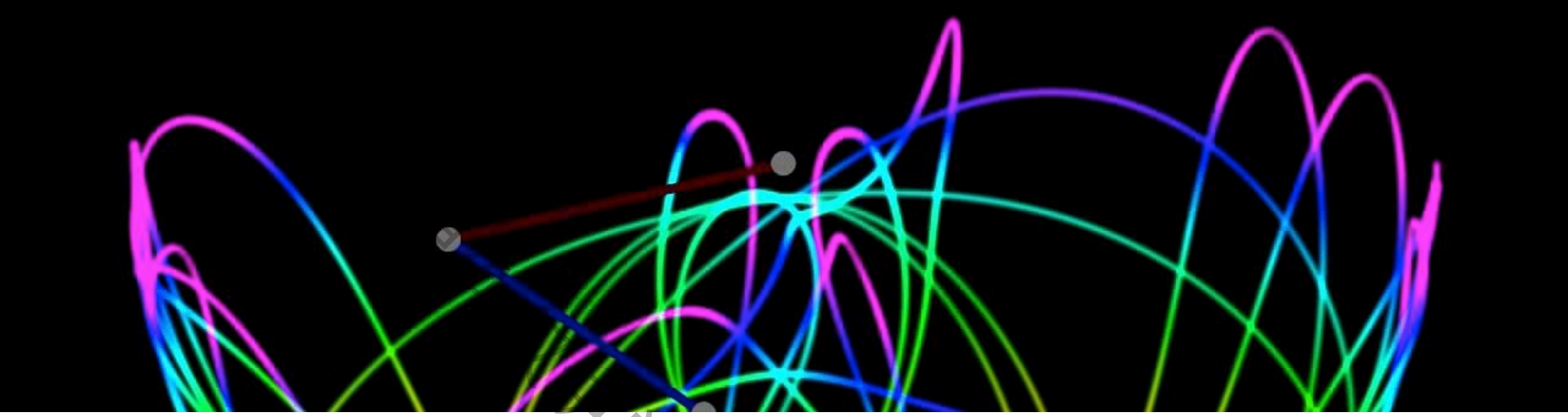
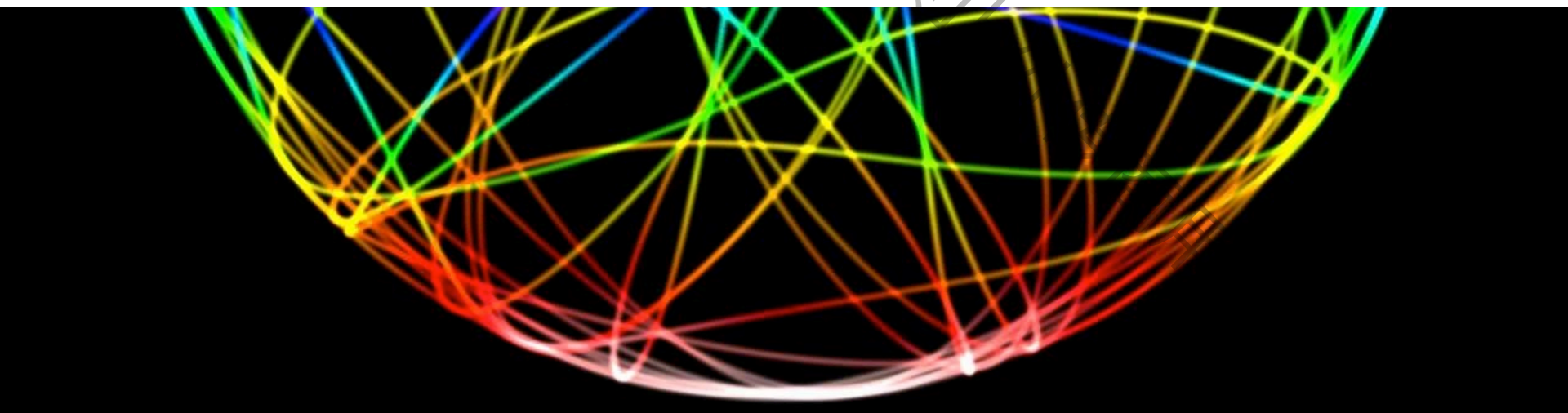


