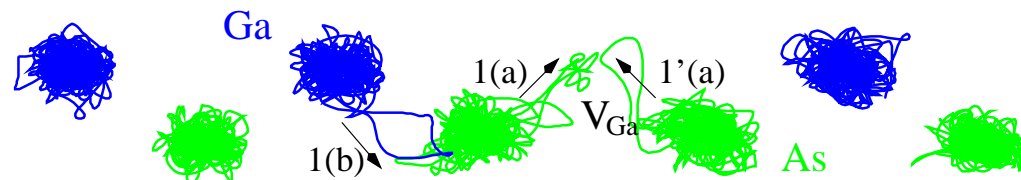


First Principles Molecular Dynamics

Michel Bockstedte

Lehrstuhl f. Theor. Festkörperphysik, Universität Erlangen-Nürnberg



Outline

First principles molecular dynamics: basic ideas

- Electrons, nuclei and the Born-Oppenheimer approximation
- First-principles molecular dynamics on the Born-Oppenheimer surface
- Car-Parrinello molecular dynamics of electrons and nuclei
- Statistical mechanics and molecular dynamics

Applications and special techniques in molecular dynamics

- Solvents: structure and electronic properties
- Phase transitions: thermodynamic quantities
- Diffusion in semiconductors: microscopic picture and transport coefficients

Born-Oppenheimer approximation revisited

Many particle Hamiltonian

$$\hat{H} = \underbrace{\frac{1}{2} \sum_I M_I \nabla_{\mathbf{R}_I}^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}_{\hat{H}_{\mathbf{R}}} + \underbrace{\frac{1}{2} \sum_i \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{ij} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}}_{\hat{H}_{\mathbf{r}}(\{\mathbf{R}\})}$$

Many particle wave function: $\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\})$

Adiabatic motion of electrons

- Mass of nuclei and electrons: $M_I/m_e \sim 1830$ (hydrogen) 10000 (semiconductors)
 \Rightarrow fast motion of electrons compared to nuclei
- Ansatz for Ψ reflects that electrons adiabatically follow the nuclei

$$\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_i\}) \approx \underbrace{\chi(\{\mathbf{R}_I\})}_{\text{nuclei}} \cdot \underbrace{\psi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})}_{\text{electrons}}$$

The Born-Oppenheimer surface

Schrödinger equations within the adiabatic approximation

$$\hat{H}_r(\{\mathbf{R}\}) \psi_\nu(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = E_\nu^e(\{\mathbf{R}_I\}) \psi_\nu(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

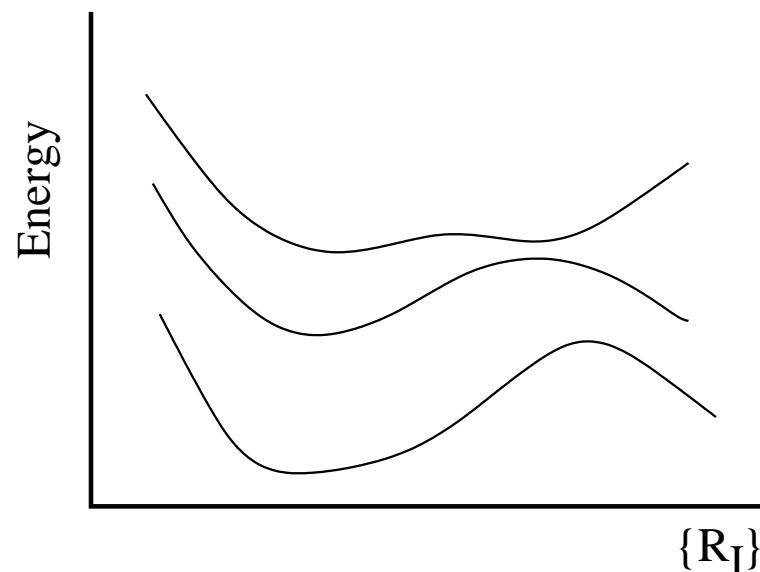
$$\psi_\nu \left\{ \hat{H}_R + E_\nu^e(\{\mathbf{R}_I\}) \right\} \chi_{\mu\nu}(\{\mathbf{R}_i\}) = \left\{ E_{\mu\nu} + \hat{H}_{na} \right\} \chi_{\mu\nu}(\{\mathbf{R}_I\}) \psi_\nu(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

in most cases the non-adiabatic coupling \hat{H}_{na} is negligible

Born-Oppenheimer surface

Potential energy surface of the nuclei

$$E_\nu^{\text{BO}}(\{\mathbf{R}_I\}) = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + E_\nu^e(\{\mathbf{R}_I\})$$



Molecular dynamics on the Born-Oppenheimer surface

First principles molecular dynamics

- Full quantum mechanical treatment of nuclei is expensive
- Nuclei are treated as classical particles
- Forces are obtained from the instantaneous many electron ground state
- Many electron ground state is described by density functional theory

Equations of motion

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial}{\partial \mathbf{R}_I} E_0^{\text{BO}}([n_0], \{\mathbf{R}_I\})$$

$$\hat{H}_{\text{KS}}(\{\mathbf{R}_I\}) \phi_i^{\text{KS}}(\mathbf{r}) = \varepsilon_i \phi_i^{\text{KS}}(\mathbf{r})$$

where $n_0(\mathbf{r}) = \sum_{i, \text{occ}} |\phi_i^{\text{KS}}(\mathbf{r})|^2$ and with $\int \phi_i^{\text{KS}}(\mathbf{r})^* \phi_j^{\text{KS}}(\mathbf{r}) d^3r = \delta_{ij}$

Literature:

- M. C. Payne, M. P. Teter, D. C. Allen, T. A. Arias and J. D. Joannopoulos, Rev. Mod.Phys., **64** (1992) 1045

Molecular dynamics on the Born-Oppenheimer surface

Constant of motion

$$E_{\text{tot}} = \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 + E_0^{\text{BO}}([n_0], \{\mathbf{R}_I\})$$

Forces between nuclei

$$F_I = -\frac{d}{d\mathbf{R}_I} E_0^{\text{BO}}([n_0], \{\mathbf{R}_i\}) = \underbrace{-\frac{\partial}{\partial \mathbf{R}_I} E_0^{\text{BO}}([n_0], \{\mathbf{R}_i\})}_{\mathbf{F}_I^{\text{HF}}} - \underbrace{\int d^3r \frac{\delta E_0^{\text{BO}}}{\delta n(\mathbf{r})} \frac{\partial n_0(\mathbf{r})}{\partial \mathbf{R}_I}}_{\mathbf{F}_I^{\text{Pulay}} + \mathbf{F}_I^{\text{Var}}}$$

- straight forward evaluation in plane wave basis set for semiconductors ($\mathbf{F}_I^{\text{Pulay}} = 0$)
- as $\mathbf{F}_I^{\text{Var}} \sim o(\delta n(\mathbf{r}))$, when $\delta E_0^{\text{BO}} \sim o(\delta n(\mathbf{r})^2)$ a high accuracy for $n(\mathbf{r})$ is needed.
- for metallic systems due to Fermi occupation additional forces appear (usually small if T_{el} is small), which are in most cases computationally expensive. When using F_I^{HF} alone $E_{\text{tot}} - \frac{1}{2}T_{\text{el}}S_{\text{el}}$ is the constant of motion.

Literature:

- F. Wagner, T. Laloyaux, and M. Scheffler, Phys. Rev. B, **57** (1998) 2102.

Molecular dynamics on the Born-Oppenheimer surface

Numerical task: solve the initial value problem for a system of Newtonian equations

Computational scheme

0. start with initial set of positions $\{\mathbf{R}_I(t_0)\}$ and velocities $\{\mathbf{V}_I(t_0)\}$

for each time $t_0 + n \delta t$ during the simulation

1. solve the Kohn-Sham equations for $\{\mathbf{R}_I(t_0 + (n - 1) \delta t)\}$ and calculate forces

2. integrate the equation of motion for nuclei to obtain $\{\mathbf{R}_I\}$ and $\{\mathbf{V}_I\}$ at $t_0 + n \delta t$

repeat 1. and 2. till the end of the simulation

Common integration schemes:

- Verlet algorithm and predictor-corrector schemes
- one evaluation of forces per time step δt is sufficient

Literature:

- M. P. Allen and D. J. Tildesley, Computer Simulations of Liquids, Clarendon Press, Oxford, 1987.
- M. E. Tuckerman *et al.*, J. Chem. Phys., **97** (1992) 1990.

