SIMULAÇÕES COMPUTACIONAIS

```
 600

O      19.524698    5.424439    2.275936
H      19.107273    6.302816    2.266253
H      20.127425    5.430228    3.072892
O      15.543904    8.452060   11.365274
H      14.631054    8.913424   11.310291
H      16.052138    8.729169   10.570819
O       6.937338   10.567258    4.931034
H       7.296381    9.654493    4.747249
H       7.424767   11.096276    4.234574
O      18.356842   17.187043    7.386380
H      17.741058   16.709966    8.082046
H      18.861264   16.437786    6.982199
O       9.518928   15.287547   16.274257
H       9.814799   15.042128   15.310577
H      10.055635   14.660002   16.859321
O      14.032806   12.868640   11.535191
H      14.306578   12.341081   10.732928
H      14.435950   12.425824   12.289672
O       9.121193    3.957660    5.846045
H       9.267975    4.076913    6.850840
H       9.621010    4.727737    5.489470
O       5.235503    7.993023    3.849965
H       5.886081    8.652885    4.084469
H       5.210007    7.491750    4.713818
O       3.405167   10.329004   12.133267
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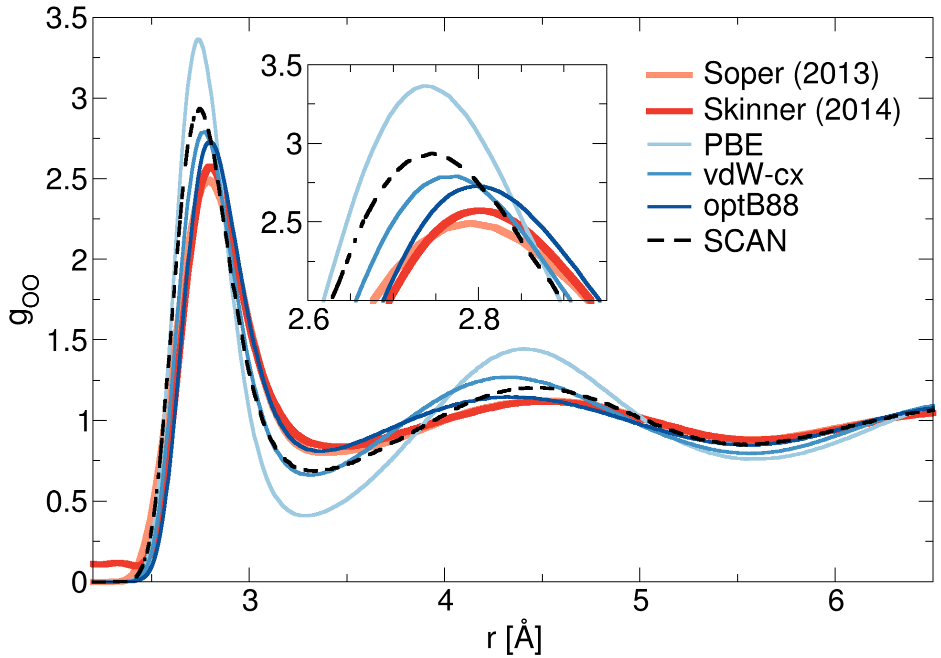
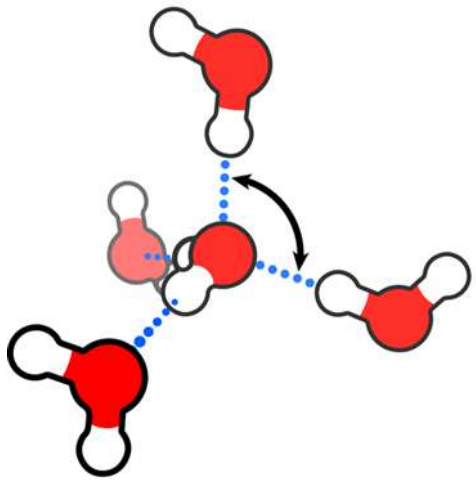
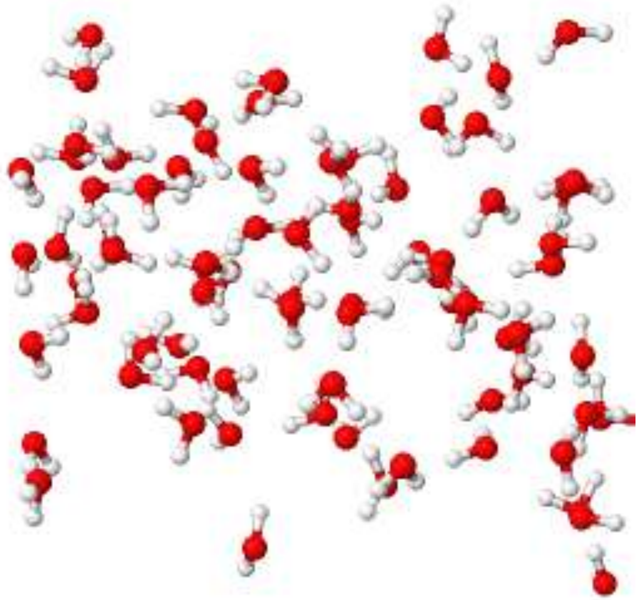
ESTRUTURA DA ÁGUA: LIGAÇÃO DE HIDROGÊNIO



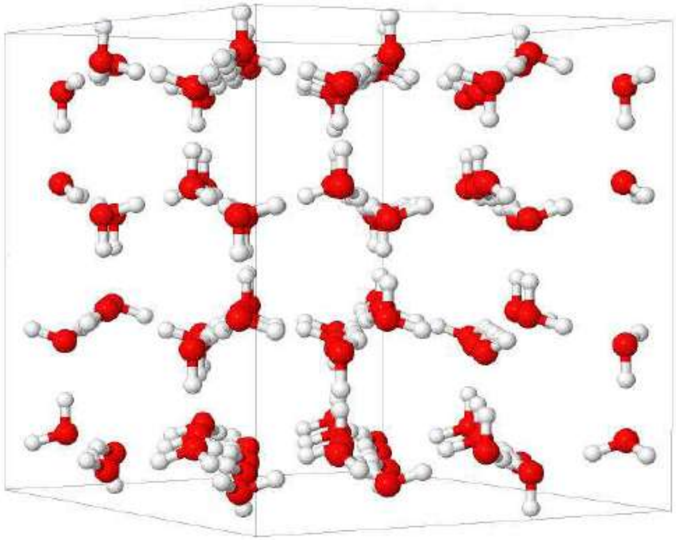


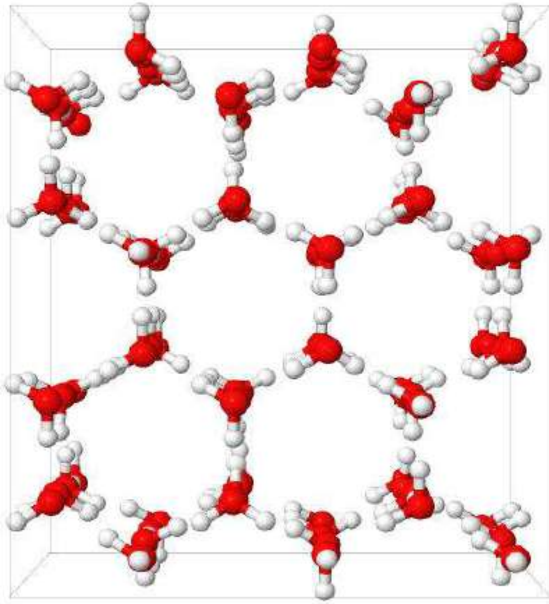
Estrutura tetraédrica



ESTRUTURA DA ÁGUA: GELO

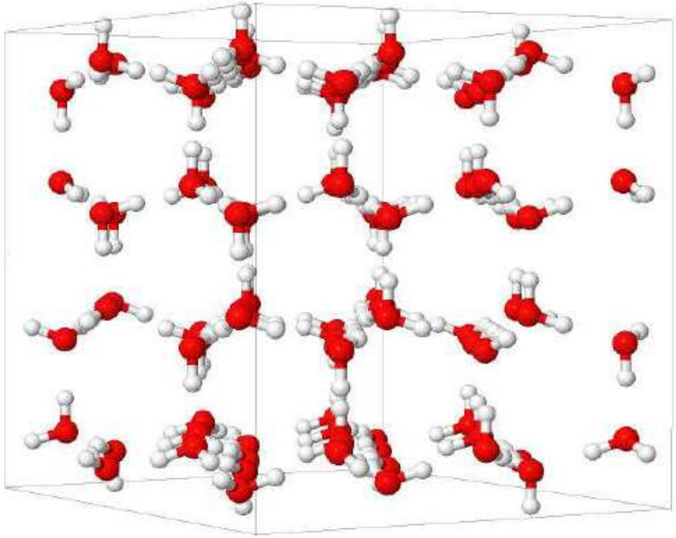
Gelo Ih

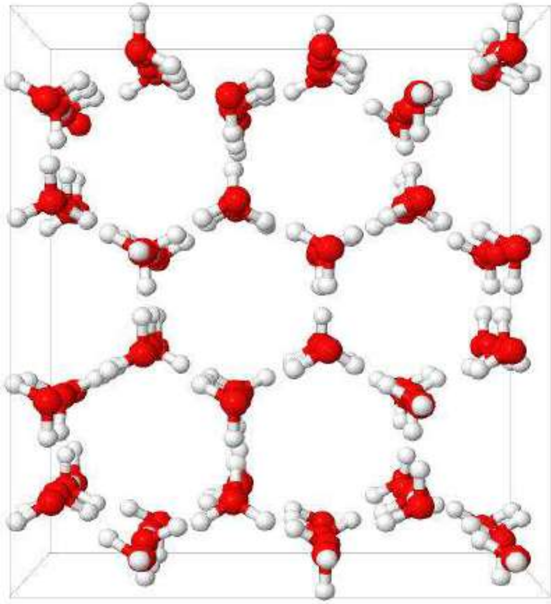


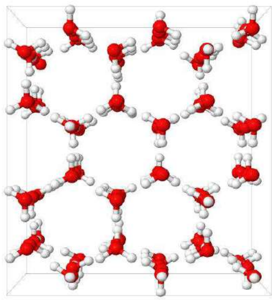


