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Introduction to Nanoscale Simulations - Part III

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

Introduction to Nanoscale Simulations

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Summary

- Density Functional Theory
- First Principles Molecular Dynamics
- Potential Energy Surfaces and Reaction Pathways
- Coarse Graining in Space and Time & other issues

Limitations of Molecular Dynamics simulations

First Principles Molecular Dynamics:

No. of atoms: < 300 Time span: < 50 ps

Computational cost ~ O(N^3)

Molecular Dynamics based on Classical Force Fields:

No. of atoms: < 10^7 Time span: < 1 μs

Computational cost ~O(N)

Coarse Graining in space and time is required to describe

phenomena that span larger time & space scales

This is common in materials simulation, even at the nanoscale

A possible way to overcome the limitations of atomistic dynamic approaches consists in adopting a kinetic approach

kinetic Monte Carlo

Continuous atomic dynamics is replaced by a **Markov** process consisting of a succession of hops with rates r_i, which must be known in advance

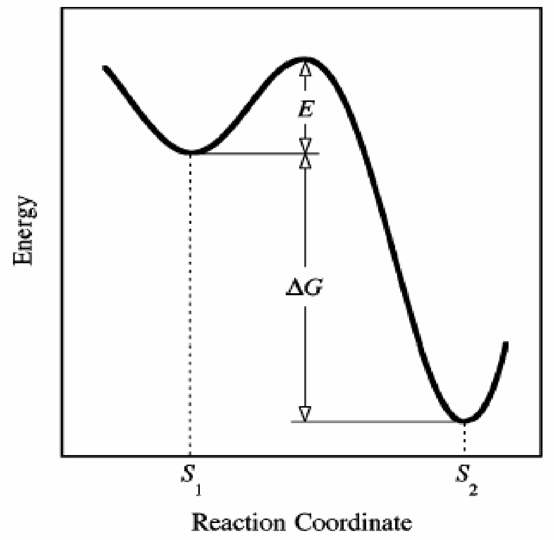


Figure 1 The energy curve for a transition between states S_1 and S_2.

$$r_i = \nu_i \exp(-E / k_B T)$$

$$\Gamma = \sum_i r_i$$

$$\frac{\sum_{j=1,i-1} r_j}{\Gamma} < \xi_1 \leq \frac{\sum_{j=1,i} r_j}{\Gamma} \qquad \Delta t = -\frac{\ln \xi_2}{\Gamma}$$

ξ_1 and ξ_2 are random numbers $\in (0,1)$

$$\langle \Delta t \rangle = -\frac{\langle \ln \xi_2 \rangle}{\Gamma} = \frac{1}{\Gamma}$$

The processes simulated by kMC can be modeled by rate or master equations that describe a continuous evolution (e.g. of chemical species)

Master equations are also useful in the quantum domain: consider for example an electron coupled to a heat bath that causes transitions between electronic states. Suppose that the coupling to the bath is weak so that the transitions can be described by Fermi's golden rule. The transition rates are:

$$W_{ij} = \frac{\pi}{\hbar} \left| \gamma_{ij} \right|^2 \delta(\varepsilon_i - \varepsilon_j)$$

Notice that the detailed dynamics of the transition is lost – like in the hops of classical kMC

A simple example: the Pauli Master equation

$$S = \sum_n |n\rangle\, p_n \,\langle n|$$

$$\dot{p}_n = \sum_{m \neq n} \left(W_{nm} p_m - W_{mn} p_n \right)$$

describes a Markovian kinetic evolution.