Molecular dynamics on the Born-Oppenheimer surface

Verlet algorithm

$$\mathbf{R}_I(t + \delta t) = 2\mathbf{R}_I(t) - \mathbf{R}_I(t - \delta t) + \frac{\mathbf{F}_I(t)}{M_I} \delta t^2 + \mathcal{O}(\delta t^4)$$
$$\mathbf{V}_I(t) = \frac{3\mathbf{R}_I(t) - 4\mathbf{R}_I(t - \delta t) + \mathbf{R}_I(t - 2\delta t)}{2\delta t} + \mathcal{O}(\delta t^2)$$

obtained by Taylor series expansion of $\mathbf{R}_i(t + \delta t)$ and $\mathbf{R}_i(t - \delta t)$ at t .

Velocity Verlet algorithm

$$\mathbf{R}_I(t + \delta t) = \mathbf{R}_I(t) + \mathbf{V}_I(t) \delta t + \frac{\mathbf{F}_I(t)}{2 M_I} \delta t^2 \quad \text{and} \quad \mathbf{V}_I(t + \delta t) = \mathbf{V}_I(t) + \frac{\mathbf{F}_I(t)}{2 M_I} \delta t + \frac{\mathbf{F}_I(t + \delta t)}{2 M_I} \delta t$$

Properties of the Verlet algorithm:

- time reversible second order scheme
- for large time steps δt strong fluctuations in the constants of motion appear

Molecular dynamics on the Born-Oppenheimer surface in practice

Choosing the time step

Example: vibration of a As₂ dimer

As ₂						
$E_{cut} = 30\text{Ry}, \nu_{stat} = 12.225\text{THz}, a_0 = 3.969\text{ Bohr}$						
	Verlet			pc 4th./6th. order		
δt [period]	0.029	0.089	0.18	0.029	0.089	0.18
ν_{dyn} [THz]	12.16	12.29	$\sim 12.45?$	12.18	12.11	11.96

Trajectory as obtained with Verlet algorithm is less accurate for large time steps

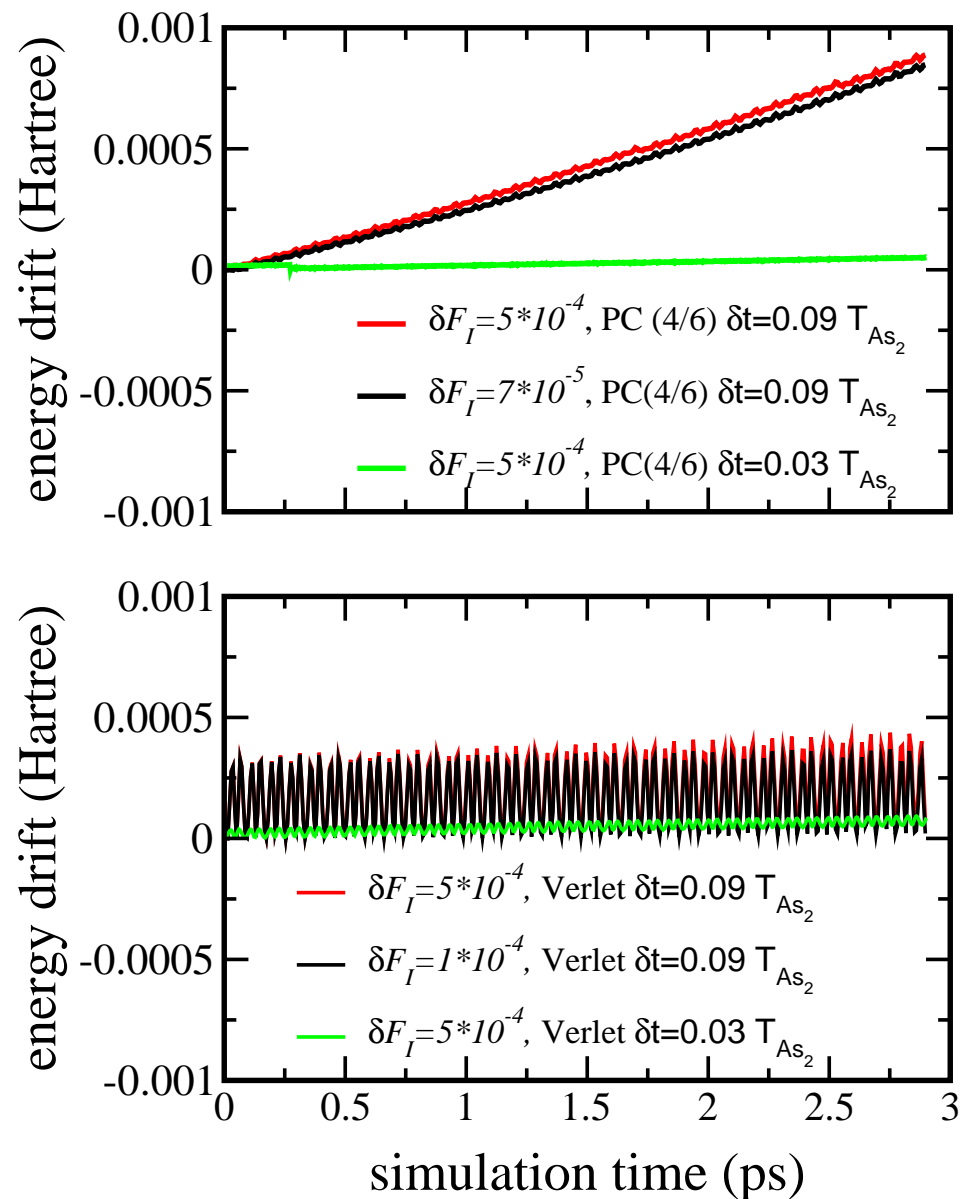
Efficiency vs. time step

As ₂ -dimer	Verlet			pc 4th./6th. order		
δt [period]	0.029	0.089	0.18	0.029	0.089	0.18
el.iter. /ionic step	12.4	13.3	13.9	19.6	29.4	32.2
el.iter/period	427.5	149.4	77.2	675.8	341.8	178.8

Molecular dynamics on the Born-Oppenheimer surface in practice

Drift in the constant of motion

- convergence of Forces $|\delta\mathbf{F}_I|/|\mathbf{F}_I|$
- time step δt
- behaviour of integration schemes
 - Verlet: fluctuations + small drift
 - Predictor-Corrector: drift only



Car-Parrinello molecular dynamics

Key idea

- Introduction of an artificial coupling between electrons and nuclei
- Kohn-Sham orbitals $\phi_i(\mathbf{r})$ are treated as classical degrees of freedom
- Kinetic energy of the new degrees is defined using an arbitrarily chosen mass μ

Extended lagrangian

$$\mathcal{L}_{\text{CP}} = \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 + \mu \sum_{i,\text{occ}} \int |\dot{\phi}_i^{\text{KS}}|^2 d^3r - E_{\text{KS}}([\{\phi_i^{\text{KS}}\}], \{\mathbf{R}_I\}) \\ + \sum_{i,\text{occ}} \Lambda_{ij} \left(\int \phi_i^{\text{KS}*} \phi_j^{\text{KS}} d^3r - \delta_{ij} \right)$$

orthogonality constraint: $\int \phi_i^{\text{KS}*} \phi_j^{\text{KS}} d^3r = \delta_{ij}$

Literature:

- D. K. Remler and P. A. Madden, Mol. Phys., **70** (1990) 921.
- G. Pastore, E. Samargiassi and F. Buda, Phys. Rev. A, **44** (1991) 6334.