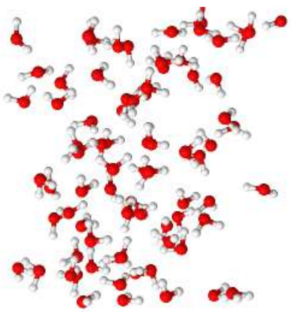
ESTRUTURA DA ÁGUA: GELO

Gelo Ih



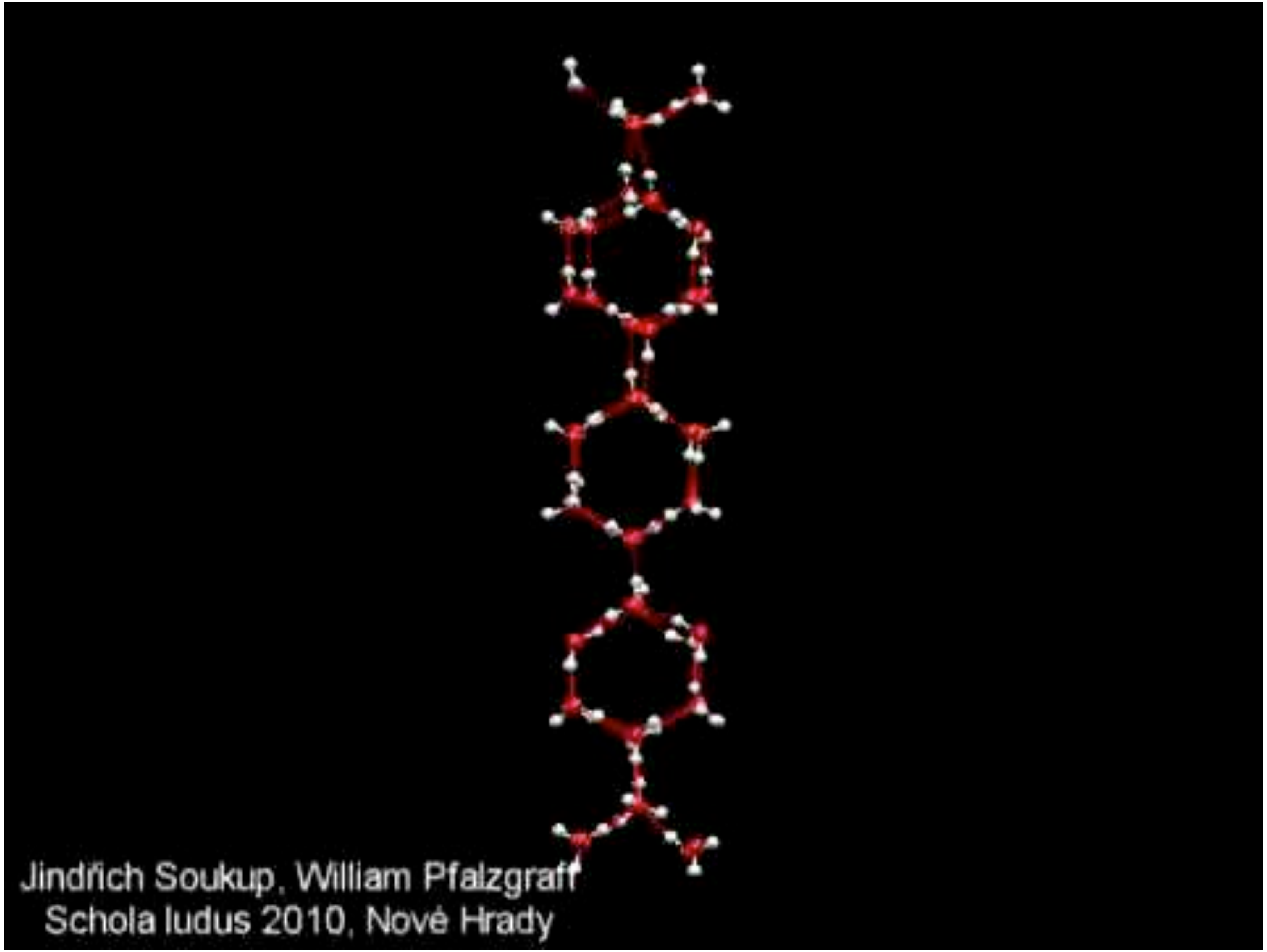




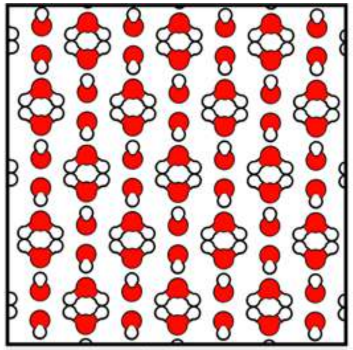


Gelo é menos denso que a água líquida

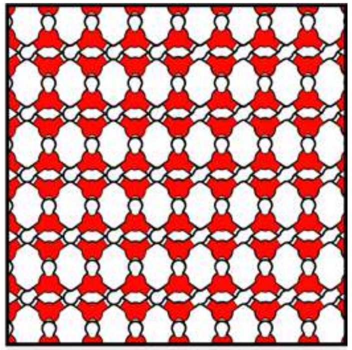
ESTRUTURA DA ÁGUA-GELO



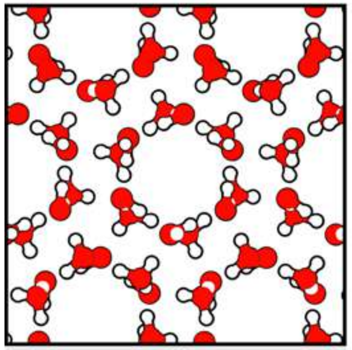
ESTRUTURA DA ÁGUA: GELO (S)



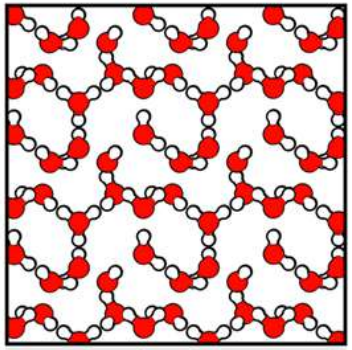
ice VIII | 1.46 g/cm^3



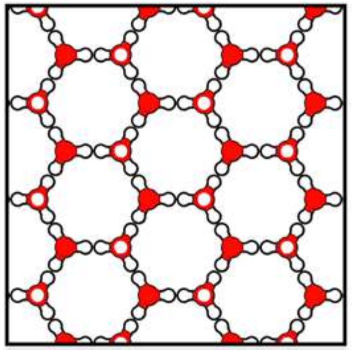
ice X | 2.51 g/cm^3



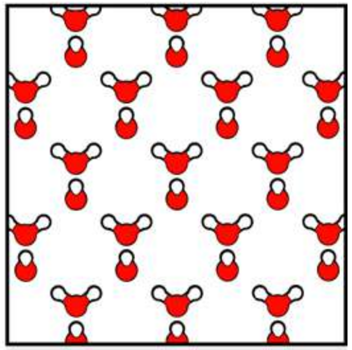
ice II | 1.17 g/cm^3



