Molekulska dinamika

Mihajlo Etinski

- Uvod
- Racunarske simulacije
- Osnove
- MD argona u NVE ansamblu
- Napredne teme
- Jos primera

Uvod

Eksperiment

- Priprema uzorka
- Merenja, osmatranja
- Skupljanje podataka
- Obrada podataka

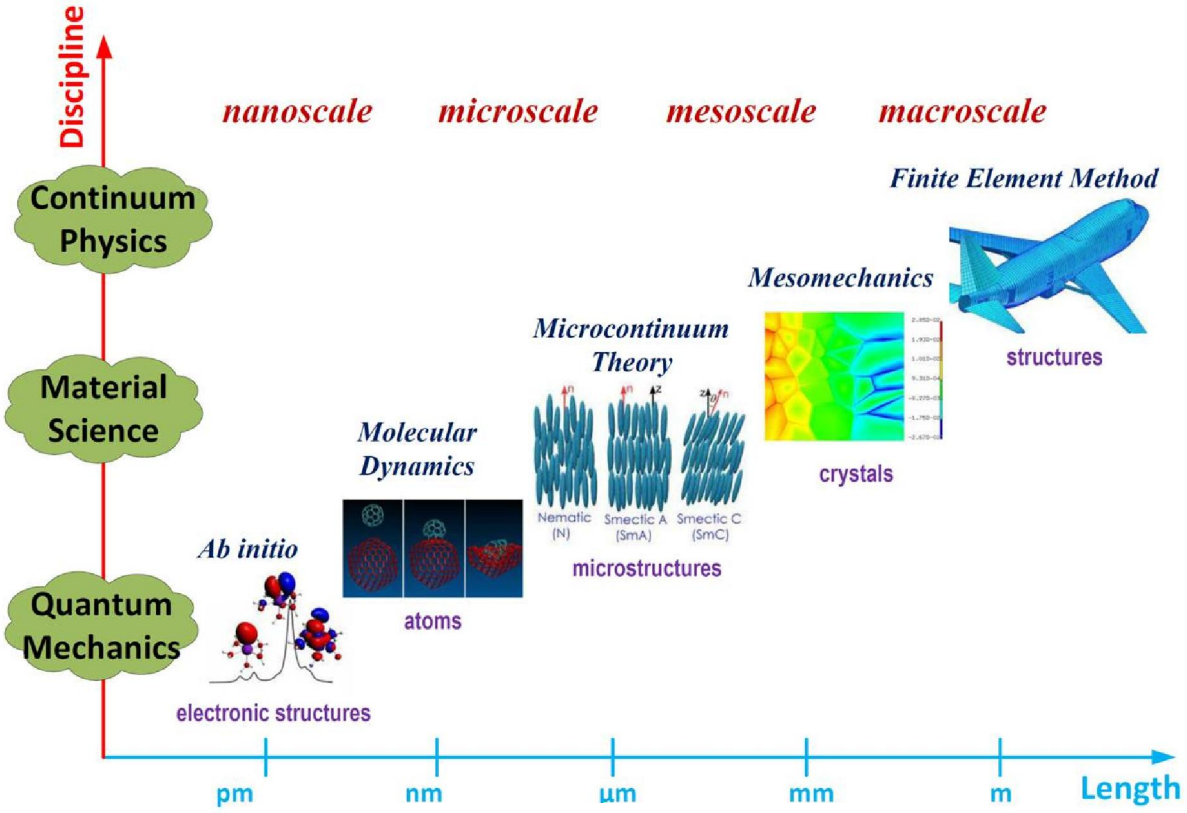
Teorija

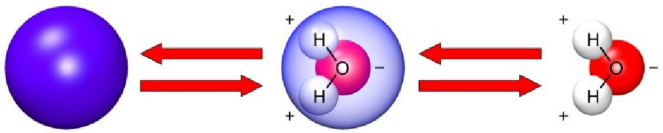
- Razvijanje modela i hipoteza
- Predikcija eksperimenata

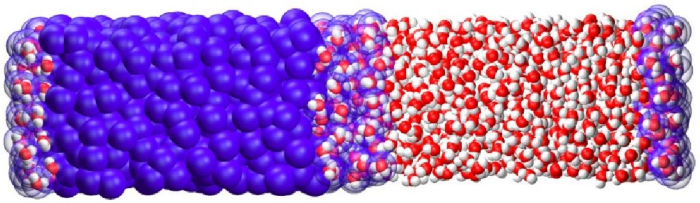
Računarske simulacije

- Priprema modela
- Obrada podataka
- Testiranje teorija
- Mogućnost simulacije eksperimenata koje je teško izvesti

Sta želimo da modelujemo?

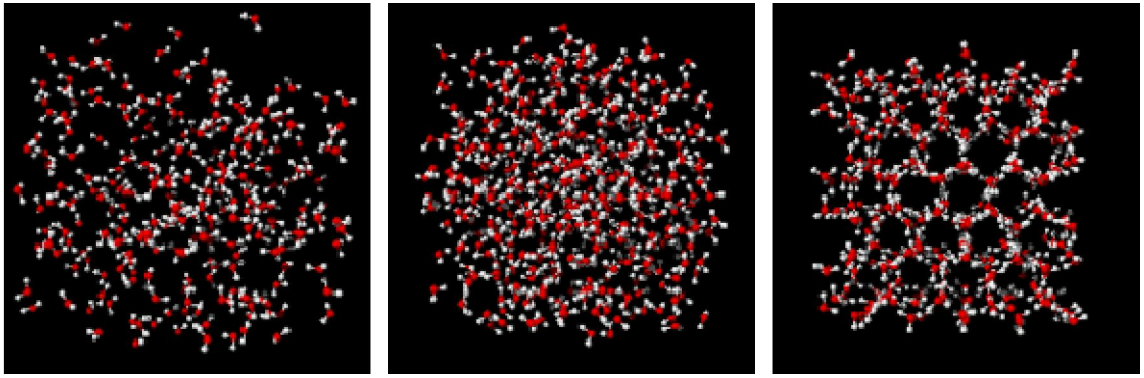




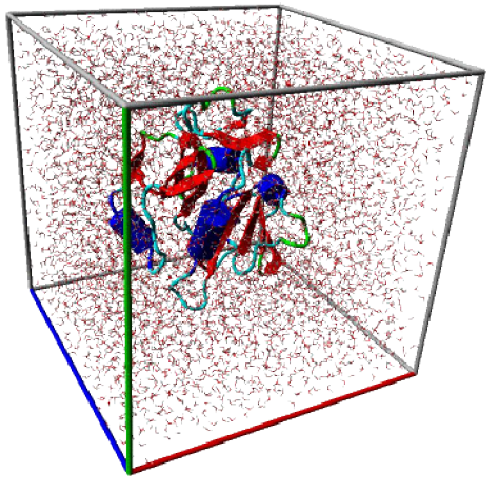


Sta želimo da modelujemo?