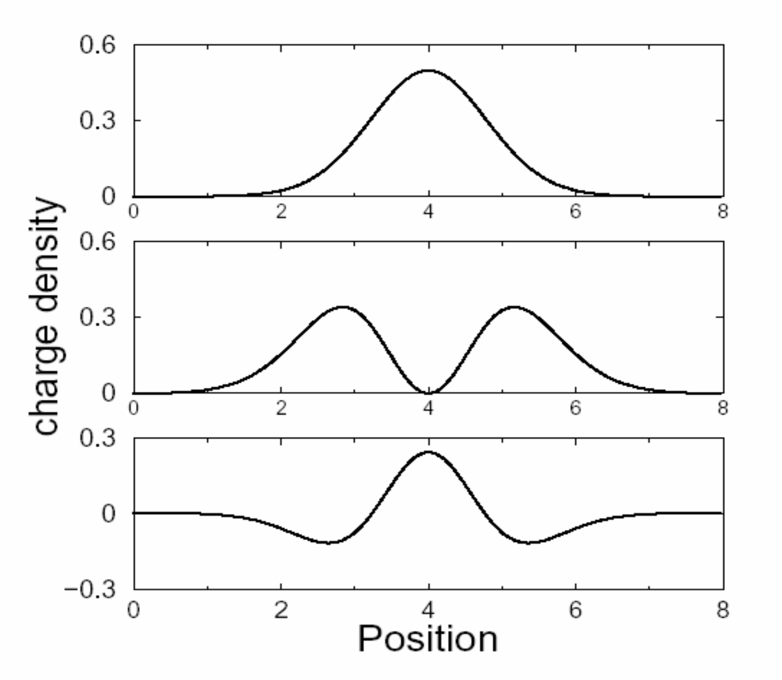
If $\dfrac{W_{nm}}{W_{mn}} = e^{-(\varepsilon_n - \varepsilon_m)/k_B T}$ (detailed balance), at equilibrium $p_n = C e^{-\varepsilon_n / k_B T}$

Coarse grained evolution: the time scale is fixed by the coupling matrix elements and has to satisfy:

$$\tau_c, \frac{1}{\varepsilon_n - \varepsilon_m} \ll t \ll \tau_R$$

A coarse graining paradox:

$$\dot{p}_m = \sum_{l \neq m} (W_{ml} p_l - W_{lm} p_m)$$



Starting from an initial non-equilibrium occupation of the eigenstates, the PME generates a redistribution among the eigenstates, and a corresponding charge density change, but *apparently* there is no current associated to this process because the eigenstates do *not* carry current

The paradox is only apparent, because if we know the Hamiltonian of the system and the coupling to the bath (which must be local), the current representing the charge flow due to the bath can be calculated:

$$j_B(x;t) = \lim_{t_0 \to t} \frac{1}{t - t_0} \int_{t_0}^{t} dt' \, j(x;t')$$

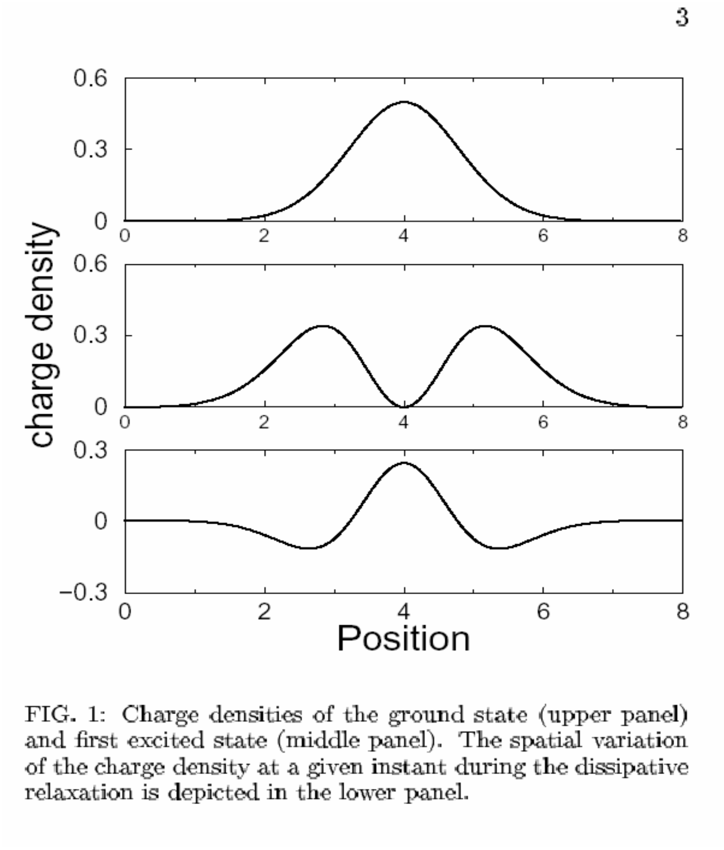


FIG. 1: Charge densities of the ground state (upper panel) and first excited state (middle panel). The spatial variation of the charge density at a given instant during the dissipative relaxation is depicted in the lower panel.