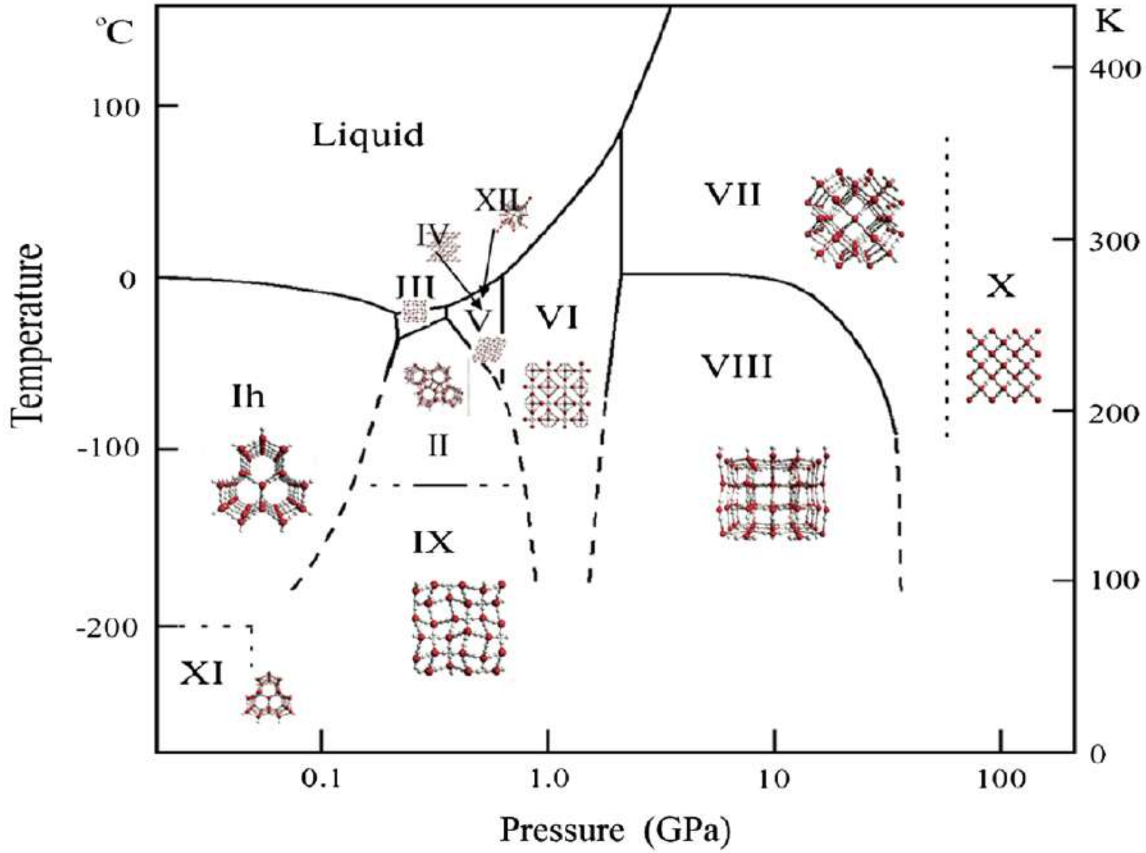
ice VI | 1.31 g/cm^3



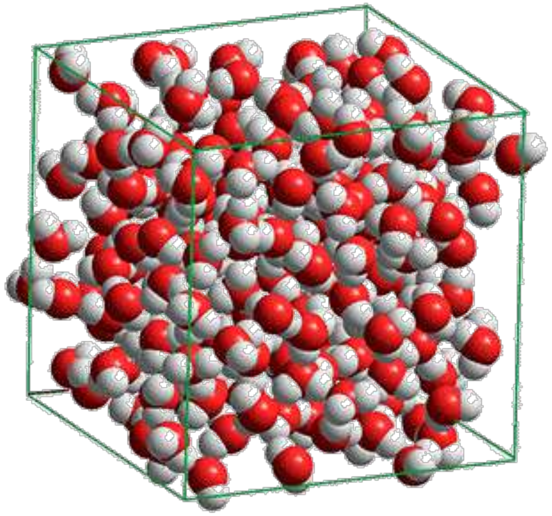
ice I_h | 0.92 g/cm^3



ice I_c | 0.93 g/cm^3

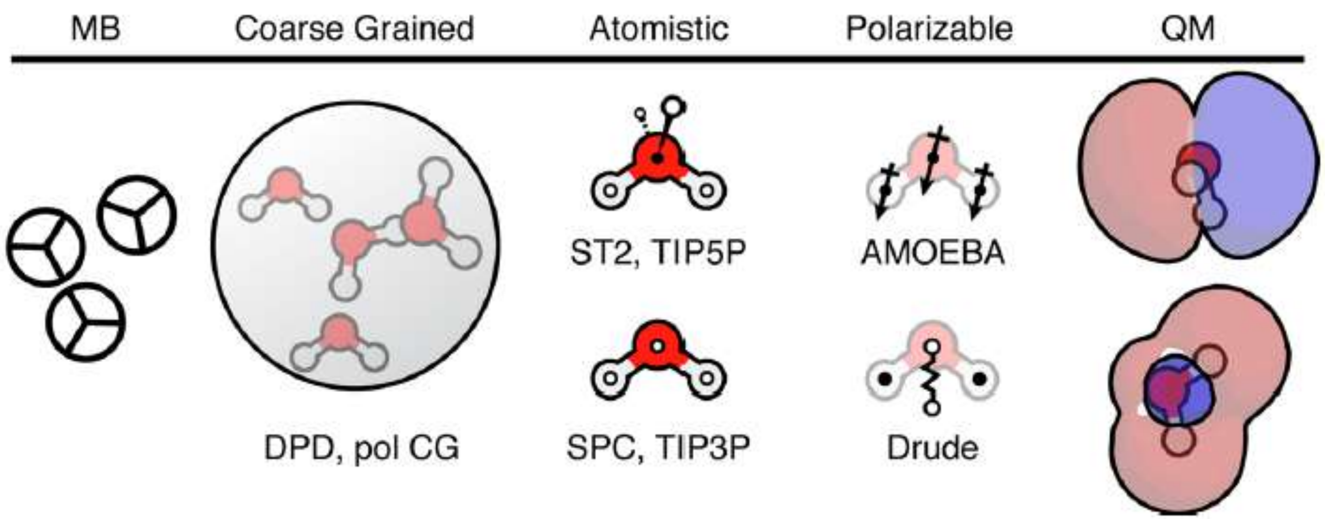


MODELOS PARA INTERAÇÕES



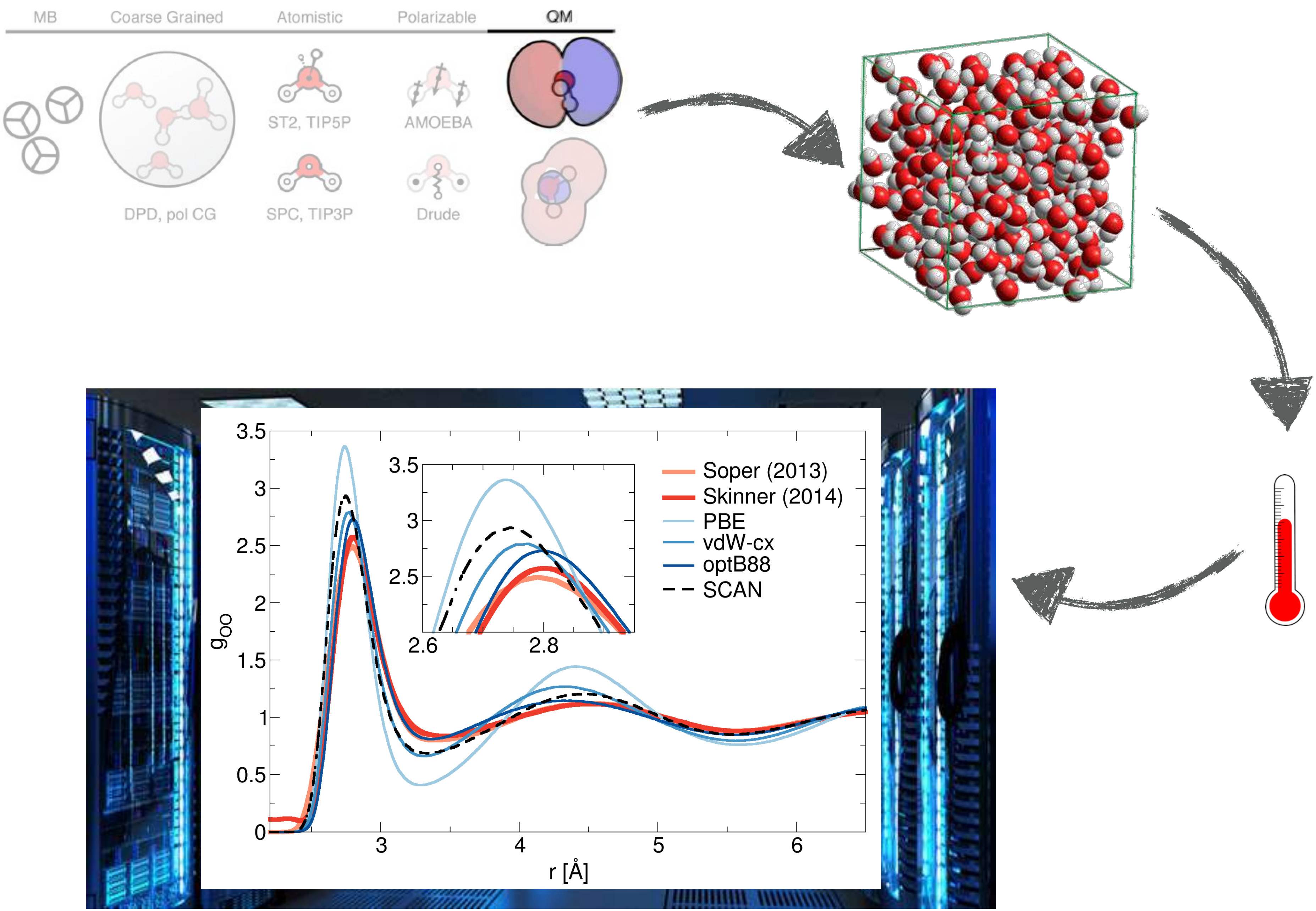
$$\left[\sum_{i}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m}+v(\mathbf{r}_i)\right)+\sum_{i<j}U(\mathbf{r}_i,\mathbf{r}_j)\right]\Psi(\mathbf{r}_1,\mathbf{r}_2\ldots,\mathbf{r}_N)=E\Psi(\mathbf{r}_1,\mathbf{r}_2\ldots,\mathbf{r}_N).$$