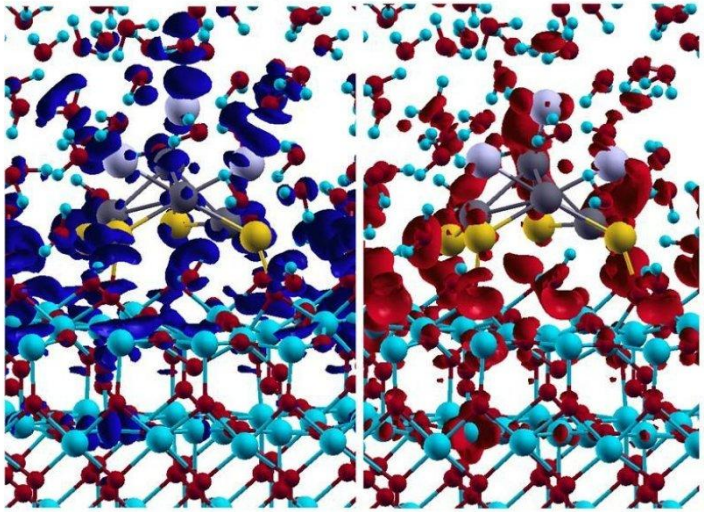
Fazni prelazi



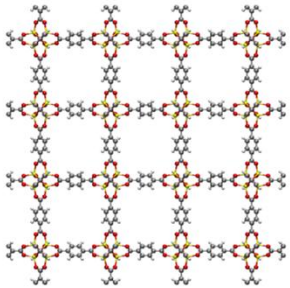
Biološke sisteme

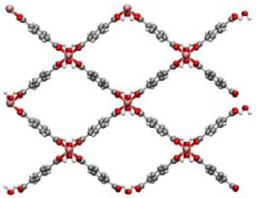


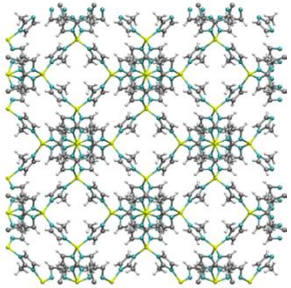
Reakcione mehanizme



Osobine materijala

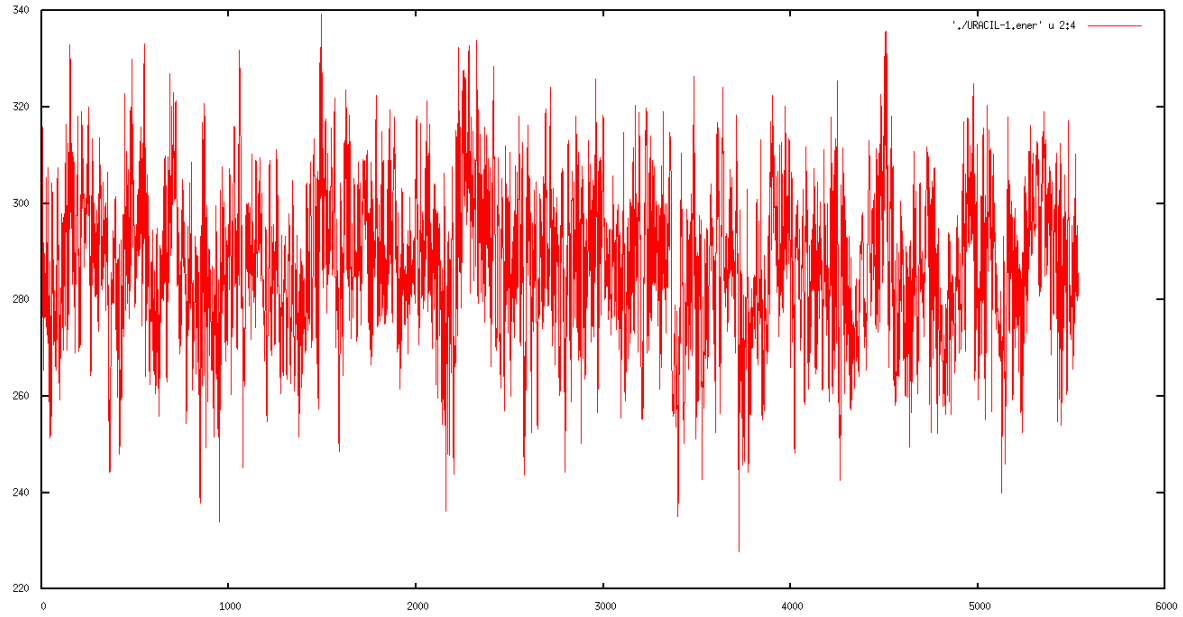






Računarske simulacije

- Računaske simulacije daju egzatno rešenje u okviru korišćenog modela
- Izbor modela sisteme zavisi od toga sta želimo da simuliramo
- Računarske simulacije zbog vremenskog ograničenja prouzrokovanim ograničenim računarskim resursima obično razmatraju sisteme od 100-10000 čestica i vremenske opsege od 10 ps do 100 ns
- Srednja vrednost dinamičke promenjive i njena statistička greška

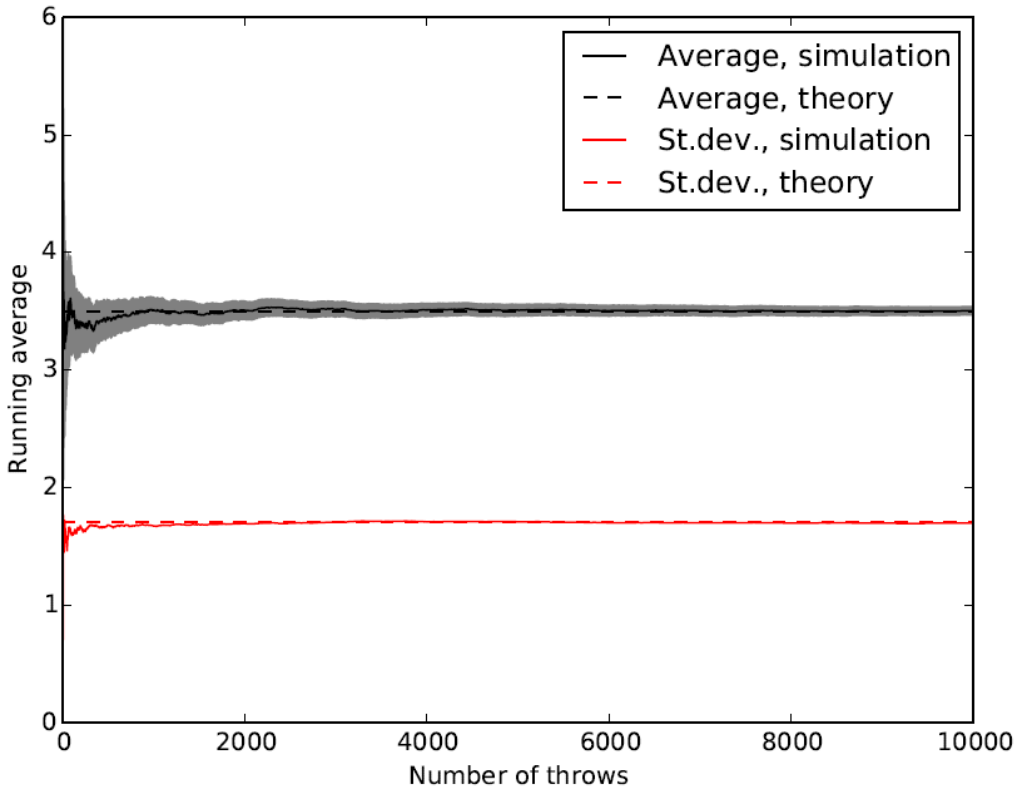


Kako proceniti kvalitet simulacije?