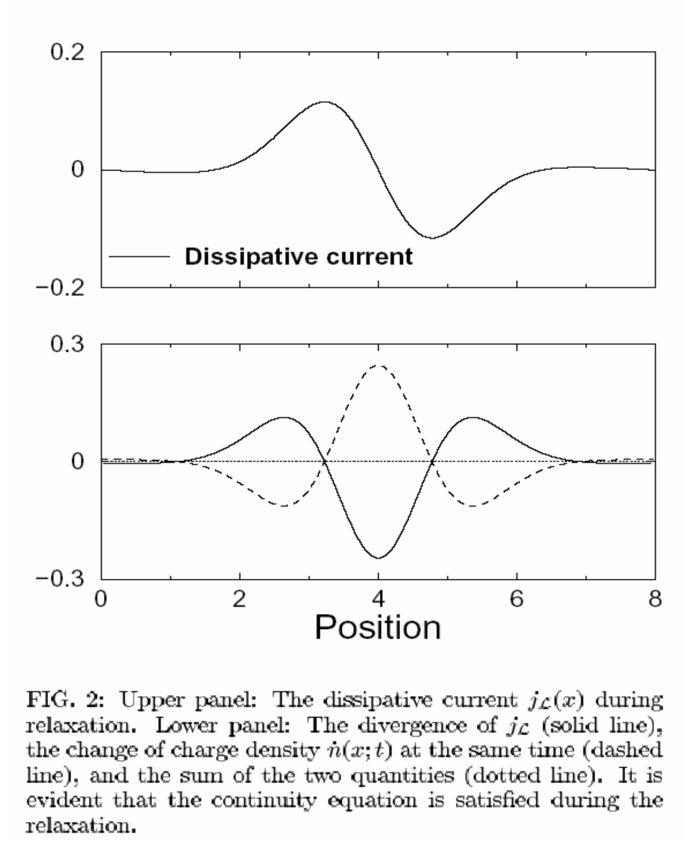


FIG. 2: Upper panel: The dissipative current $j_{\mathcal{L}}(x)$ during relaxation. Lower panel: The divergence of $j_{\mathcal{L}}$ (solid line), the change of charge density $\dot{n}(x;t)$ at the same time (dashed line), and the sum of the two quantities (dotted line). It is evident that the continuity equation is satisfied during the relaxation.

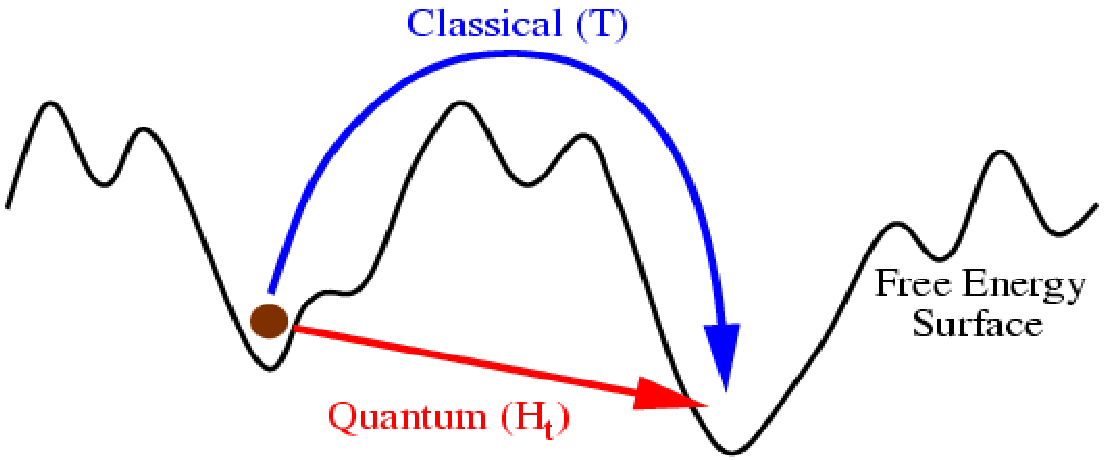
Continuity equation is satisfied exactly (within the numerical accuracy of the calculation). This has important implications in the study of quantum transport in presence of dissipative coupling.

Global Optimization

Natural Evolution, a long time-scale process, leads to global optimization

Can we achieve global optimization on a computer?