$$E_{ab}=\sum_{ij}\frac{q_i q_j e^2}{r_{ij}}+4\varepsilon_0\left[\left(\frac{\sigma_0}{r_{OO}}\right)^{12}-\left(\frac{\sigma_0}{r_{OO}}\right)^{6}\right]$$

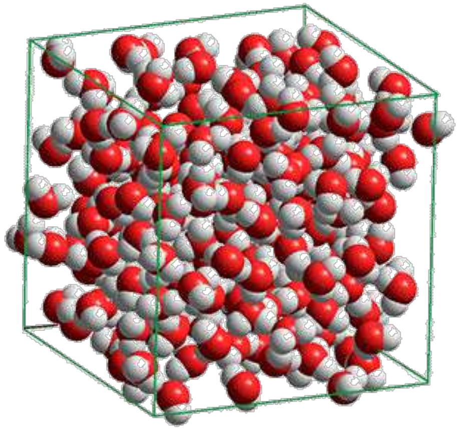


E. Brini *et al*, Chem. Rev. 2017, 117, 12385−12414

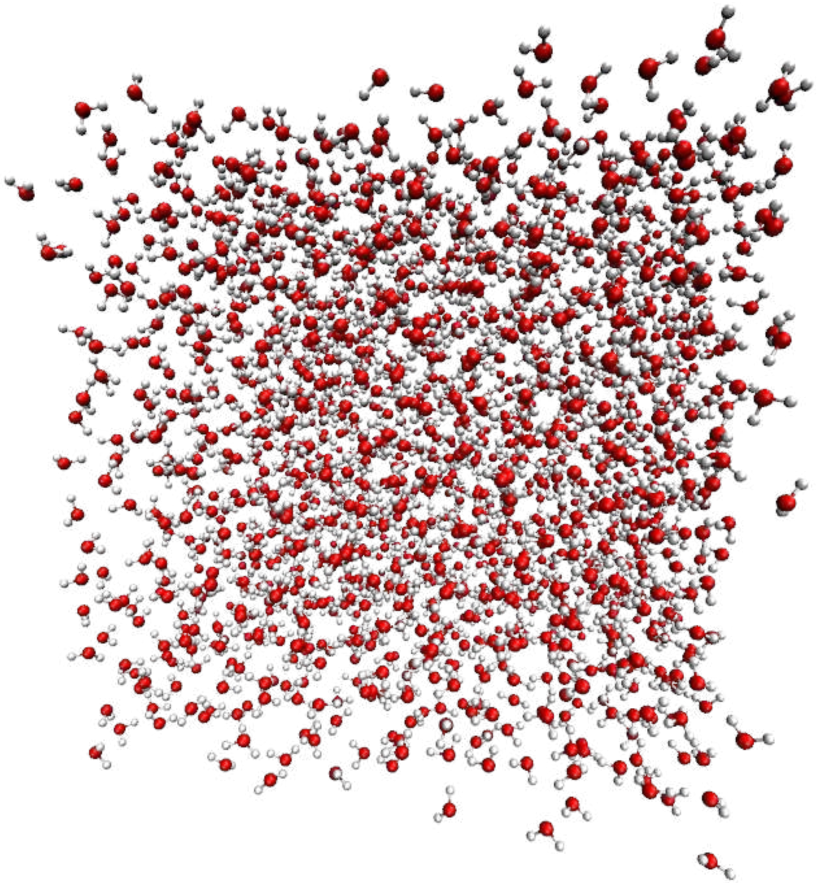
SIMULAÇÕES COMPUTACIONAIS



Água - Redes Neurais

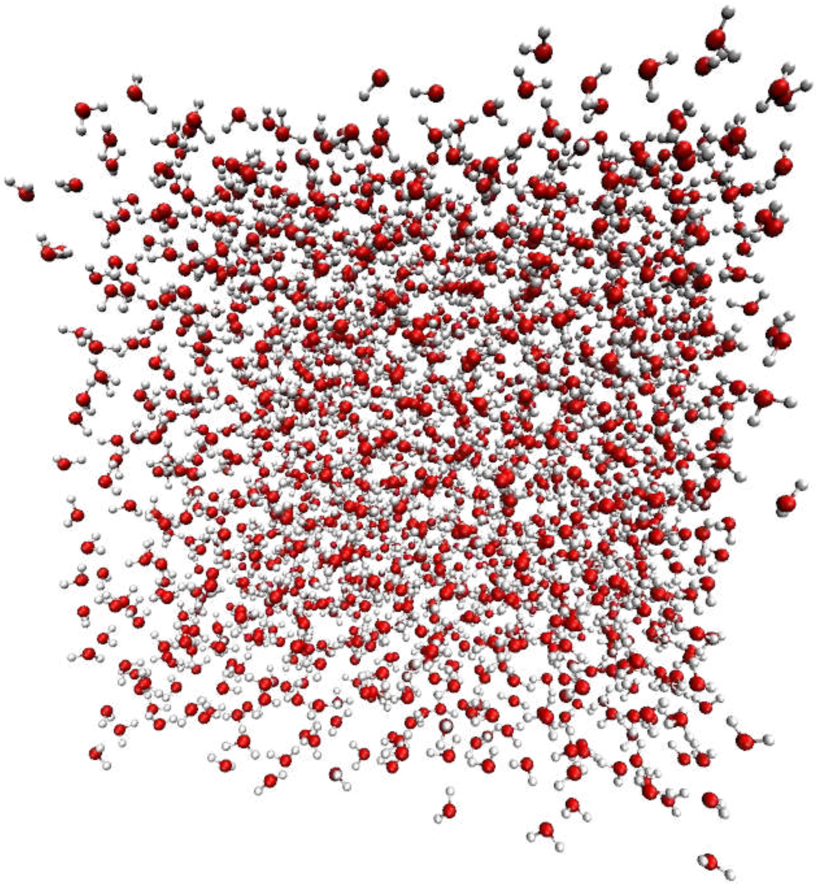


64 molecules



up to 1728 molecules

Água



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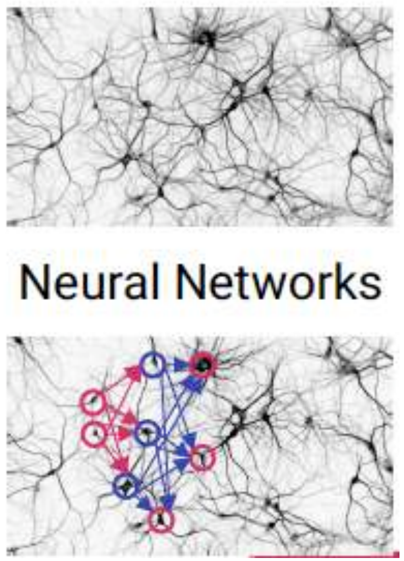