Car-Parrinello molecular dynamics: equations of motion

Equations of motion

$$M_I \ddot{\mathbf{R}}_I = - \underbrace{\frac{\partial E_{\text{KS}}([\{\phi_i^{\text{KS}}\}], \{\mathbf{R}_I\})}{\partial \mathbf{R}_I}}_{\mathbf{F}_I^{\text{HF}}} \quad \text{and} \quad \mu \ddot{\phi}_i^{\text{KS}} = - \underbrace{\frac{\partial E_{\text{KS}}([\{\phi_i^{\text{KS}}\}], \{\mathbf{R}_I\})}{\partial \phi_i^{\text{KS}}}}_{\hat{H}_{\text{KS}} \phi_i^{\text{KS}}(\mathbf{r})} - \sum_{j, \text{occ}} \Lambda_{ij} \phi_j^{\text{KS}}$$

Constant of motion in CP dynamics

$$E_{\text{const}} = \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 + \underbrace{\mu \sum_{i, \text{occ}} \int |\dot{\phi}_i^{\text{KS}}|^2 d^3r}_{\text{additional kinetic energy}} + E_{\text{KS}}([\{\phi_i^{\text{KS}}\}], \{\mathbf{R}_I\})$$

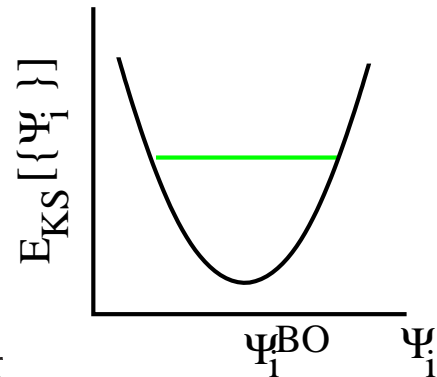
Idea:

- for small μ adiabatic decoupling is achieved \Rightarrow true MD trajectories are obtained

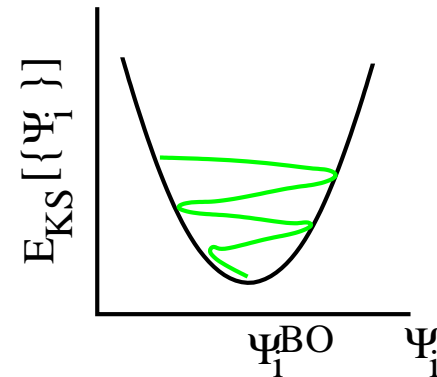
Car-Parrinello molecular dynamics: interpretation

Interpretation of CP molecular dynamics

assume nuclei are at rest, i.e. $\ddot{\mathbf{R}}_I = 0$



no damping



with damping

Full dynamics

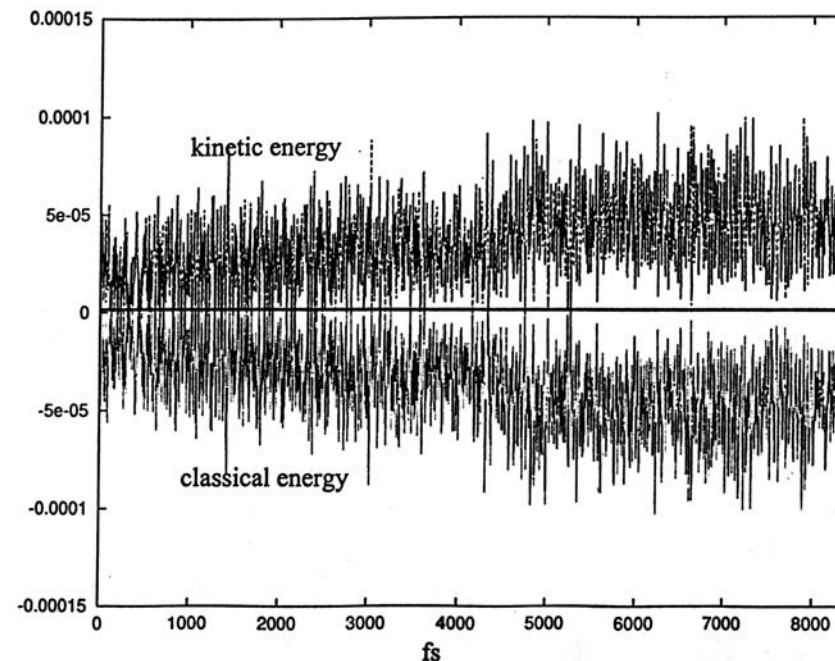
Evolution of

$$\mu \sum_{i, \text{occ}} \int |\dot{\phi}_i^{\text{KS}}|^2 d^3r$$

and

$$\frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 + E_{\text{KS}}([\{\phi_i^{\text{KS}}\}], \{\mathbf{R}_I\})$$

Classical and fictitious kinetic energy



Car-Parrinello molecular dynamics: adiabaticity

Restrictions for mass μ

- Oscillatory motion of Kohn-Sham orbitals is given by μ and ε_{Gap} (adiabatic limit)

$$\omega_{\phi_i^{\text{KS}}} \leq \sqrt{\frac{\varepsilon_{\text{Gap}}}{\mu}}$$

ε_{Gap} is the Kohn-Sham energy gap between highest occupied and lowest unoccupied state

- Adiabatic decoupling between nuclei and Kohn-Sham orbitals
 - Electrons are close to the BO-surface:

$$\mu \sum_{i,\text{occ}} \int |\dot{\phi}_i^{\text{KS}}|^2 d^3r \ll \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 + E_{\text{KS}} \left(\left[\left\{ \phi_i^{\text{KS}} \right\} \right], \left\{ \mathbf{R}_I \right\} \right)$$

- Kohn-Sham orbitals should oscillate faster than nuclei (phonons)

$$\omega_{\phi_i^{\text{KS}}} > \omega_{\text{nuclei}}$$

- No energy transfer between nuclei and Kohn-Sham orbitals:

$$\mu \sum_{i,\text{occ}} \int |\dot{\phi}_i^{\text{KS}}|^2 d^3r \sim \text{const}$$

Car-Parrinello molecular dynamics in practice

- choice of the time step:

Systems with a large energy gap ε_{gap} allow for a larger mass μ and time step

$$\Delta t \sim 1/\omega_{\phi_i^{\text{KS}}} \sim \sqrt{\mu/\varepsilon_{\text{Gap}}}$$

- Low drift in constants of motion:

oscillatory motion of electrons allows for a small drift in E_{CP} .

- system with a small gap:

A small gap requires a small mass μ and hence a small time step

However, a failure in adiabaticity is reduced by thermostats (P. Blöchl and M. Parrinello Phys. Rev. B, **45**).

- Metallic systems:

Kohn-Sham orbitals $\{\phi_i^{\text{KS}}\}$ do not correspond to eigenstates, hence occupation by a Fermi-distribution is not suitable.

Comparing the first principles approaches

Molecular dynamics on the Born-Oppenheimer surface

- + efficient as it allows for a large time step
- + no additional parameters to guarantee adiabaticity
- + efficient even for small gap systems, metallic systems
 - drift in the constant of motion (i.e. E_{tot})
 - inefficient, when convergence is an issue

Car-Parrinello molecular dynamics

- + negligible drift in the constants of motion
- + efficient when force evaluation is inexpensive
 - less suited for metallic systems
 - inefficient for small gap systems and when level crossings occur

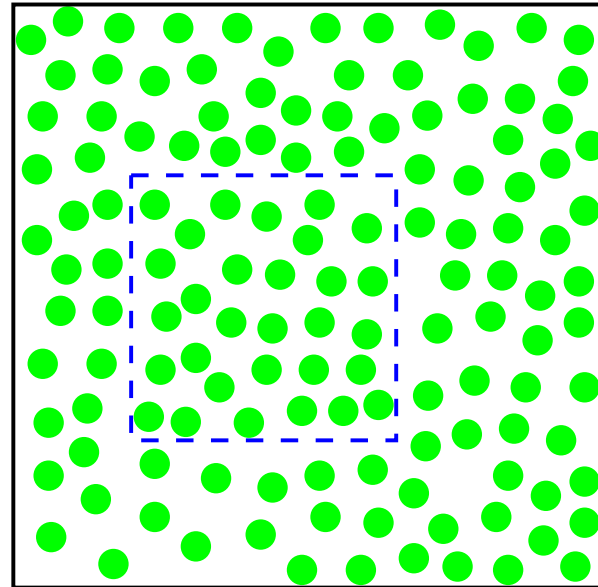
The Nosé-Hoover thermostat

Microcanonical ensemble

- * closed system
- * constant energy

Canonical ensemble

- * energy exchange with a reservoir
- * constant temperature



Small systems:

- microcanonical ensemble averages \neq canonical ensemble averages

Nosé-Hoover thermostat:

- allows for simulations within the canonical ensemble
- corrects for a drift in the energy as a side effect

Nosé-Hoover thermostat: The extended system

Additional degree of freedom x_R simulates heat bath:

$$M_I \frac{d^2}{dt^2} \mathbf{R}_I = - \frac{\partial}{\partial \mathbf{R}_I} E_0(\{\mathbf{R}_J\}_N) - M_I \mathbf{V}_I \frac{d}{dt} x_R$$

$$Q \frac{d^2}{dt^2} x_R = \sum_I M_I \mathbf{V}_I^2 - g k_B T_{\text{ext}}$$

and the constant of motion

$$E'_{\text{tot}} = \underbrace{\sum_I \frac{1}{2} M_I \mathbf{V}_I^2 + E_0(\{\mathbf{R}_J\}_N)}_{E_{\text{tot}}} + \frac{1}{2} Q \left(\frac{d}{dt} x_R \right)^2 + g k_B T_{\text{ext}} x_R$$

- Nosé-Hoover thermostat simulates a canonical ensemble
- Choice for the extended system is unique
- Thermostat parameters Q (thermostat mass) and $g = 3N$ (degrees of freedom)

Literature:

- S. Nosé, J. Chem Phys., **81** (1984) 511.
- W.G. Hoover, Phys. Rev. A, **31** (1985) 1695.