Two heuristic approaches to GO: Classical (thermal) and Quantum Annealing



Simulated Annealing (classical) : S.Kirkpatrick, C.D.Gelatt Jr, M.P. Vecchi, *Science* **220**, 671 (1983)

First QA paper (to my knowledge): A.B.Finnila, M.A.Gomez, C.Sebenik, C.Stenson, J.D.Doll, *Chem. Phys. Lett.* **219**, 343 (1994)

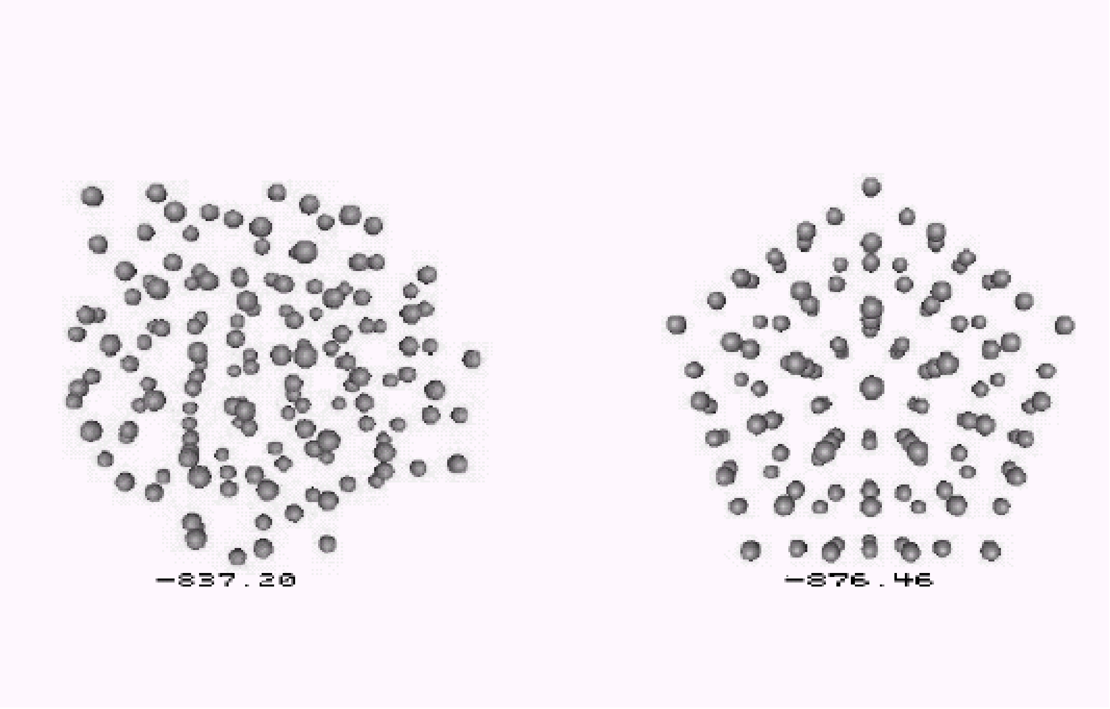
$$H = -\frac{\hbar^2}{2M}\sum_I \nabla_I^2 + \Phi(\{R_I\})$$

Using $\frac{\hbar^2}{2M}$ as an annealing parameter they found the global minimum of Lennard-Jones clusters with up to 19 atoms by Diffusion Quantum Monte Carlo