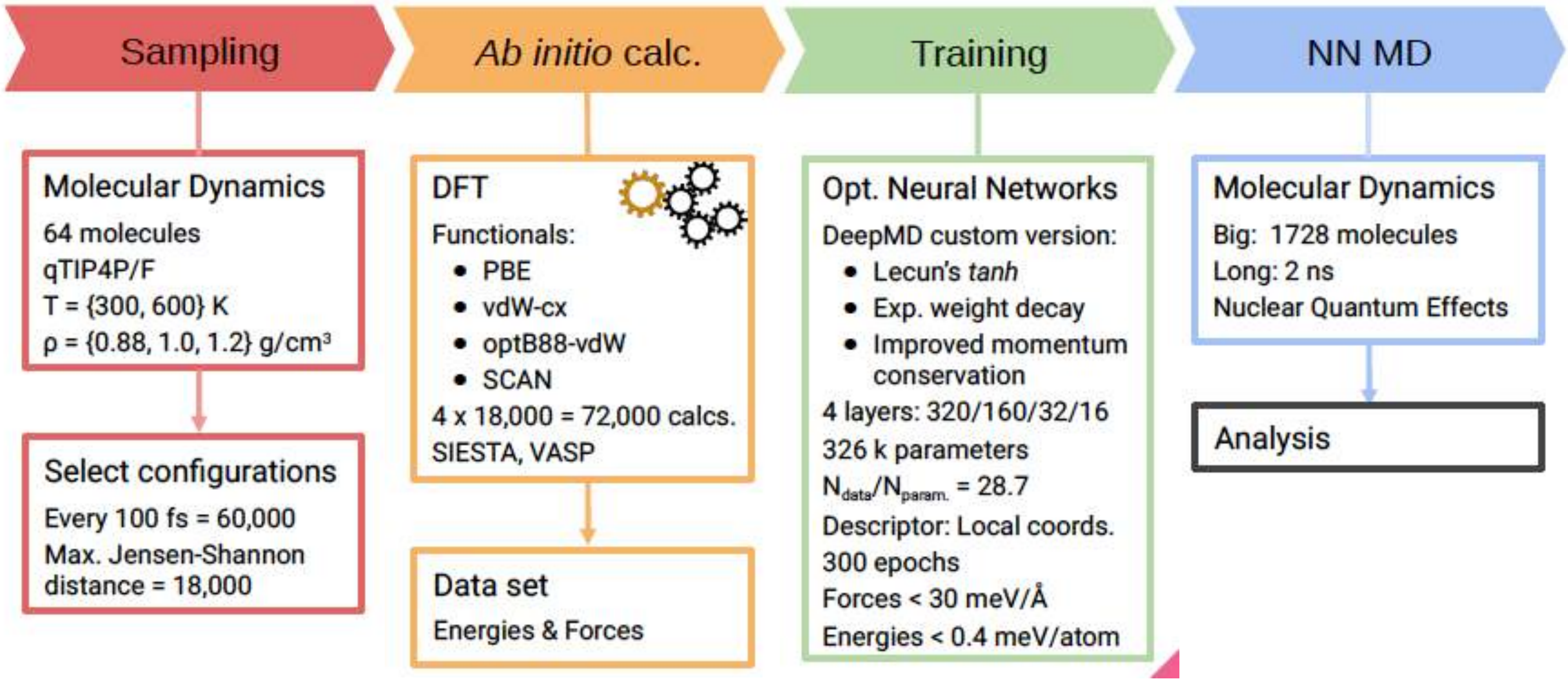


Água - Redes Neurais

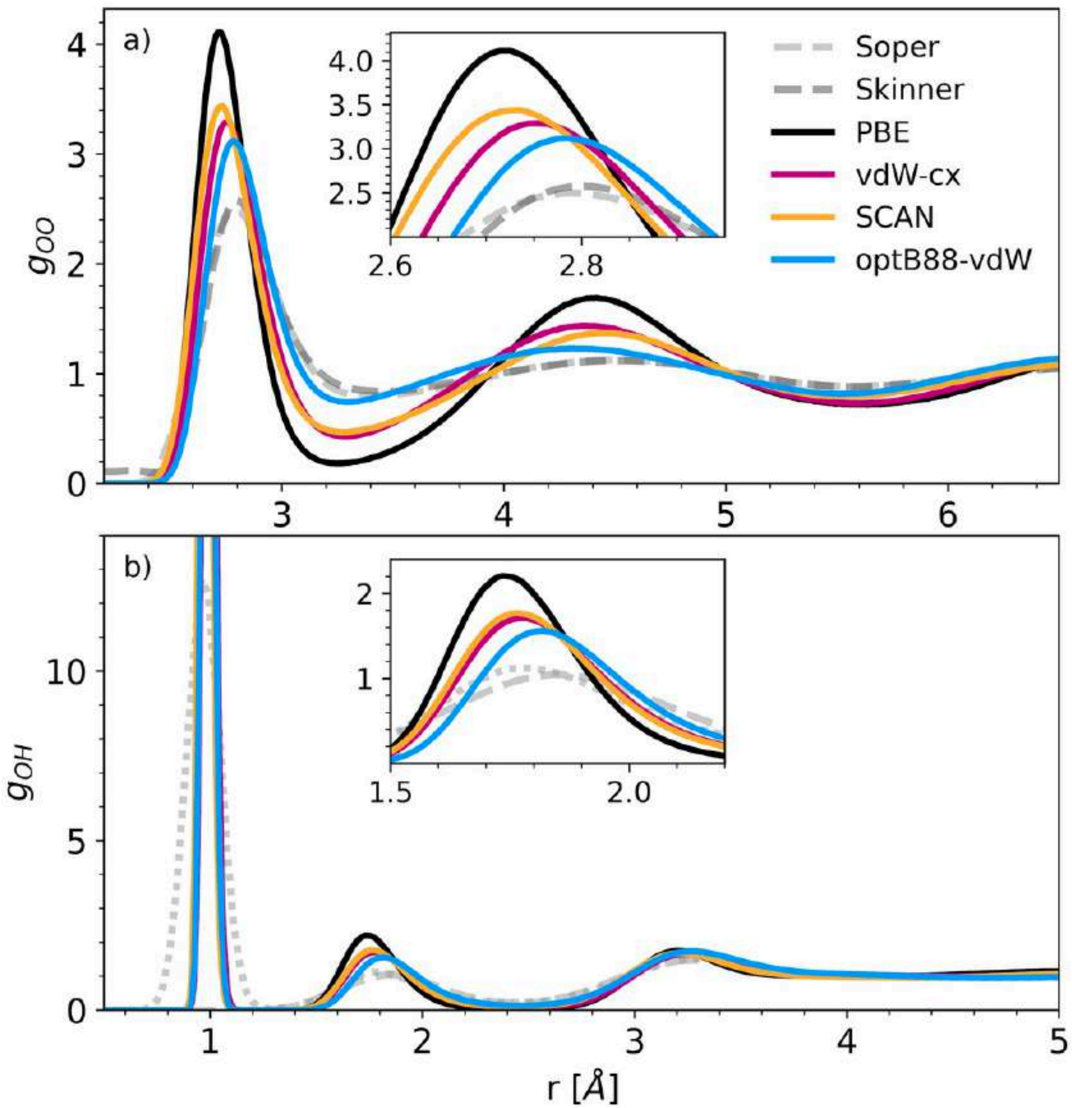


A. Torres, LSP, M. Fernandez-Serra, A. Rocha, JPCB 125, 10772 (2021)

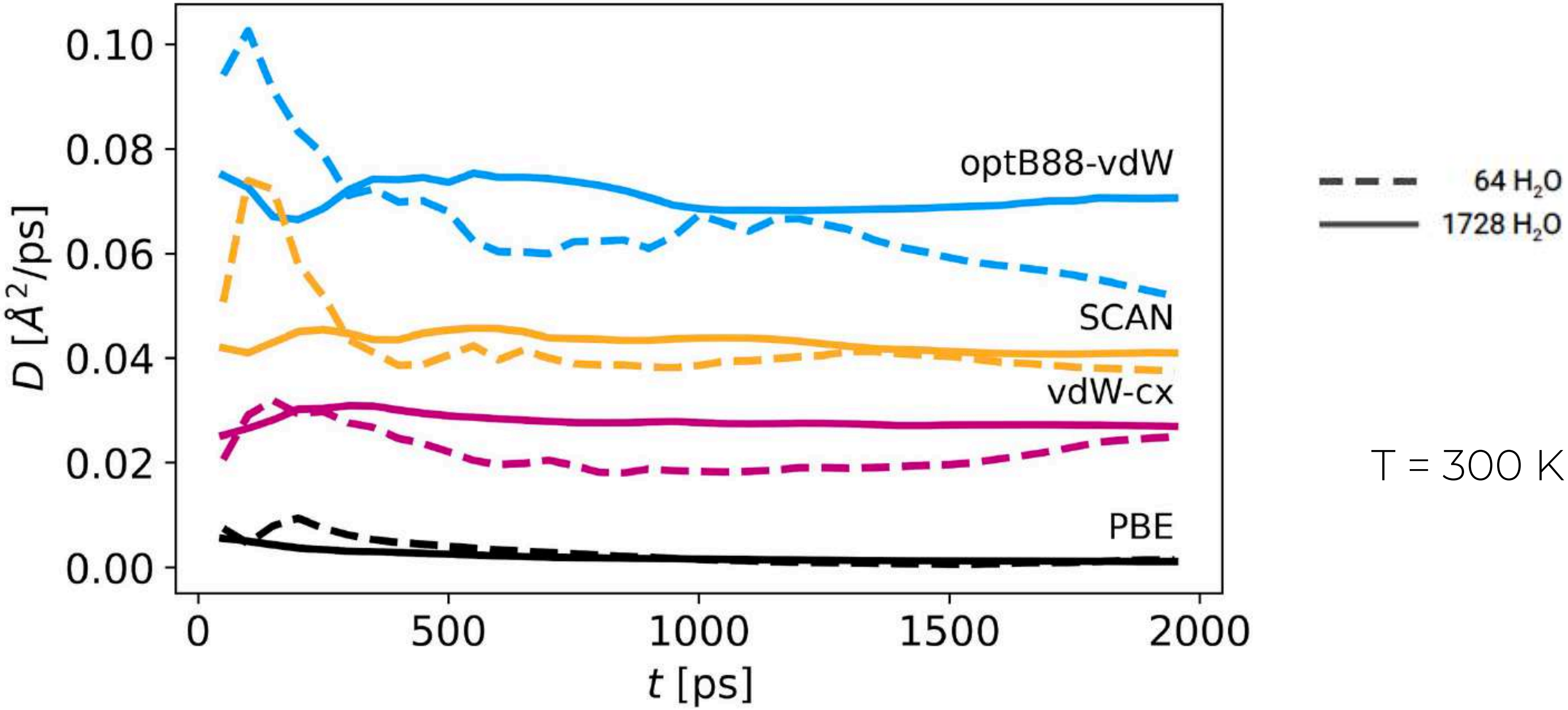
Água - NN MD

1728 molecules

2 ns NVT NN-MD



Water - NN MD - Self-diffusion coefficient

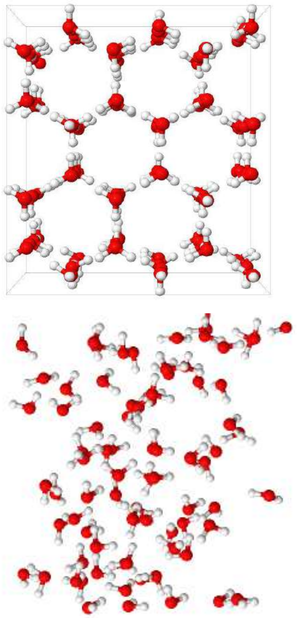


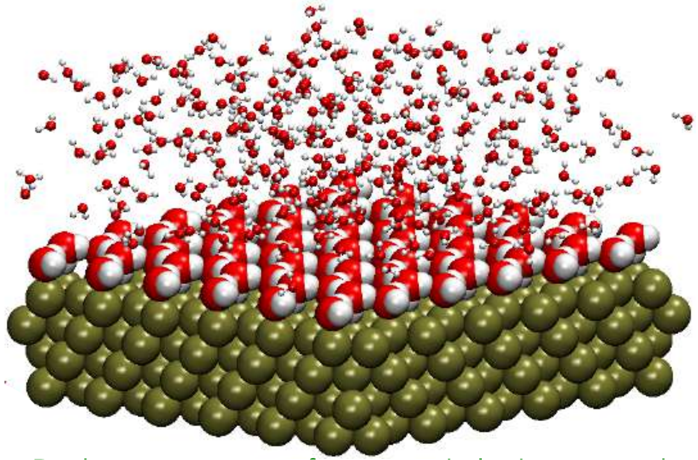
T = 300 K

Mecânica quântica

$$\left[\sum_{i}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m}+v(\mathbf{r