Statistical averages from the ergodic hypothesis

Calculation of averages (Ergodic hypothesis):

$$\begin{aligned}\langle A(\{\mathbf{P}_I, \mathbf{R}_I\}_N) \rangle &= \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau A(\{\mathbf{P}_I(t), \mathbf{R}_I(t)\}_N) dt \\ &\approx \frac{1}{\tilde{\tau}} \int_0^{\tilde{\tau}} A(\{\mathbf{P}_I(t), \mathbf{R}_I(t)\}_N) dt\end{aligned}$$

for a sufficiently long simulation time $\tilde{\tau}$.

Example: Average kinetic energy and higher order moments:

$$\langle E_{\text{kin}} \rangle = \left\langle \sum_I \frac{M_I}{2} \mathbf{v}_I^2 \right\rangle = \frac{3N}{2} k_B T \quad \text{and} \quad \langle E_{\text{kin}}^m \rangle_C = \langle (E_{\text{kin}} - \langle E_{\text{kin}} \rangle)^m \rangle = \frac{3N}{2} (k_B T)^m$$

used to test the choice of the thermostat mass Q and the simulation time $\tilde{\tau}$

The thermostat mass Q

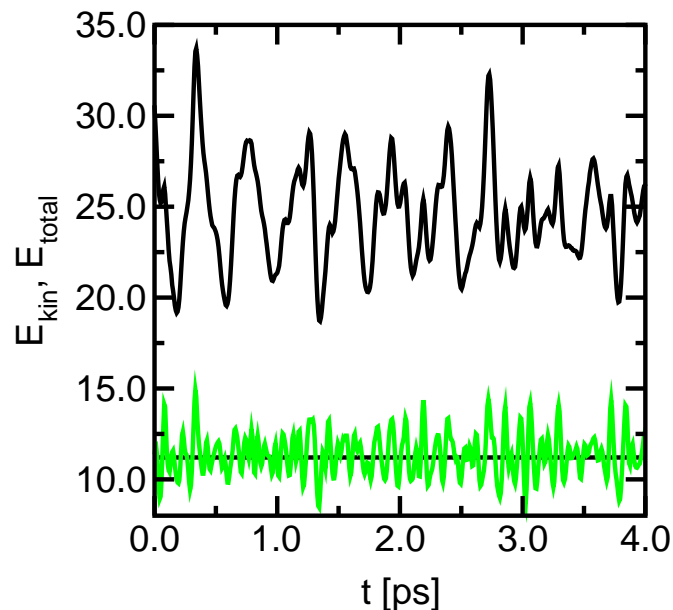
- Q determines motion of the thermostat and coupling to the system
- characteristic time in the weak coupling:

$$\tau = 2\pi \sqrt{\frac{Q}{6N k_B T}}$$

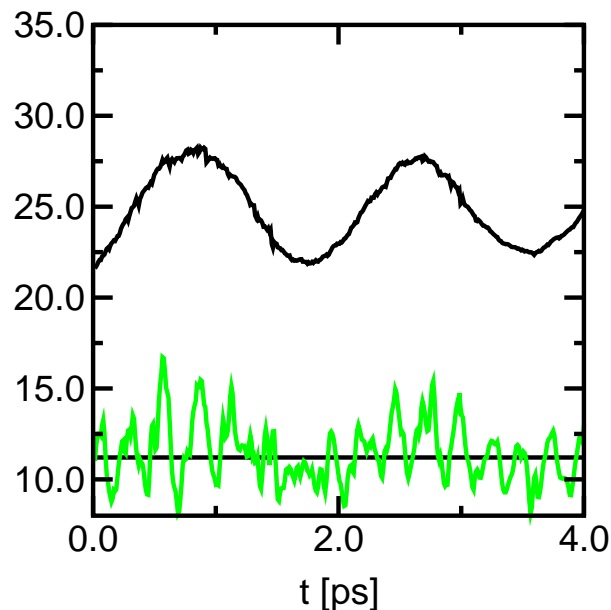
Example: GaAs 64 atoms at $T=1400$ K

phonon time scale: $\nu_{\text{TO}} = 8.8$ THz \rightarrow 0.1 ps and $\nu_{\text{X,TA}} = 2.5$ THz \rightarrow 0.4 ps

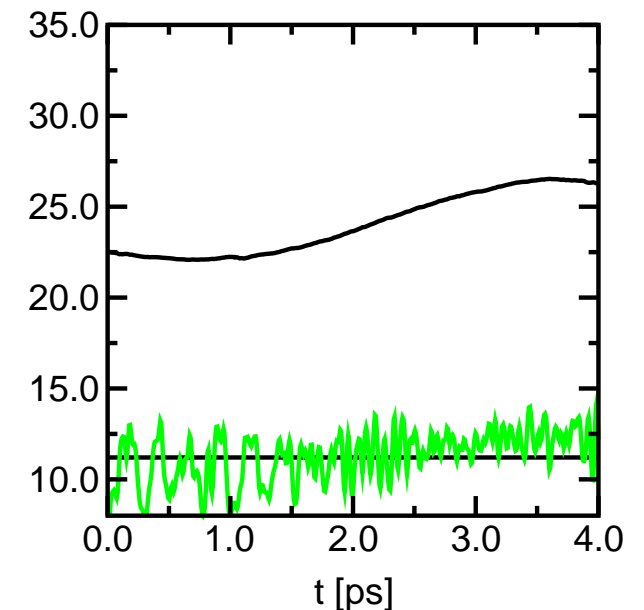
Simulations for different Q :



$Q = 10^7 a.u.$ $\tau = 0.3$ ps



$Q = 10^8 a.u.$ $\tau = 2.5$ ps



$Q = 10^9 a.u.$ $\tau = 7.9$ ps

Statistical ensemble techniques: overview

General approach

- additional degrees of freedom simulate heat bath or applied pressure
- modified equations of motion are solved for given external variables
- thermodynamic quantities in the desired ensemble are obtained from time averages
- but: actual trajectories are only relevant on a time scale below the interaction time with additional degrees of freedom

Examples:

- constant pressure dynamics: H. C. Andersen, J. Chem. Phys., **72** (1980) 2384.
- Parrinello-Rahman method: M. Parrinello and A. Rahman, Phys. Rev. Lett., **45** (1980) 1196.
- canonical ensemble: Nosé-Hoover thermostat

Application of Molecular dynamics

Applications

- Structural properties of liquids
- Phase transitions
- Diffusion in semiconductors

Special simulation techniques

- Spatial and time correlation functions
- Free energies and thermodynamic integration
- Rare events and the blue moon ensemble

Example: Structure and properties of liquids

Water above the critical point

(M. Boreo *et al.* Phys. Rev. Lett., **85** (2000) 3245)

Critical point:

$$T = 647 \text{ K} \quad P = 22.1 \text{ MPa} \quad \text{and} \quad \rho = 0.32 \text{ g/cm}^3$$