Primer: bacanje kockice

Srednje vrednost $\langle x \rangle = \Sigma i \; pi * xi = 3.5$

Standardna devijacije $\sigma = \langle x^2 \rangle - \langle x \rangle^2 \approx 2.92$



Osnove

Izračunati sile koje deluju na čestice i rešiti Njutnove jednačine kretanja

Srednja vrednost termodinamičkih promenjivih se računa koristeći vremensku usrednjenost

Mogu se računati vremeski nezavisne (termodinamičke i strukturne) ali i vremenski zavisne (kinetički koeficienti) osobine sistema

Koraci tokom izvođenja simulacije:

Inijalizacija sistema

Uravnotežnjenje sistema

Proizvodnja rezultata

Obrada podataka

Koraci tokom izvodjena eksperimenta:

Priprema uzorka

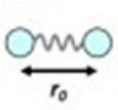
Merenje

Obrada podataka

Born-Openhajmerova aproksimacija za molekule:
Atomska jezgra se kreću na površi potencijalne energije

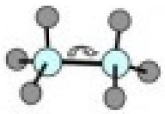
Molekulska mehanika

$$V = \sum_{veze} k_r(r - r_{eq})^2$$

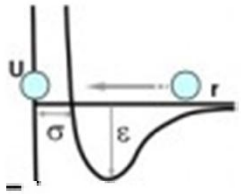


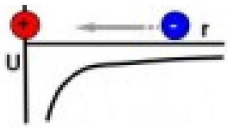
$$+ \sum_{uglovi} k_\theta(\theta - \theta_{eq})^2$$

$$+ \sum_{diedralniuglovi} \frac{1}{2}\pi_n(1 + \cos(n\varphi - \varphi_0))$$



$$+ \sum_{i<j} \left(\frac{a_{ij}}{r_{ij}^{12}} - \frac{b_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{\varepsilon r_{ij}}\right)$$



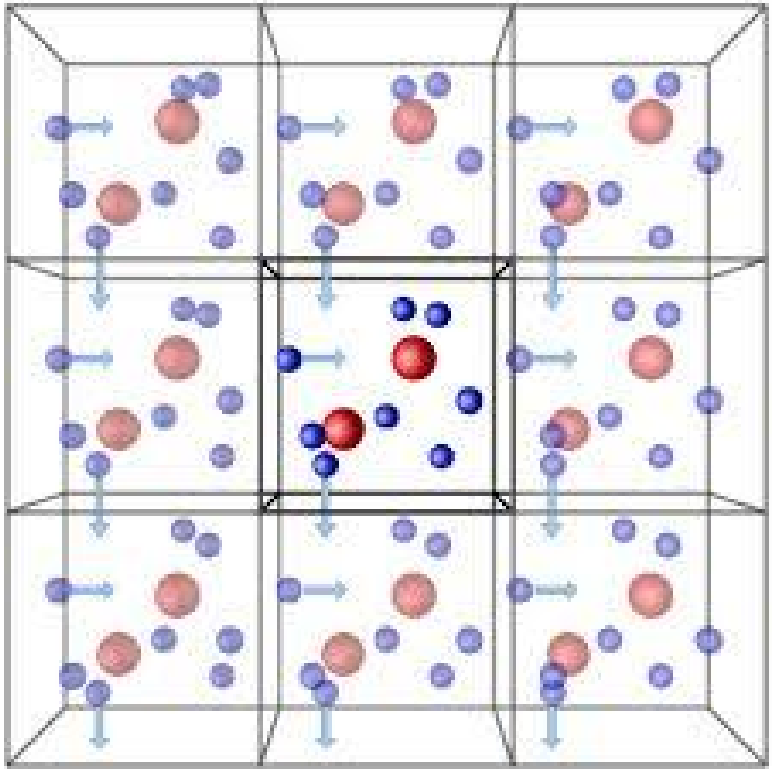


Ab initio potencijal

Potrebno je rešiti elektronsku Šredingerovu jednačinu u svakom koraku (BOMD)
Kretanje elektrona se uključuje preko fiktivnih stepeni slobode (CPMD)

Periodični uslovi

Potrebni su da bi se izbegao uticaj površinskih efekata na simulaciju



Čestice interaguju sa svim (beskonačno mnogo) replikama čestica

Ograničavanje interakcija

Da bi se izbeglo računanje interakcije sa beskonačno mnogo replika, obično se potencijali koji brzo opadaju ograničavaju do nekog rastojanja r_c.
Izuzeci su Kulonov potencijal i interakcije dipolnih momenta.

Od posebnog interesa je slučaj $r_c=L/2$ – posmetra se interakcija čestice samo sa najbližom replikom ostalih čestica

Ipak, moramo dodati korekciju za ukupnu potencijalnu energiju

$$U = \sum_{i<j} u_c(r_{ij}) + \frac{N\rho}{2} \int_{r_c}^{\infty} u(r) d^3 r$$

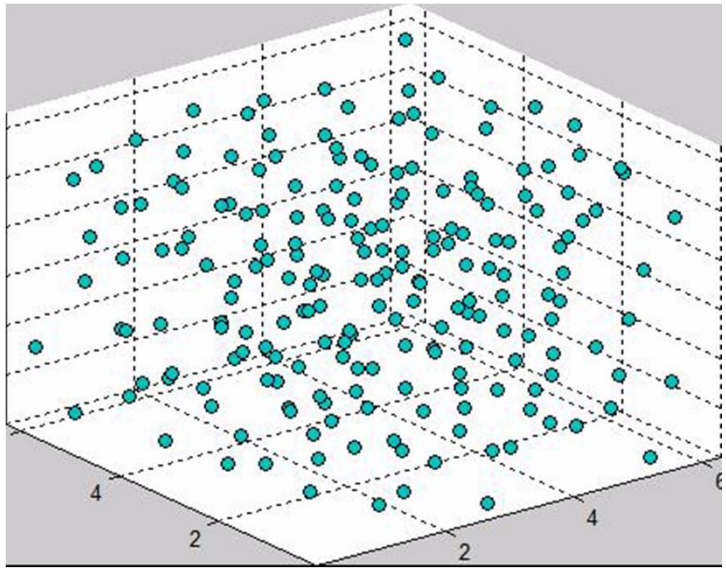
Primer: Molekulska dinamika argona u NVE ansamblu

Atomi argona su sfernosimetrični te stoga interaguju međusobno samo Lenard-Džonsovim potencijalom

$$u(\vec{r}_1, \vec{r}_2) = u(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$

Ukupna potencijalna energija za sistem atoma argona:

$$V\left(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N\right) = \sum_{i=1}^{N} \sum_{j<i} u(\vec{r}_i, \vec{r}_j)$$



Ograničen i pomeren potencijal

Ograničeni LJ potencijal

$$u(r) = \begin{cases} u(r) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

Ograničeni i pomereni LJ potencijal

$$u(r) = \begin{cases} u(r) - u(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

Uslov minimalne slike $r_c = L/2$

Korekcije repa za potencijalnu energiju po atomu i pritisak

Trenutna temperatura u sistemu se izračunava iz kinetičke energije (N_{tr} je broj stepeni slobode):

$$T(t) = \frac{2K}{kN_{tr}}$$

Pritisak argona se izračunava pomoću dinamičke promenjive virijal:

$$P = \frac{kTN}{V} + \frac{vir(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)}{3V}$$

$$vir(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \sum_{i=1}^{N} \sum_{j<i} \vec{F}(\vec{r}_i, \vec{r}_j) \cdot (\vec{r}_i - \vec{r}_j)$$

x-komponenta sile između dva atoma: $F_x = \frac{48x\epsilon}{r^2} \left(\left(\frac{\sigma}{r} \right)^{12} - \frac{1}{2} \left(\frac{\sigma}{r} \right)^{6} \right)$

$$\vec{F}(\vec{r}_i, \vec{r}_j) \cdot (\vec{r}_i - \vec{r}_j) = F_{x_{i,j}} \cdot x_{i,j} + F_{y_{i,j}} \cdot y_{i,j} + F_{z_{i,j}} \cdot z_{i,j} =$$

$$= 48\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \frac{1}{2} \left(\frac{\sigma}{r} \right)^{6} \right)$$

Inicijalizacija:

Izabrati broj čestica, gustinu, dužinu vremenskog koraka za dinamiku,...