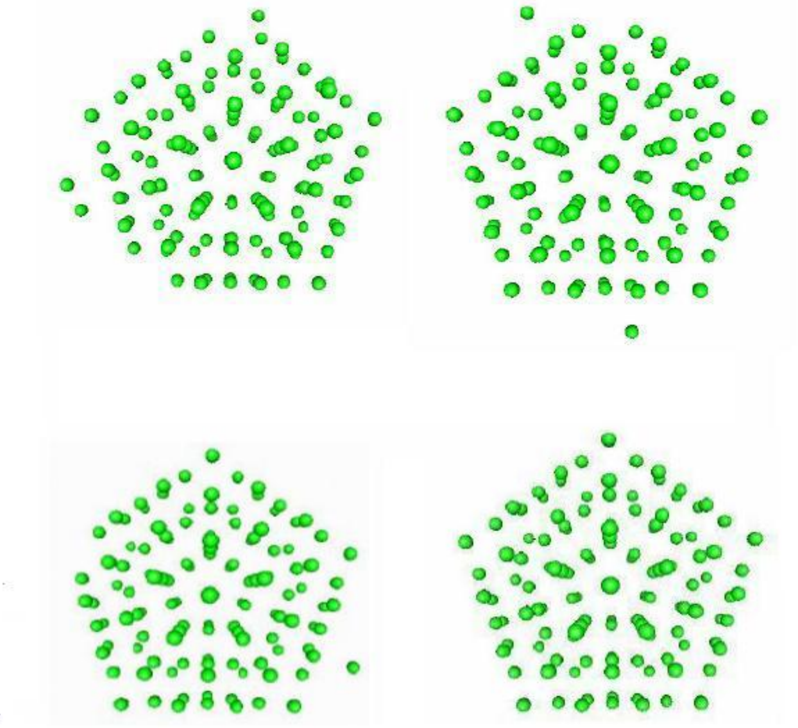
- For clusters with more than 20 atoms both SA and QA (with simple linear schedules) find increasingly difficult to reach the global minimum within practical annealing schedules

- By improving the procedure we were able to optimize significantly larger clusters (finding that QA is superior to CA)

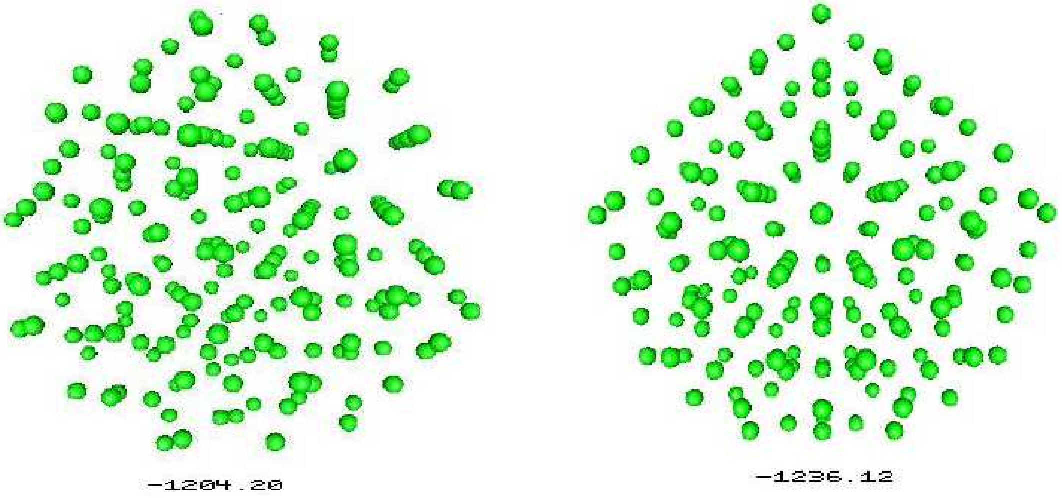
RPQA: initial (left) and final (right) structures for LJ147



RPQA: defects are successively eliminated by quantum tunneling



RPQA: a disordered (left) and the final (right) structures for LJ201



RPQA does not always work - for multifunnel potential energy surfaces the method is not able to avoid ergodicity breaking

Multifunnel potential energy surfaces occur for LJ clusters due to the competition between icosahedral and fcc growth sequences - while icosahedral motifs dominate the lowest energy minima of small LJ clusters exceptions occur for N=38 and N=75, 77 for instance

RPQA and sampling methods find the minimum of LJ38 but none of them is able to find the minimum of LJ75 (in a reasonable time)

- Quantum methods appear superior to classical methods for global optimization but both schemes fail due to loss of ergodicity

- It seems very difficult to overcome the difficulty posed by multifunnel surfaces by retaining the total energy as the only objective function (some way to bias fcc vs icosahedral nucleation seems necessary)

- In other words: in a maze when the search gets hard, you can get out only if you know at least approximately where to go

In order to better explore potential energy surfaces, searches must be biased by our incomplete knowledge of the system and by physical intuition.

A very powerful approach using a set of order parameters to bias the exploration of the PES has been recently proposed by Laio and Parrinello. This approach uses a non-Markovian evolution in order to refine the knowledge of the PES.