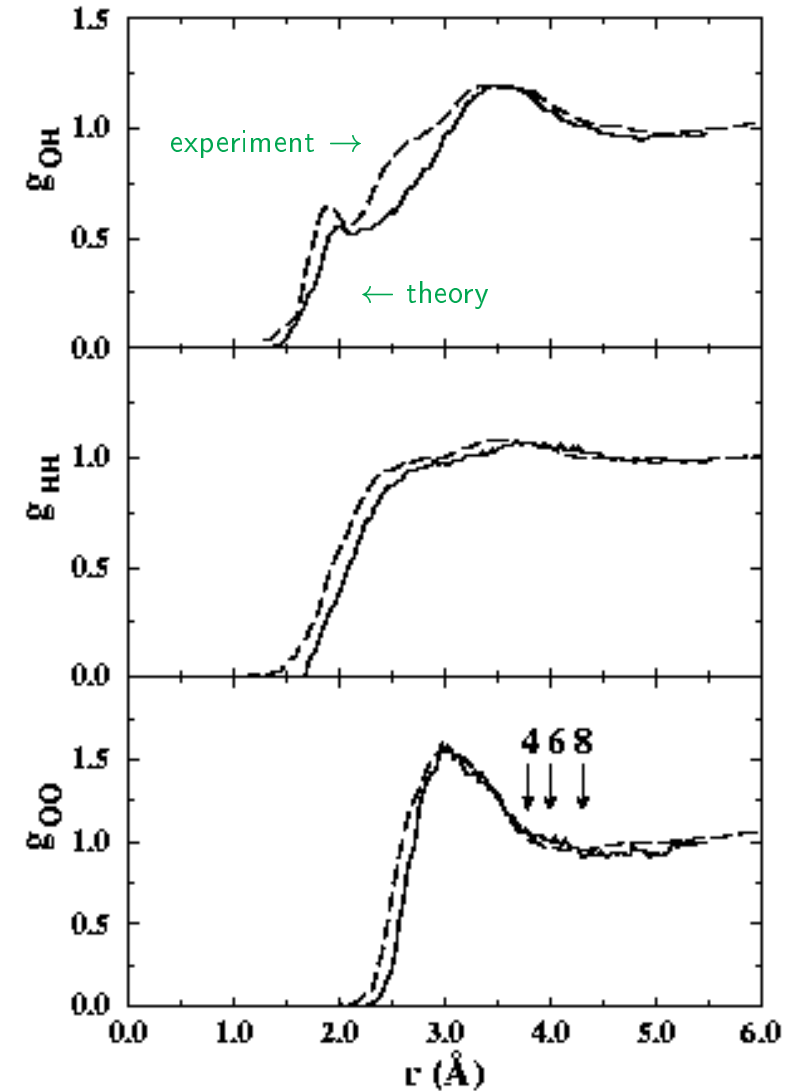
Structure

- pair correlation function

$$g(r) = \frac{1}{\rho N} \int \langle n(\tilde{\mathbf{r}}) n(\mathbf{r} - \tilde{\mathbf{r}}) \rangle d^3 \tilde{\mathbf{r}}$$

- Coordination number

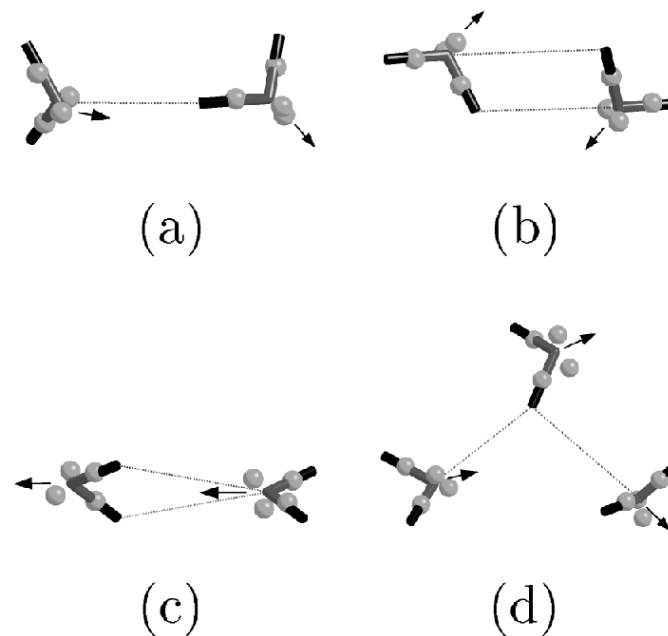
$$N_c = 4\pi \int_0^{r_{\min}} g(r) r^2 dr$$



Example: Structure and properties of liquids

Local bonding

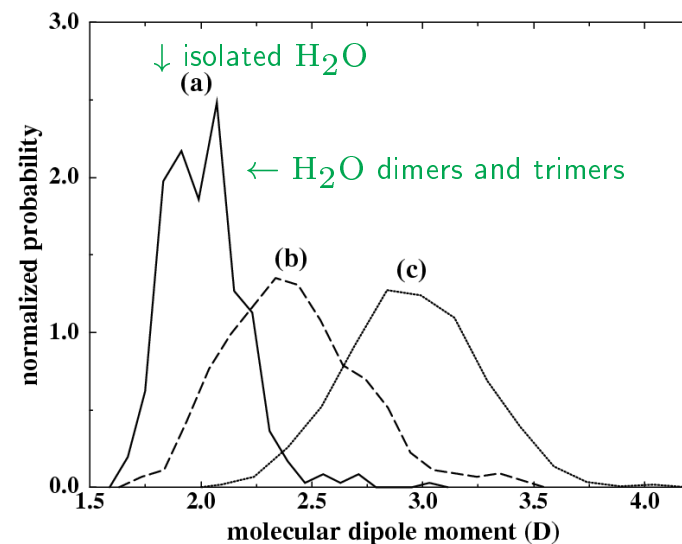
- Liquid water: only linear H bonds (a) form
- sc water: a large fraction of unbonded molecules
- 1%-3% of H bonds are of type (b)-(d)



Distribution of dipole moments

local dipole moments are calculated by maximally localised Wannier function and Wannier function centres technique (N. Mazari and D. Vanderbilt, Phys. Rev. B, **56** (1997) 12847)

- (a) $\rho = 0.32 \text{ g/cm}^3$
(b) $\rho = 0.73 \text{ g/cm}^3$
(c) liquid water



Example: Structure and properties of liquids

IR-spectra of liquid water

(P. L. Silvestrelli *et al.* Chem. Phys. Lett., **277** (1997) 478)

Infrared adsorbtion coefficient

$$\alpha(\omega) = \frac{4\pi \tanh(\hbar\omega/2kT)}{3\hbar n(\omega) c V} \int dt \exp(-i\omega t) \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle$$

where \mathbf{M} is the total dipole moment, $n(\omega)$ the refractive index, c the speed of light and V is the volume.

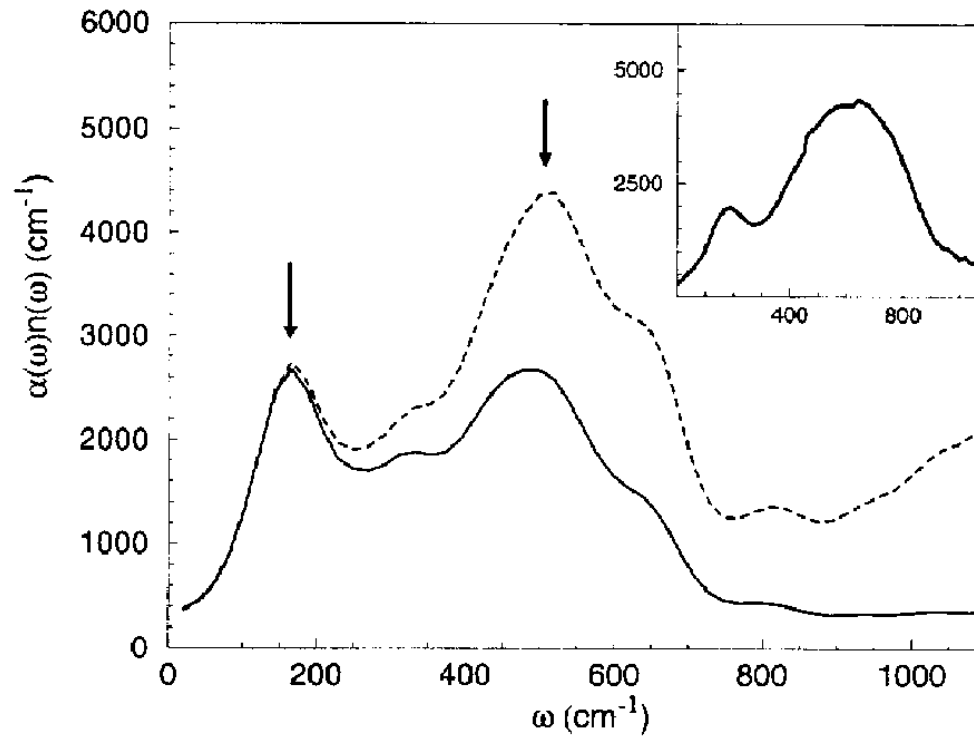
Electronic contribution to dipole moment from berry phase R. D. King-Smith and D. Vanderbilt, Phys. Rev. B, **47** (1993) 1651