Izabrati početni položaj čestica. Poželjno je da se čestice ne preklapaju. Dobra početna konfiguracija je npr. kada se čestice nalaze u čvorovima jednostavne kubne kristalne rešetke

Brzine čestica u početku biramo na slučajan način, pogodno iz Maksvelove raspodele za zadatu temperaturu. Ukupni linearni moment treba da je jednak nuli (time smanjujemo broj stepeni slobode za 3)

Uravnoteženje:

Početno stanje je malo verovatno stanje za termodinamičke parametre koje želimo da simuliramo. Stoga je potrebno pripremiti sistem u stanje koje odgovara željenim parametrima. Tome služi uravnotežnjenje sistema.

Iako se koristiti NVE ansambl za uzorkovanje stanja, pogodno je pripremiti sistem na željenu temperaturu. U tu svrhu koristimo skaliranje brzina čestica na odabranu temperaturu tokom ovog dela simulacije sa faktorom $\sqrt{\frac{T}{T(t)}}$

Ovakvo skaliranje temperature ne oponaša NVT ansambl, ali je pogodno kao brz metod za uravnotežnjenje sistema

Jednačine kretanja

$$\vec{r}(t+\Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{\Delta t^2}{2m}\vec{f}(t) + \frac{\Delta t^3}{3!}\dddot{\vec{r}}(t) + O(\Delta t^4)$$

$$\vec{r}(t-\Delta t) = \vec{r}(t) - \vec{v}(t)\Delta t + \frac{\Delta t^2}{2m}\vec{f}(t) - \frac{\Delta t^3}{3!}\dddot{\vec{r}}(t) + O(\Delta t^4)$$

$$\vec{r}(t+\Delta t) + \vec{r}(t-\Delta t) = 2\vec{r}(t) + \frac{\Delta t^2}{m}\vec{f}(t) + O(\Delta t^4)$$

Verleov algoritam

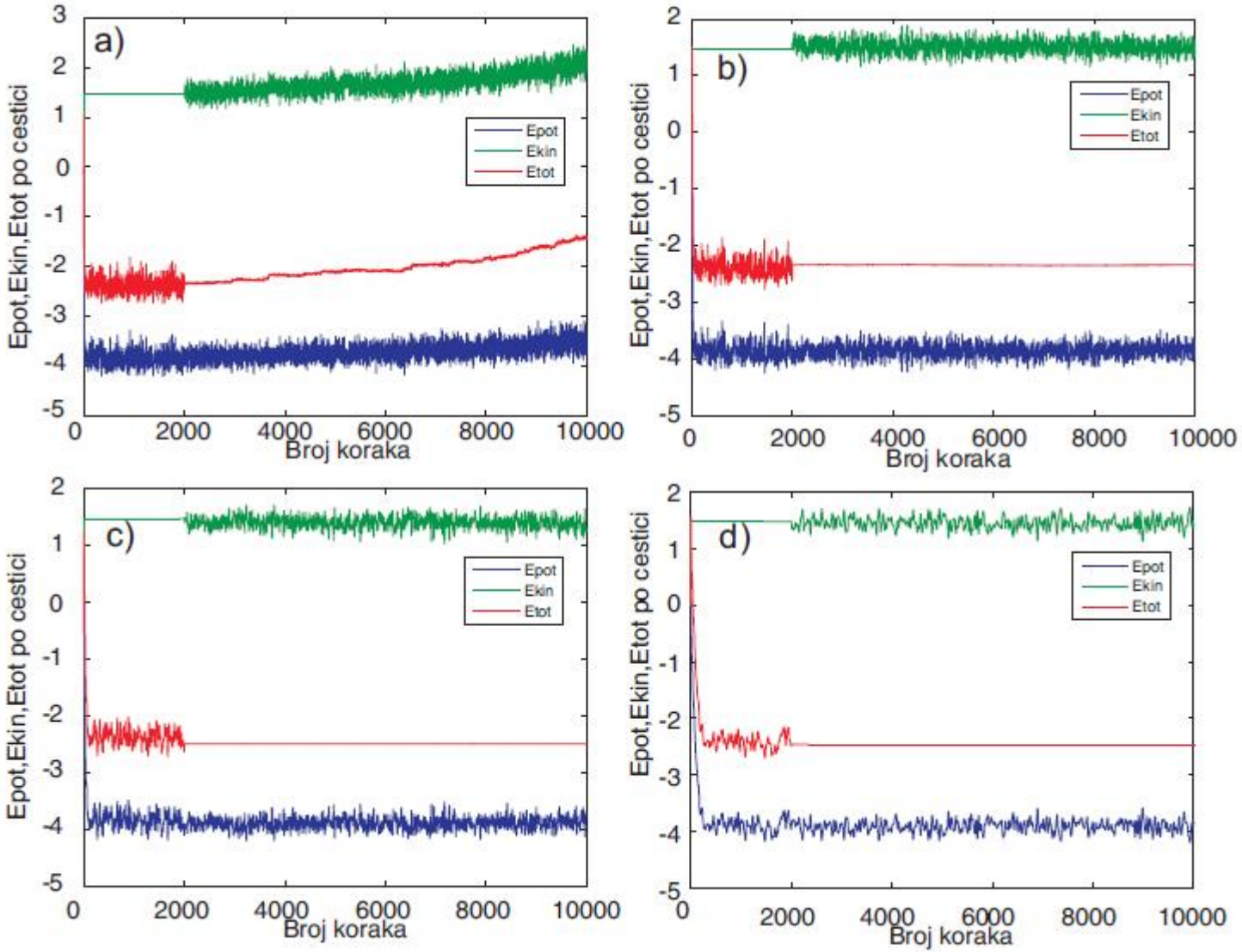
$$\vec{r}(t+\Delta t) \approx 2\vec{r}(t) + \vec{r}(t-\Delta t) + \frac{\Delta t^2}{m}\vec{f}(t)$$

Verleov algoritam ne koristi brzine da bi se odredili položaji čestica u sledećoj tački. Brzine se mogu odrediti na sledeći način:

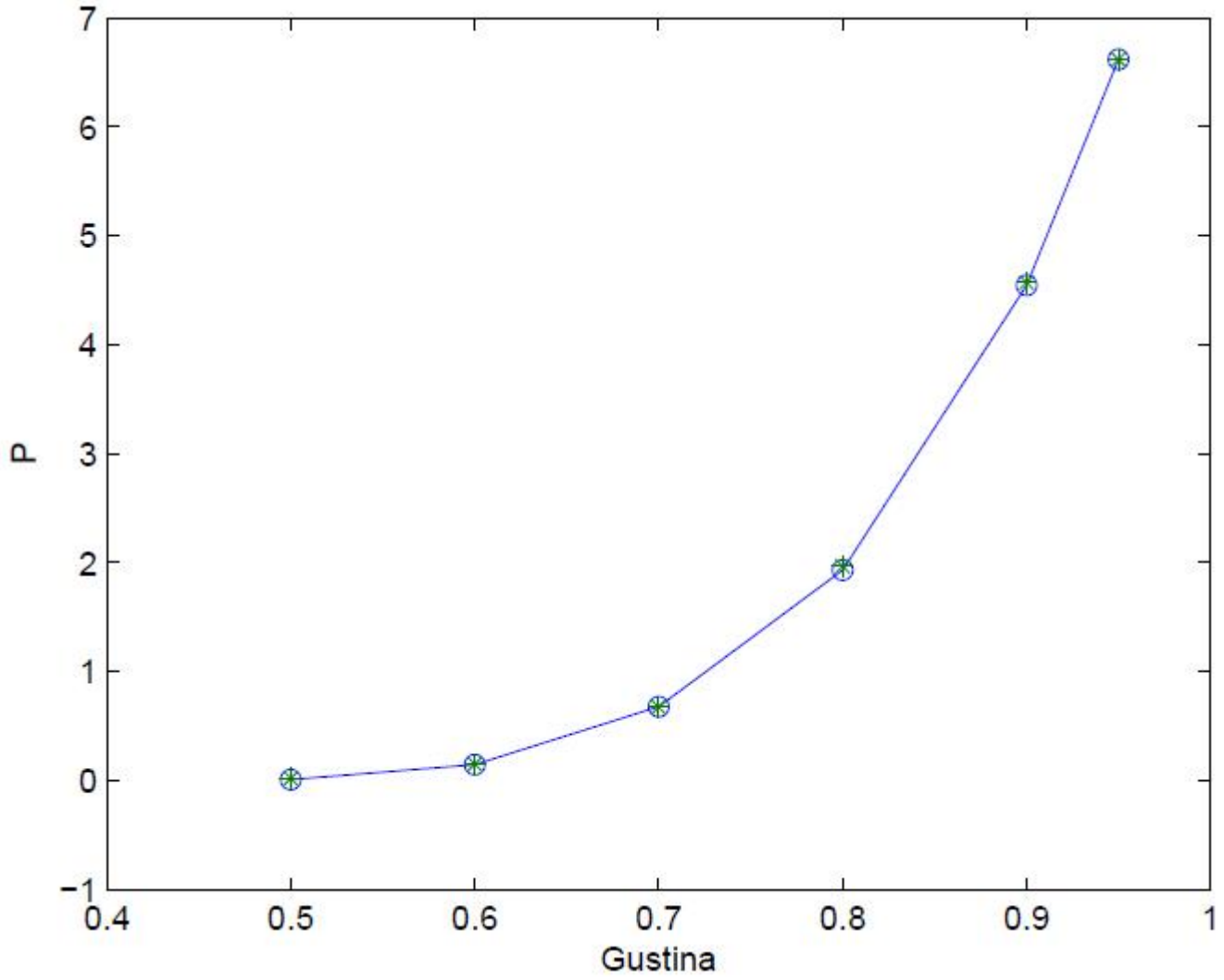
$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$$

Najviše vremena potrebno je izračunavanje sila

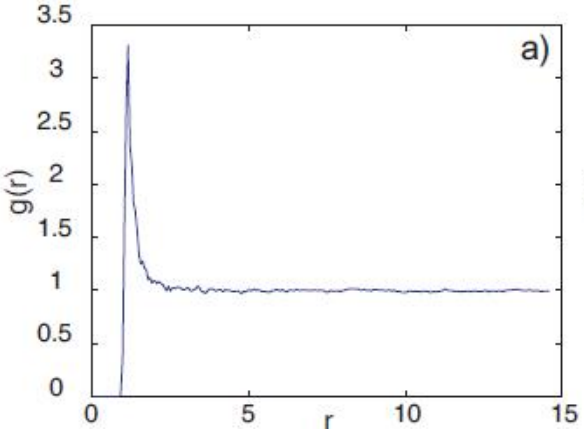
Kako odrediti dužinu vremenskog koraka za integraciju jednačina kretanja?

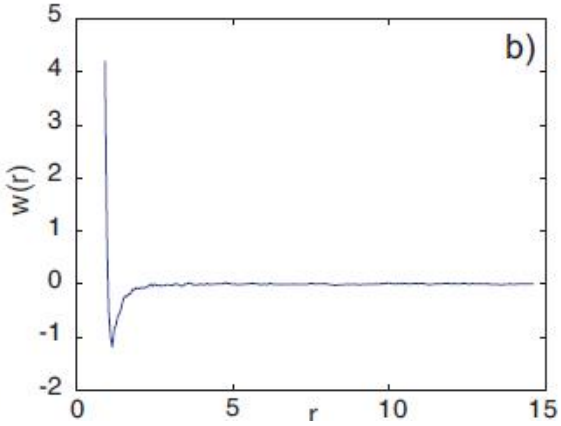


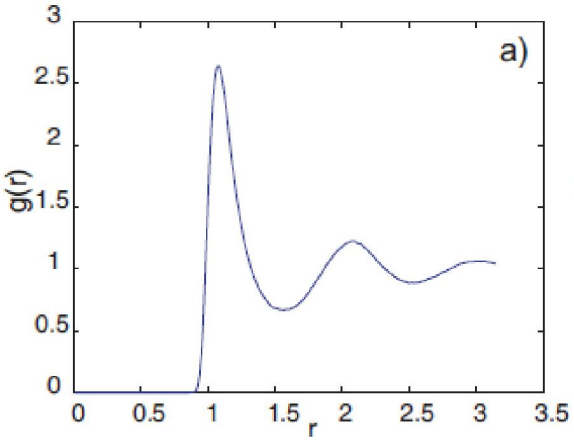
Izračunati pritisak (kružići) i vrednosti koje su dobili Džonson i saradnici (zvezdice) Mol. Phys. 591 78 1993, T=1,2

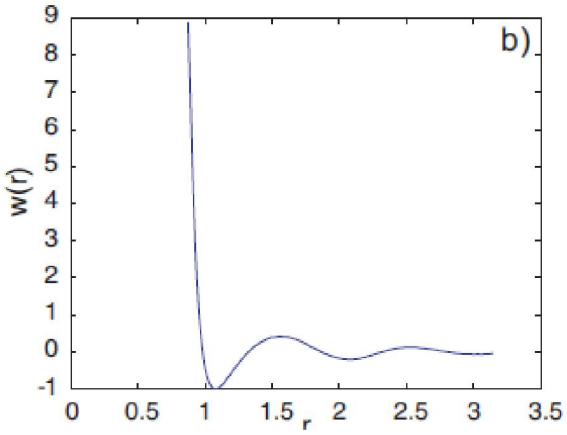


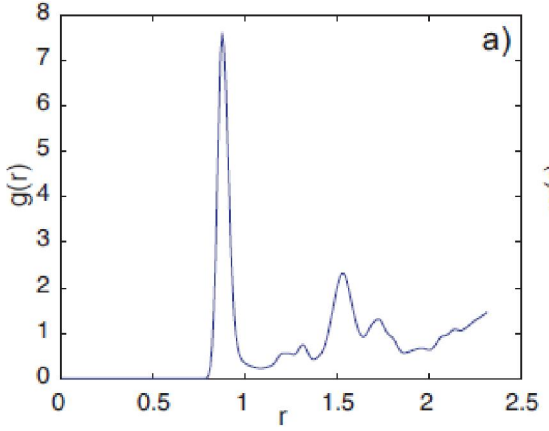
Radijalne funkcije raspodele i potencijali srednje sile