计算物理导论

李永乐/物理系/ICQMS

上海大学



Part 2

MOLECULAR DYNAMICS SIMULATIONS

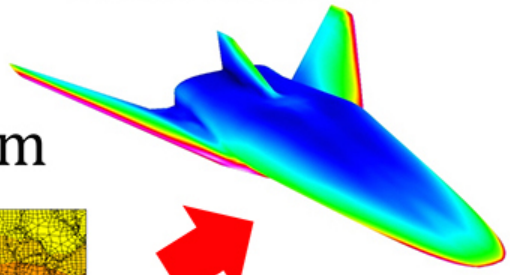
Content

1. History
2. Basic technique
3. References

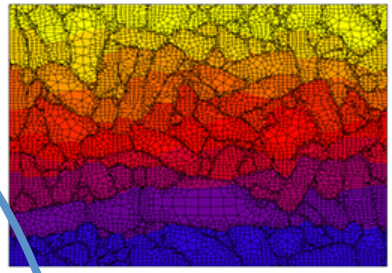
A textbook, as opposed to a treatise, should include everything a student must know, not everything the author does know.

Kenneth Johnson, quoted by Francis Low (1997)

Macroscale



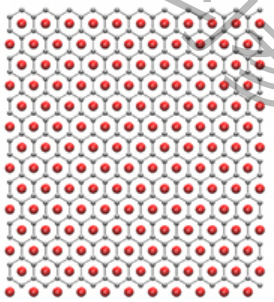
Continuum



Detailed microstructural analysis

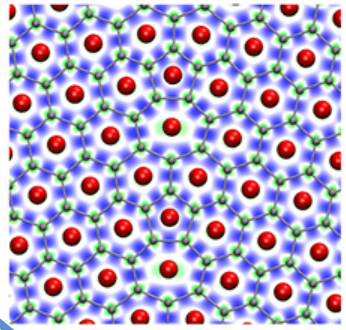
To understand macroscopic phenomena from microscopic view

Atomistic



Large scale, parallel simulations
Structural, thermal, mechanical properties

Ab Initio



High accuracy, numerically intensive computations
Insight into chemistry and physics

Time

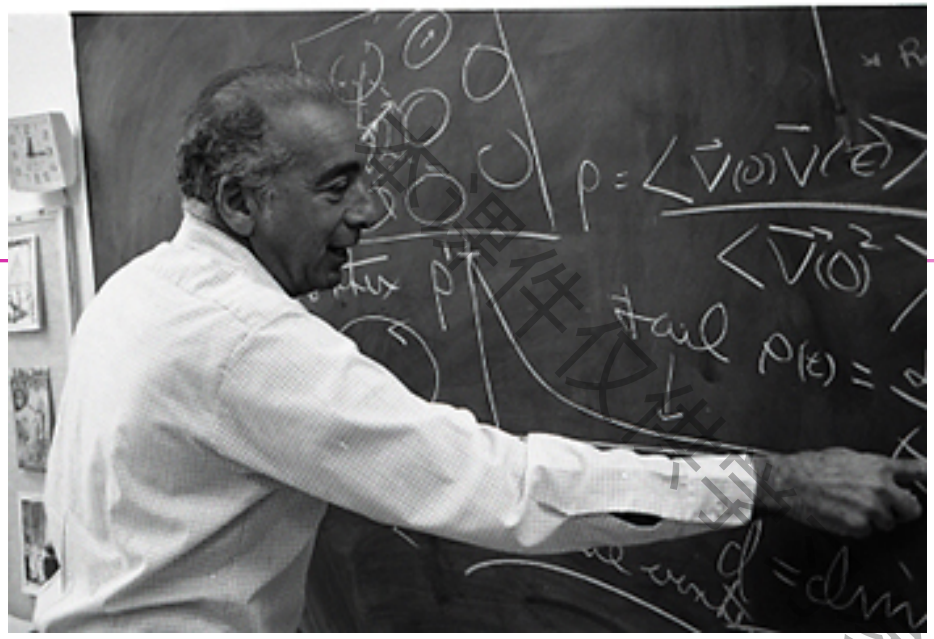
Length

MD： History

Berni Alder, 1925-2020

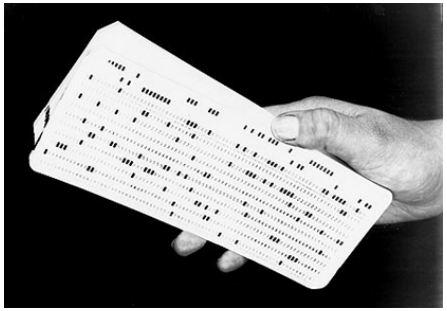
https://www.nature.com/articles/d41586-020-02858-5