$$M_i^{\text{el}} = \frac{2|e|}{|\mathbf{b}_i|} \phi(\mathbf{b}_i) \quad \text{with} \quad \phi(\mathbf{b}_i) = \Im \ln \det S \quad \text{and} \quad S_{mn} = \langle \psi_m | \exp -i\mathbf{b}_i \cdot \mathbf{r} | \psi_n \rangle$$

where \mathbf{b}_i are the reciprocal basis vectors and $i = 1, 2, 3$

Example: Structure and properties of liquids

Calculated IR-spectrum



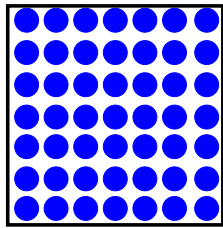
Example: First order phase transition

Melting of silicon

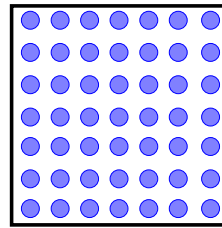
(O. Sugino and R. Car, Phys. Rev. Lett., **74** (1995) 1823)

First order phase transition occurs if chemical potentials coincide

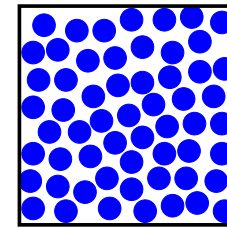
$$\Delta\mu_{\text{solid}}(T, P) = \Delta\mu_{\text{liquid}}(T, P)$$



solid



reservoir



liquid

Task:

$$\mu \sim -kT \ln \int d\mathbf{Q} d\mathbf{P} \exp(-H/kT)$$

Thermodynamic integration:

$$H(\lambda) = \lambda H_1 + (1 - \lambda) H_{\text{reservoir}}$$

$$\Delta\mu = \int_0^1 \frac{\partial\mu}{\partial\lambda} d\lambda = \int_0^1 \left\langle \frac{\partial H(\lambda)}{\partial\lambda} \right\rangle_{\lambda} d\lambda = \int_0^1 \langle H_1 - H_{\text{reservoir}} \rangle_{\lambda} d\lambda$$

Example: First order phase transition

Calculated properties of the phase transition

- simulation in a canonical ensemble with constant pressure (Nosé-Hoover and Andersen techniques)
- ensemble averages are obtained as time averages by slowly switching from $\lambda = 0$ to $\lambda = 1$

$$\Delta\mu = \frac{1}{T} \int_0^T (H_1 - H_{\text{reservoir}}) \frac{d\lambda}{dt} dt$$

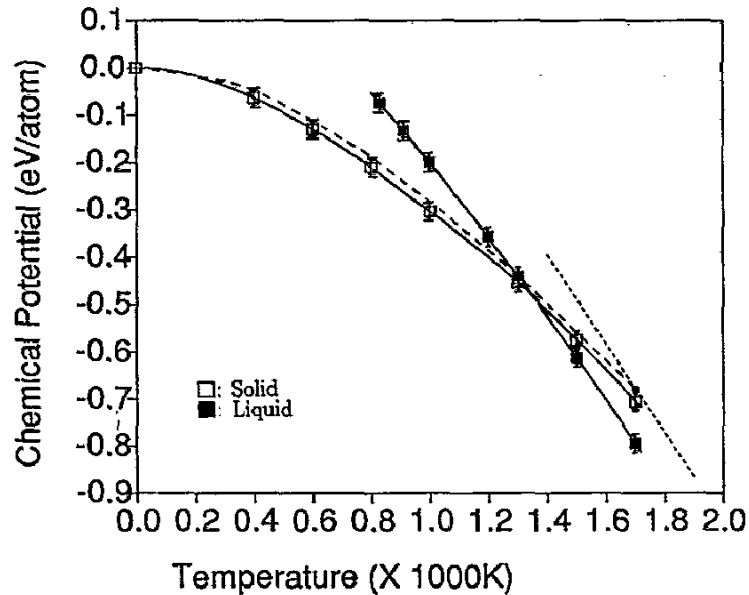


TABLE I. Thermodynamic properties at the theoretical and at the experimental melting point.

	This work (LDA)	Experiment
T_m (K)	$1.35(10) \times 10^3$	$1.685(2) \times 10^3$ ^a
S_s	$6.9(1)k_B$	$7.4k_B$ ^b
S_l	$9.9(2)k_B$	$11.0k_B$ ^b , $10.7k_B$ ^c
H_s (eV/atom)	$H_s(0 \text{ K}) + 0.33(2)$	$H_s(0 \text{ K}) + 0.41$ ^b
ΔH_{sl} (eV/atom)	0.35(2)	0.52 ^b , 0.47 ^c
C_s (eV/K atom)	$3.0(4) \times 10^{-4}$	3.03×10^{-4} ^d
C_l (eV/K atom)	$2.7(4) \times 10^{-4}$	3.03×10^{-4} ^d
V_s [(a.u.) ³ /atom]	$1.350(5) \times 10^2$	1.380×10^2 ^a
$\Delta V/V_s$	10(1)%	11.9% ^c , 9.5% ^c
α_s (K ⁻¹)	$0.3(1) \times 10^{-5}$	0.44×10^{-5} ^a
α_l (K ⁻¹)	$4.8(5) \times 10^{-5}$	5.2×10^{-5} ^d
dT_m/dp (K/GPa)	-50(5)	-38 ^a

^aRef. [23].

^bRef. [24].

^cRef. [25].

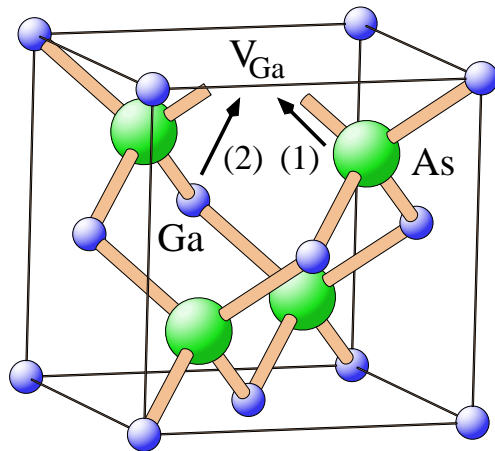
^dFrom Ref. [4].

^eRef. [26].

Example: Diffusion in semiconductors

Gallium self diffusion mediated by vacancies

(M. Bockstedte and M. Scheffler, Z. Phys. Chem., **200** (1997) 195)

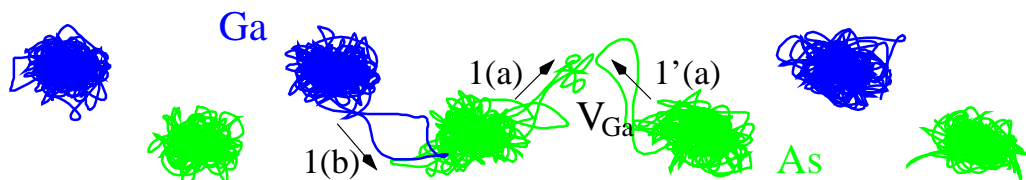


Microscopic picture of diffusion:

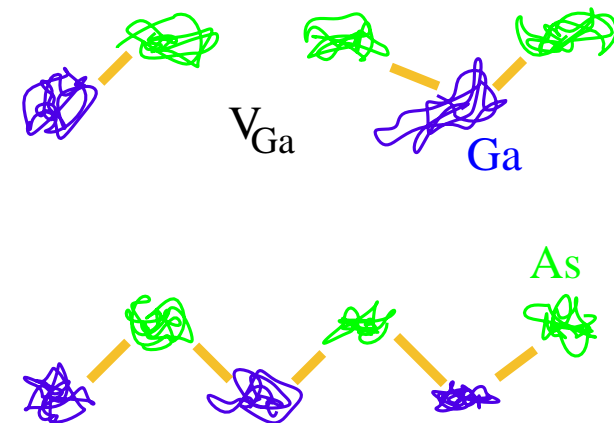
- Mechanism of vacancy diffusion
 - (1) nearest-neighbour hops
 - (2) second-nearest-neighbour hops
- Contribution to the gallium self diffusion

Molecular dynamics simulations ($T=1700$ K)

(1) nearest-neighbour hops



(2) attempted second-nearest-neighbour hop

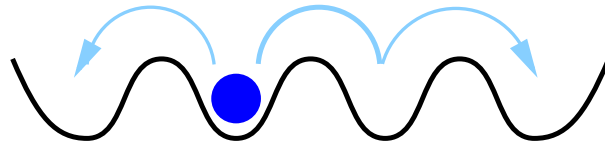


Example: Diffusion in semiconductors

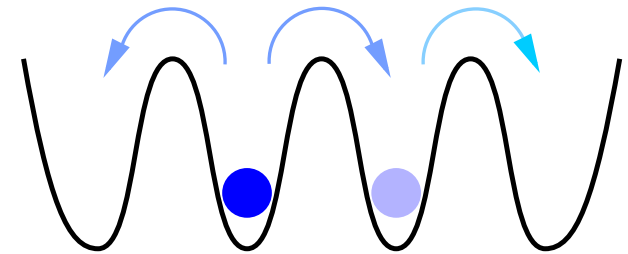
Diffusion and rate processes

Migration barrier E_m determines timescale of diffusion:

$$E_m < 4k_B T$$



$$E_m \sim 10 k_B T$$



Diffusion constant:

$$D = \frac{1}{6t} \langle (\mathbf{R}(t) - \mathbf{R}_0)^2 \rangle$$

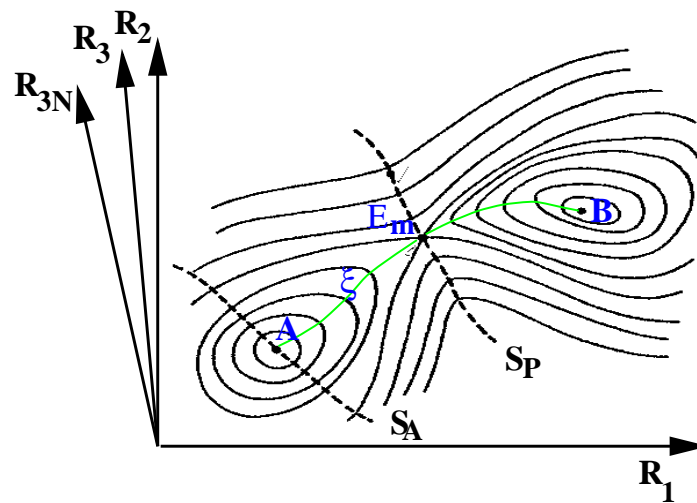
for a large simulation time t

$$D = \frac{1}{6} n \Gamma d^2$$

with the hopping rate $\Gamma \sim e^{-\frac{E_m}{k_B T}}$

Example: Diffusion in semiconductors

Reaction coordinates and potential energy surfaces



- potential energy surface depends on many coordinates $\{R_i\}_N$
- only a few coordinates describe the hop

Reaction coordinate ξ (c.f. C H Bennett 1975 and 1977):

- reaction coordinate determines the migration path

$$R_i(A) = R(\xi_A) \quad \text{and} \quad R_i(B) = R(\xi_B)$$

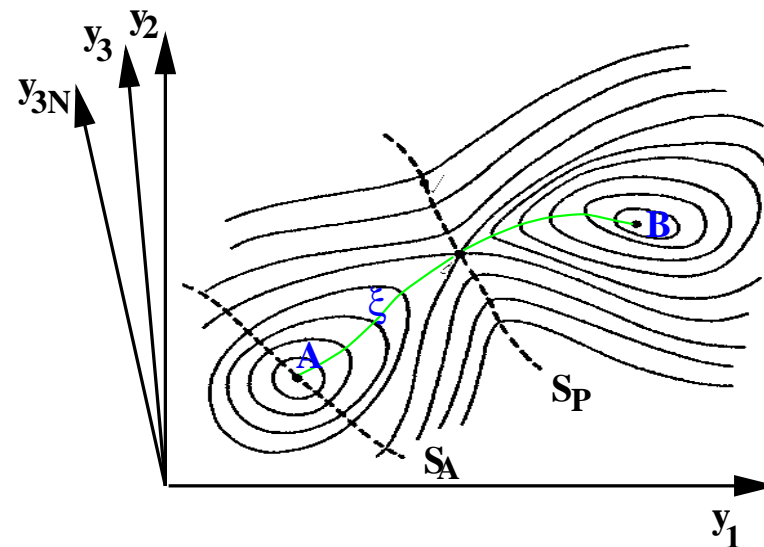
- potential energy has a local minimum for each value of ξ is at the path

$$E(\xi) = \min_{\{R_i\}_N, \xi=const.} E(\{R_i\}_N)$$

Example: Diffusion in semiconductors

Transition state theory (Vineyard 1957):

$$\Gamma_{\text{TST}} = \frac{I_{A \rightarrow B}}{Q_A} = \sqrt{\frac{k_B T}{2\pi}} \frac{\int_{S_P} e^{-\frac{U(\{\mathbf{R}_i\})}{k_B T}} dS}{\int_A e^{-\frac{U(\{\mathbf{R}_i\})}{k_B T}} d^{3N} R}$$



Blue moon ensemble for the calculation of rare events (Carter et al 1989):

- probability density $P(\xi) = \langle \delta(\xi - \xi^\dagger) \rangle$ is the key quantity:

$$P(\xi) = \langle \delta(\xi - \xi^\dagger) \rangle = C \exp\left(-\frac{V(\xi)}{k_B T}\right) \quad \text{and} \quad \int P(\xi) d\xi = 1$$

- $P(\xi)$ and $V(\xi)$ do not represent an ensemble average, but

$$\frac{\partial}{\partial \xi} V(\xi) = -k_B T \frac{\partial}{\partial \xi} \langle \delta(\xi - \xi^\dagger) \rangle = \frac{\langle (\partial E(\xi, \{\mathbf{R}, \mathbf{V}\}) / \partial \xi - k_B T \partial \ln |J| / \partial \xi) \delta(\xi - \xi^\dagger) \rangle}{\langle \delta(\xi - \xi^\dagger) \rangle}$$

Example: Diffusion in semiconductors

Blue Moon Ensemble for Calculation of Rare Events

- $P(\xi)$ and $V(\xi)$ are calculated from $\partial V(\xi)/\partial \xi$ by integration
- Evaluate $\partial V(\xi)/\partial \xi$ by molecular dynamics with constraint:
Problem: constraint $\delta(\xi - \xi^\dagger)$ implies $\partial \xi / \partial t = 0$
Solution: introduce statistical weights to exactly compensate for $\partial \xi / \partial t = 0$

$$\frac{\langle A(\xi, \{\mathbf{R}, \mathbf{V}\}) \delta(\xi - \xi^\dagger) \rangle}{\langle \delta(\xi - \xi^\dagger) \rangle} = \frac{\langle |\mathbf{Z}|^{-\frac{1}{2}} A(\xi, \{\mathbf{R}_i, \mathbf{V}_i\}) \rangle_{\xi^\dagger}}{\langle |\mathbf{Z}|^{-\frac{1}{2}} \rangle_{\xi^\dagger}}$$

Statistical weights $|\mathbf{Z}|$: $|\mathbf{Z}| = \sum_i \frac{1}{M_i} |\partial \xi / \partial \mathbf{R}_i|^2$

Example: Diffusion in semiconductors

Gallium self-diffusion constant

$$D_{\text{Ga}} = D_0 \exp\left(-\frac{Q(\mu_{\text{F}}) - \Delta\mu(T)}{k_{\text{B}}T}\right)$$

$$D_0 = \frac{1}{6} n_{\text{lat}} d^2 f_{\text{C}} \Gamma_{\text{V}_{\text{Ga}}}^0 \exp(S_{\text{D}}/k_{\text{B}})$$