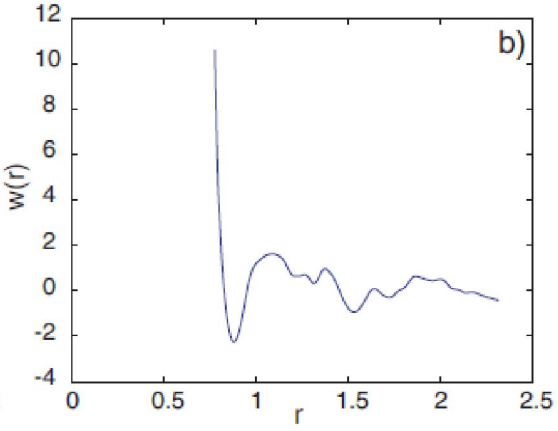












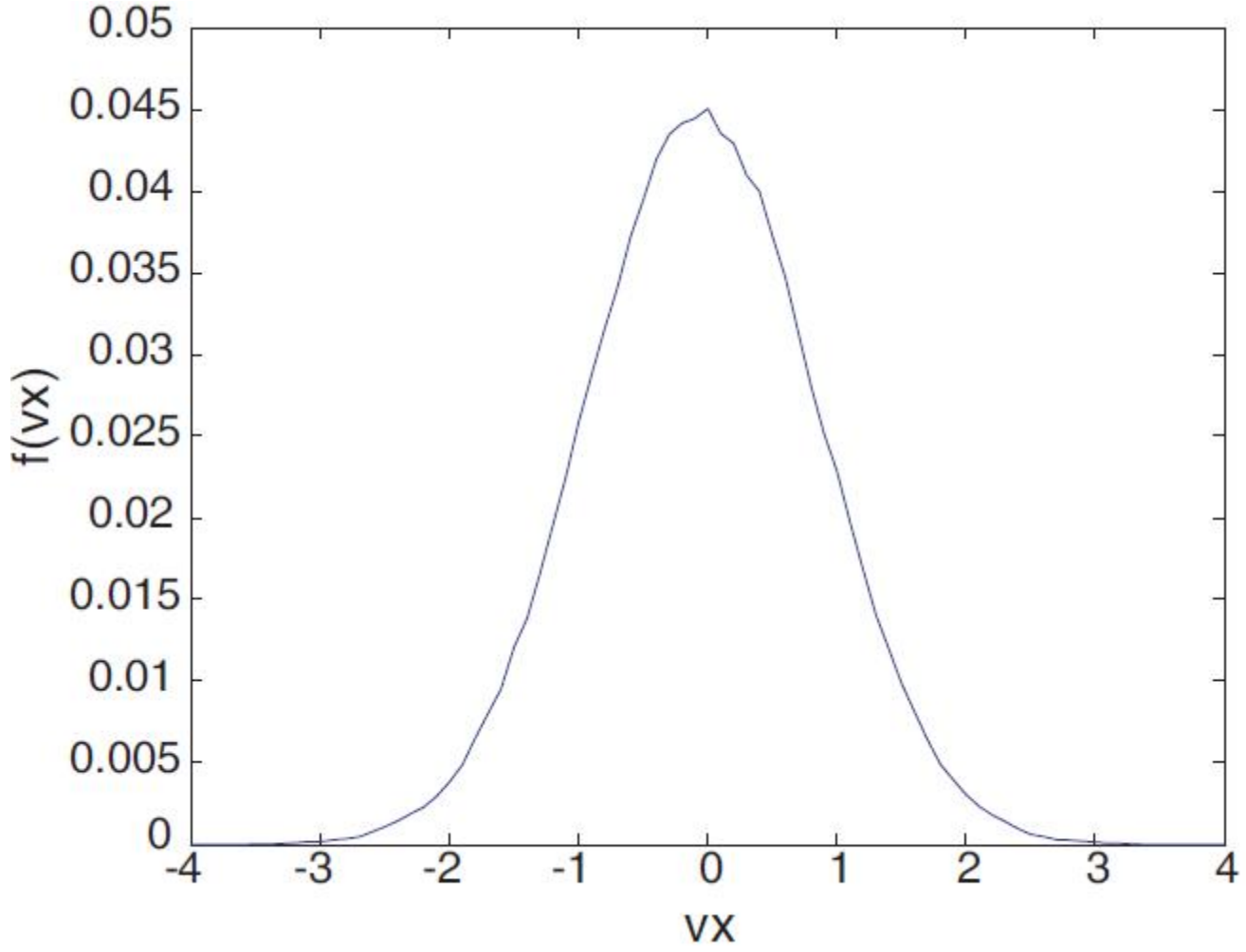
Radijalna funkcija raspodele:

$$g(r) = \frac{\langle N(r \pm \Delta r/2) \rangle}{\Omega(r \pm \Delta r/2)} \frac{1}{\rho}$$

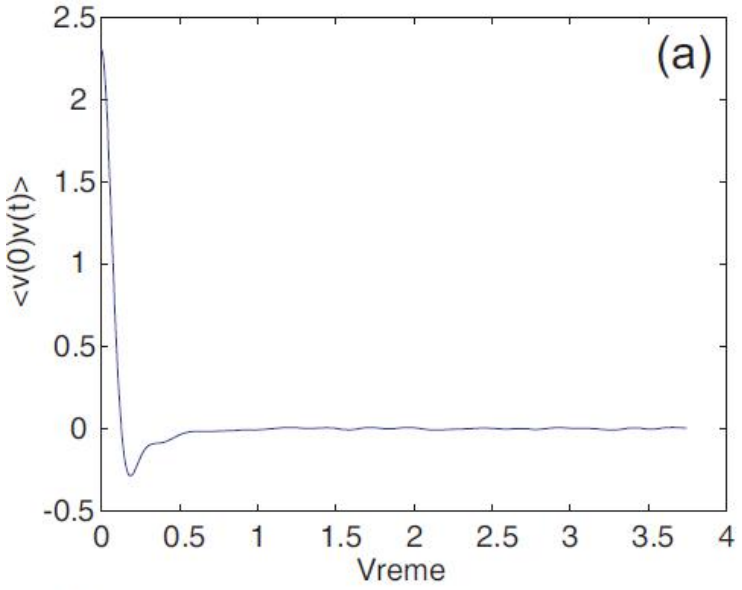
Potencijal srednje sile:

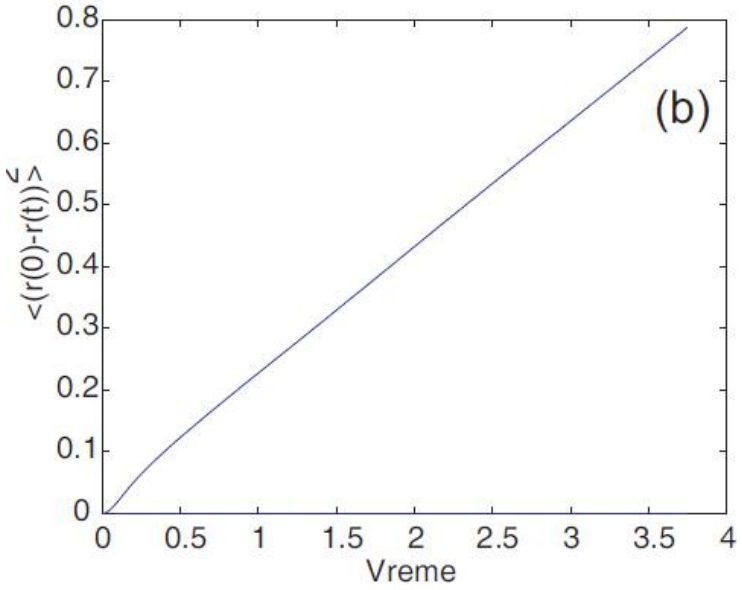
$$w(r) = -kT \ln g(r)$$

Raspodela x-komponente brzine argona



Autokorelaciona funkcija brzine i srednji kvadratni pomeraj atoma argona





Koeficijent difuzije: $D = \frac{1}{3}\int_0^\infty \langle \vec{v}(0)\vec{v}(t)\rangle \, dt$ $D = \lim_{t\to\infty} \frac{\langle |\vec{r}(0) - \vec{r}(t)|^2 \rangle}{6t}$

Napredne teme

Velocity Verlet algoritam

$x(t+dt)=x(t)+v(t)dt+0.5*a(t)*dt^2$
$v(t+dt)=v(t)+(a(t)+a(t+dt))*dt/2$

a(t+dt) se izracunava iz potencijala u konfiguraciji x(t+dt)

Leap Frog, Bimanov, prediktor-korektor algoritam

Molekulska dinamika u različitim ansamblima?