}_i)\right)+\sum_{i<j}U\left(\mathbf{r}_i,\mathbf{r}_j\right)\right]\Psi=E\Psi$$

Computação alto desempenho

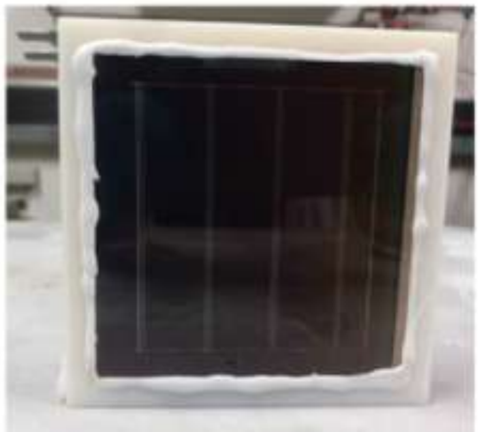




Mecânica quântica

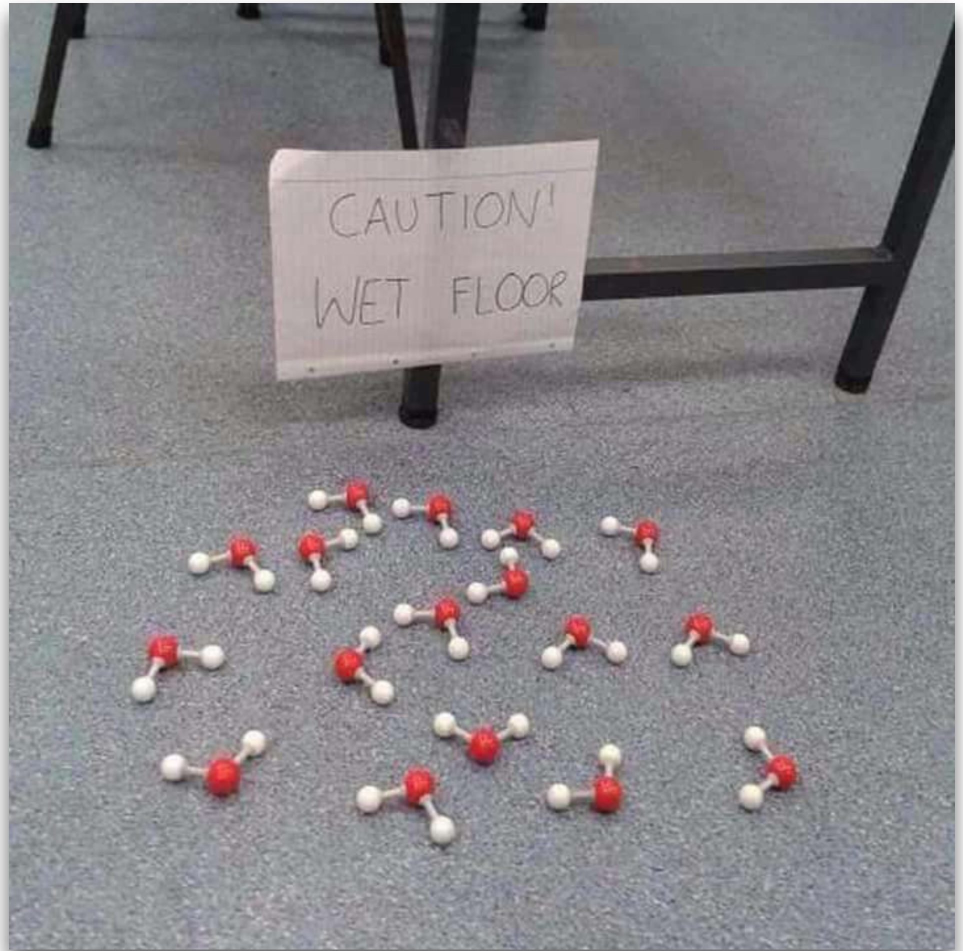
$$\left[\sum_{i}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m}+v(\mathbf{r}_i)\right)+\sum_{i<j}U\left(\mathbf{r}_i,\mathbf{r}_j\right)\right]\Psi = E\Psi$$

Computação alto desempenho



Adv. Sustainable Syst. 4, 2000070 (2020)

Obrigada!



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