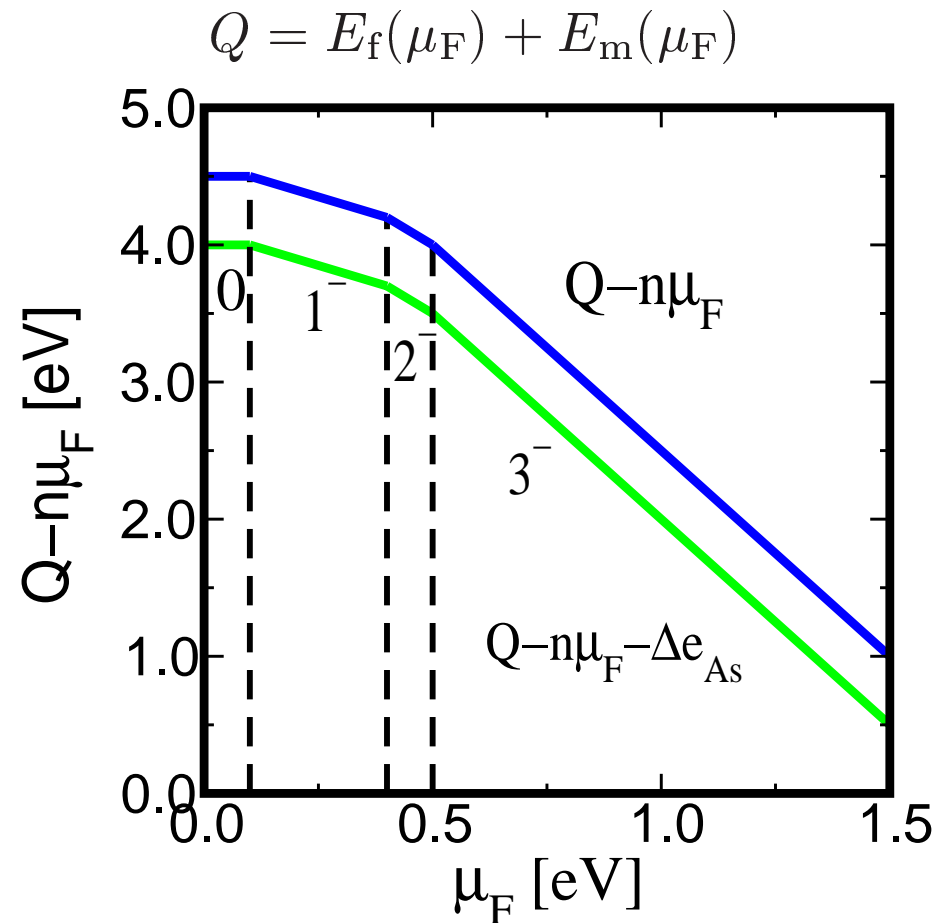
Reservoir As_4 -Gas: $\Delta\mu = \Delta e_{\text{As}} - T \Delta s_{\text{As}}$

$$\tilde{D}_0 = D_0 \exp\left(\frac{\Delta s_{\text{As}}}{k_{\text{B}}}\right) \left(\frac{P}{1\text{atm}}\right)^{1/4} \left(\frac{T}{298\text{K}}\right)^{1/2}$$

typically $P \sim 1\text{ atm}$ and $T \sim 800\text{ K} - 1500\text{ K}$

$$\text{V}_{\text{Ga}}^0: \tilde{D}_0 = 0.8 - 1.0\text{ cm}^2\text{s}^{-1}$$

$$\text{V}_{\text{Ga}}^{3-}: \tilde{D}_0 = 2.5 - 3\text{ cm}^2\text{s}^{-1}$$



Example: Diffusion in semiconductors

Self diffusion constant: as calculated from rate constant and free formation energy

- Calculation

$$D_{\text{Ga}} = (0.8 - 3) \text{ cm}^2 \text{ s}^{-1} e^{-\frac{Q}{k_B T}}$$

with $Q = 4.0 \text{ eV} - 3.0 \text{ eV}$

- GaAs/GaAlAs-heterostructures:

- Tan and Gösele (1988):

$$D_{\text{Ga}} = 2.9 \cdot 10^8 e^{-\frac{6 \text{ eV}}{k_B T}} \text{ cm}^2 \text{ s}^{-1}$$

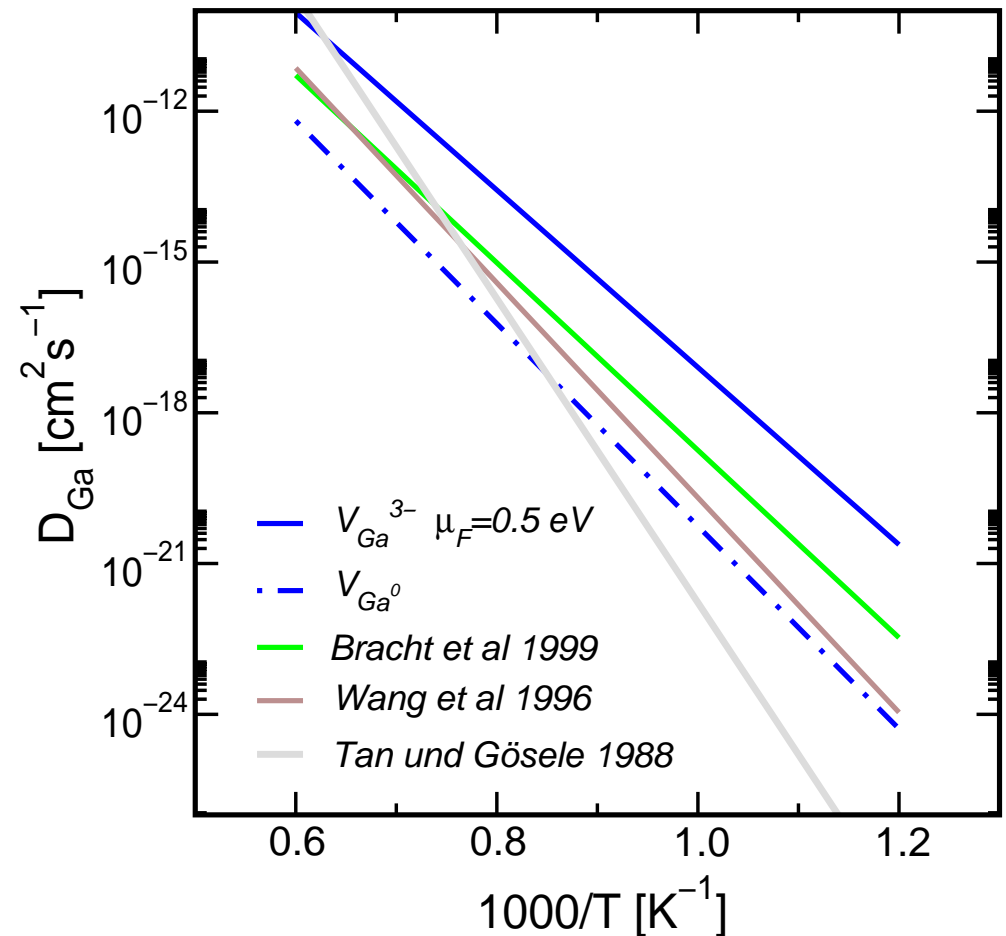
- Bracht *et al* (1999):

$$\text{Al}_0\text{Ga}_1\text{As}: D_{\text{Ga}} = 0.6 e^{-\frac{3.7 \text{ eV}}{k_B T}} \text{ cm}^2 \text{ s}^{-1}$$

- Isotope-heterostructures

- Wang *et al* 1996:

$$D_{\text{Ga}} = 48 e^{-\frac{4.2 \text{ eV}}{k_B T}} \text{ cm}^2 \text{ s}^{-1}$$



Summary

- First principles molecular dynamics
- Molecular dynamics on the Born-Oppenheimer surface
- Car-Parrinello molecular dynamics
- Simulation techniques
 - Canonical ensemble: Nosé-Hoover thermostat
 - Thermodynamic properties: phase space averages and free energies
 - Rare events: blue-moon ensemble
- Applications of MD-techniques
 - Solvents: pair correlation and adsorption spectra
 - Phase transitions: thermodynamic properties
 - Diffusion in semi conductors: diffusion mechanisms and transport coefficients