Ansambl	Konstantne veličine	Termodinamičke funk.
Mikrokanonski	N,V,E	$S=k \ln \Gamma(N,V,E)$
Kanonski	N,V,T	$\beta F= - \ln Q(N,V,T)$
Izobarski-izotermski	N,P,T	$\beta G= - \ln \Delta(N,P,T)$

Rezervoari

Andersenov termostat

Toplotno kupatilo deluje stohasticki na brzine slucajno izabranih cestica.
Izmedju menjanja brzina cestica, sistem ima konstantnu energiju.
Algoritam:

1. Integraliti jednacine kretanja na intervalu dt
2. Odredjeni broj cestica se izabere da interaguje sa rezervoarom. Verovatnoca da se cestica izabere u vremenskom intervalu dt je vdt, v je frekvencija interakcije rezervoara sa sistemom.
3. Ako je cestica izabrana da interaguje sa rezervoarom, njena nova brzina se dodeljuje iz Maksvelove raspodele na temperaturi T.

Noze-Huverov termostat – deterministicki termostat
Barostat – menja se zapremina simulacione kutije

Jos primera

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Impeding ^{99}Tc(IV) mobility in novel waste forms

Mal-Soon Lee[1], Wooyong Um[2,3], Guohui Wang[2], Albert A. Kruger[4], Wayne W. Lukens[5], Roger Rousseau[1] & Vassiliki-Alexandra Glezakou[1]

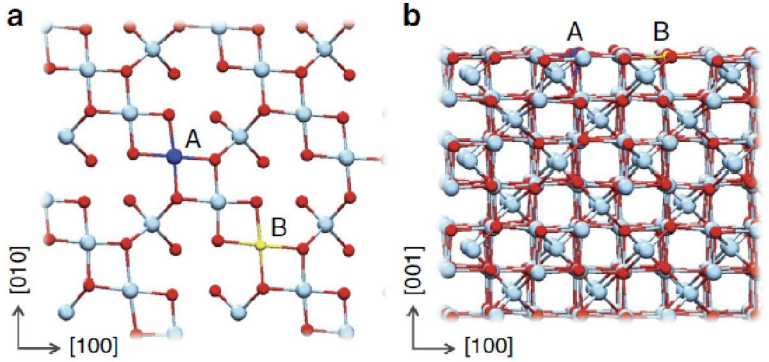

Figure 1 | The B-truncated (octahedral Fe) Fe_3O_4(001) structure. (**a**) Top view and (**b**) side view of surface structure. Red and cyan circles represent oxygen and iron, respectively. A (blue circle) can be either Fe or Tc and B (yellow circle) can be either Fe or an impurity atom (Ni/Zn/Co).

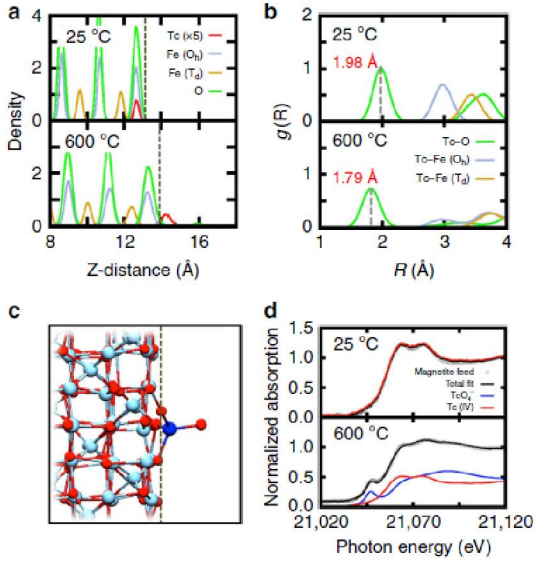

Figure 2 | Structural properties and XANES spectra in the presence of Tc. (**a**) Atomic-density profile showing atomic arrangement along the *z*-direction at 25 and 600 °C obtained from AIMD simulations, where dotted vertical line denotes the magnetite surface. (**b**) Pair distribution function g(R) obtained from AIMD simulation trajectories at 25 and 600 °C. (**c**) Snapshot of the structure at 600 °C from AIMD trajectories where a blue circle represents Tc, red for O and cyan for Fe. The dotted vertical line denotes the magnetite surface. (**d**) Normalized XANES spectra at 25 and 600 °C.

"AIMD simulations were performed with and without Tc at 25 C and with the dopants Co/Ni/Zn at 600 C, with the Nose´-Hoover thermostat for NVT ensemble and a time step of 1.0 fs. Each simulation was equilibrated for at least 20–28 ps, and the last 10–12 ps of the trajectories was used for the analysis."

"This work highlights the power of modern, state-of-the-art simulations to provide essential insights and generate theory-inspired design criteria of complex materials at elevated temperatures."

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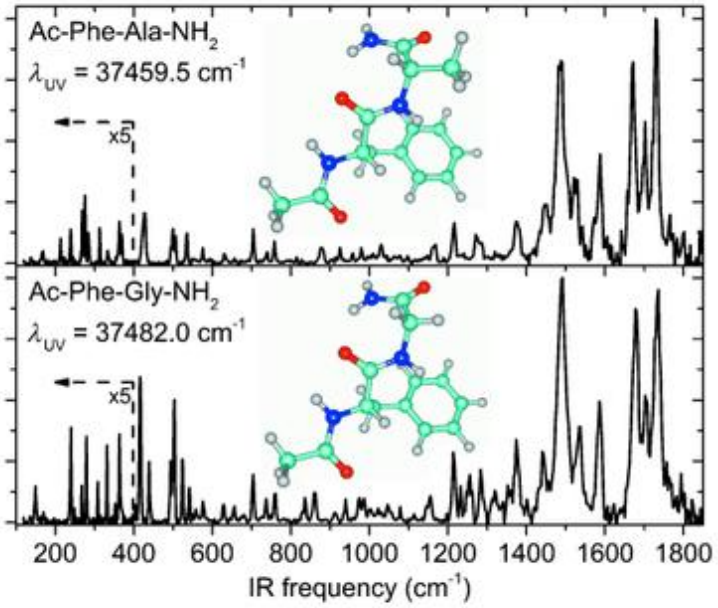
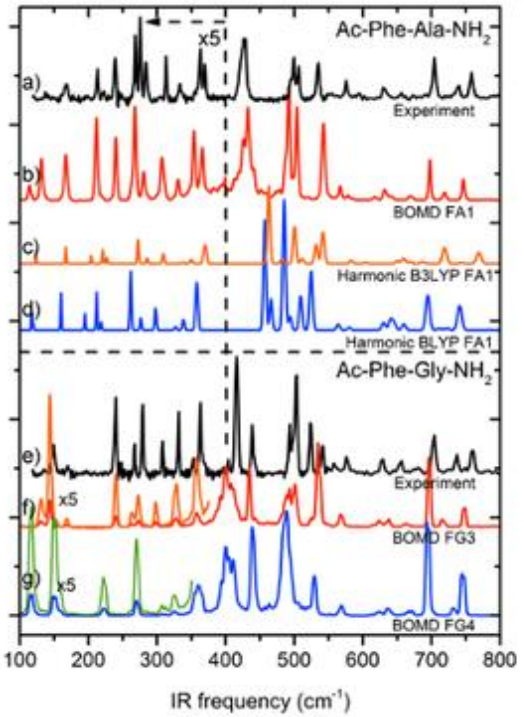
Far-IR Spectroscopy

Gas-Phase Peptide Structures Unraveled by Far-IR Spectroscopy: Combining IR-UV Ion-Dip Experiments with Born–Oppenheimer Molecular Dynamics Simulations**

Sander Jaeqx, Jos Oomens, Alvaro Cimas, Marie-Pierre Gaigeot, and Anouk M. Rijs**





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Ab initio molecular dynamics simulations of liquid water using high quality meta-GGA functionals†

Luis Ruiz Pestana,[a] Narbe Mardirossian,[b] Martin Head-Gordon[b] and Teresa Head-Gordon*[abc]

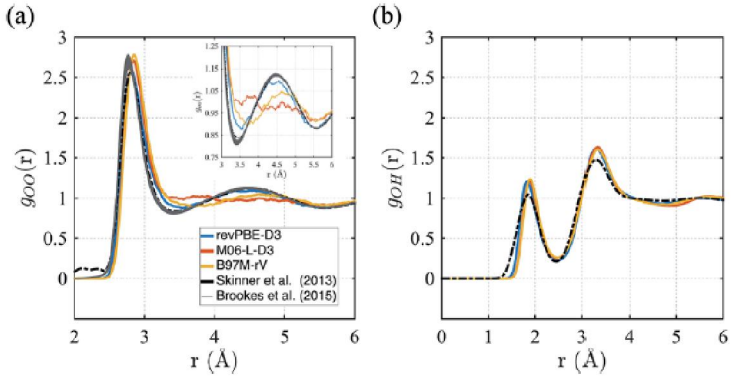

Fig. 1 Radial distribution functions for revPBE-D3, M06-L-D3, and B97M-rV compared to recent experimental results.[116,117] (a) $g_{OO}(r)$, the inset in panel (a) focuses on the region corresponding to the interstitial region and the 2nd hydration shell. (b) $g_{OH}(r)$.

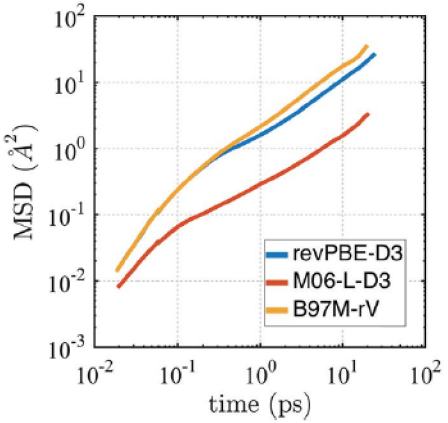

Fig. 4 Mean squared displacement (MSD) from AIMD simulations in the NVE ensemble for revPBE-D3, M06-L-D3, and B97M-rV on a log–log scale.

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Ligand binding to telomeric G-quadruplex DNA investigated by funnel-metadynamics simulations

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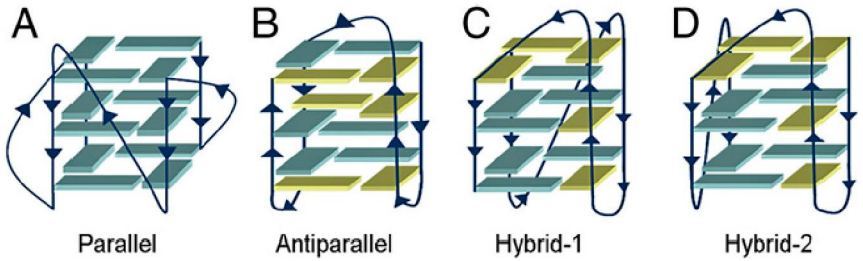

Fig. 1. Schematic representation of the human telomeric G4-DNA folding topologies. (*A*) Parallel or propeller type, as identified by X-ray in presence of K^+; (*B*) antiparallel or basket-like, as detected in Na^+ solution; (*C*) hybrid type 1 and (*D*) hybrid type 2, both found in K^+ solution. *Syn* and *anti* guanines glycosidic bond orientation are colored in yellow and cyan, respectively.

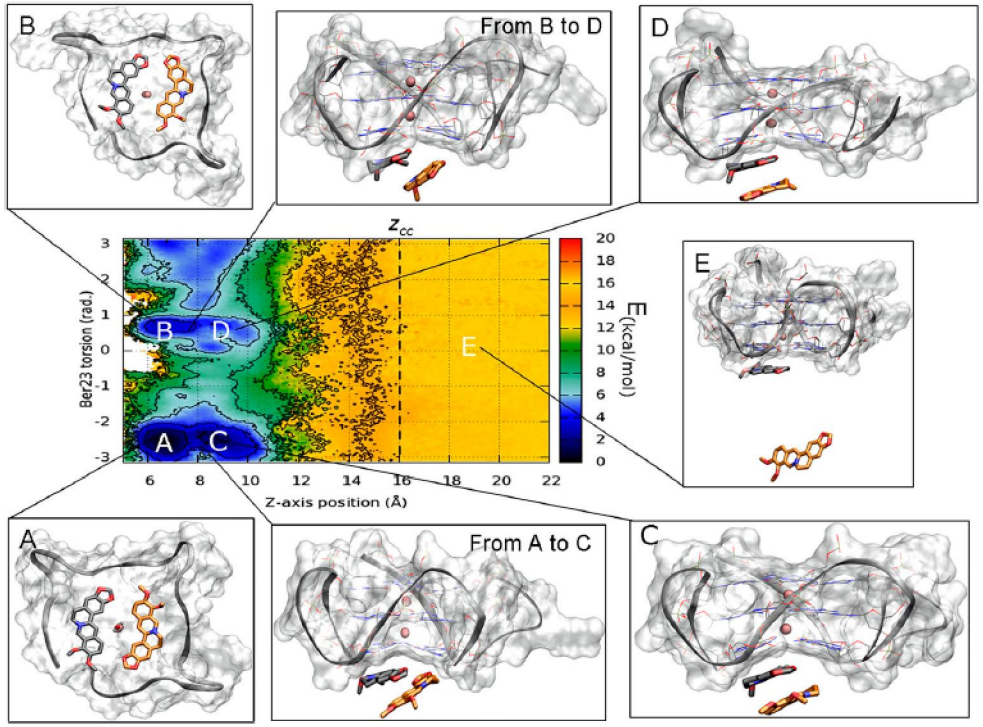

Fig. 6. The binding FES calculated using the reweighting algorithm as a function of Ber23 π (in radians) CV and the funnel *z*-axis position. Isosurfaces are shown every 2 kcal/mol. Beyond the minima (*A*) and (*B*), in which the simil X-Ray and the alternative conformations are respectively found, in this FES representation two further energy basins (*C*) and (*D*) appear, elucidating the binding mechanism of Ber23 to DNA. (*E*) Representation of one of the isoenergetic conformations found in the unbound state when $z_{cc} > 16$ Å. Here, the ligand has no contacts with the target and can assume a wide number of isoenergetic conformations. Ber25 and Ber26 are omitted for clarity.