Lawrence Livermore scientist **Berni Alder** will celebrate his 90th birthday and his 60th anniversary at the Laboratory. He still comes into the Laboratory twice a week in the afternoon. Photo by Julie Russell/LLNL (https://www.llnl.gov/news/berni-alder-pioneer-times) （2012）



Phase Transition for a Hard Sphere System

B. J. ALDER AND T. E. WAINWRIGHT
University of California Radiation Laboratory, Livermore, California
(Received August 12, 1957)



Journal of Chemical Physics, **1957**, 27, 1208

Two major legacies from Alder

- Changing from liquid to solid is nothing about attraction, (even hard-sphere system can condensation!) but rather the maximization of entropy.
- The fluctuation of one non-eq. system back to eq. system will not decay quickly. If a sphere is given an initial push, its average velocity is found to decay much more slowly.

Content

1. History
2. Techniques
3. References

Basic thought

$$\vec{F} = m\vec{a}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

Basic thought

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

$$\hat{H} = \hat{T}_{nuc} + \hat{T}_{ele} + \sum_{I=1}^{N_n}\sum_{J=I+1}^{N_n}\frac{Z_I Z_J}{\left|\boldsymbol{R}_I - \boldsymbol{R}_J\right|} + \sum_{i=1}^{N_e}\sum_{j=i+1}^{N_e}\frac{1}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j\right|} - \sum_{I=1}^{N_n}\sum_{i=1}^{N_e}\frac{Z_I}{\left|\boldsymbol{R}_I - \boldsymbol{r}_i\right|}$$

Born-Oppenheimer approximation

$$\Psi(r,R) = \chi(\boldsymbol{R})\psi(\boldsymbol{R};\boldsymbol{r})$$

Pre-determined

$$\hat{H} = \hat{T}_{nuc} + \hat{V}(\boldsymbol{R}) \Rightarrow H = T_{nuc} + E_0(\boldsymbol{R})$$

1. The motion of electrons and nuclei can be described separately.

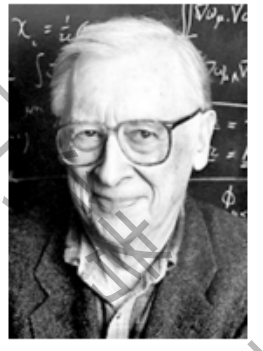
2. After separating electron and nuclear motion, use classical dynamics to describe nuclei

$$M_p = 1836 m_e$$

X. Z. Li & E. G. Wang, *Computer Simulations of Molecules and Condensed Matter*, World Science Press & Peking University Press, 2013

The Nobel Prize in Chemistry 1998

Walter Kohn
Prize share: 1/2



John A. Pople
Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn *"for his development of the density-functional theory"* and John A. Pople *"for his development of computational methods in quantum chemistry"*.

Ab initio determination of the crystalline benzene lattice energy to sub-kilojoule/mole accuracy

Jun Yang,[1] Weifeng Hu,[1] Denis Usvyat,[2] Devin Matthews,[3] Martin Schütz,[2] Garnet Kin-Lic Chan[1]*

Unit: kJ/mol

Contributions	Estimates in this work
$\Delta H_{sub}^{298.15K}$	$44.7 \pm 0.2^{*}$
$\Delta H_{sub}^{0\rightarrow 298.15K}$	$-5.8 \pm 1.0^{\dagger}$
ΔE_{ZPE}	$-4.8 \pm 1.0^{\ddagger}$
$\mathbf{E}_{exp,\,latt}^{0K}$	-55.3 ± 2.2
$\mathbf{E}_{theor,\,latt}^{0K}$	$-55.90 \pm 0.76 \pm 0.1$

*Data in (*34*). †Mean value from data in (*9*, *33*). ‡Data in (*10*) accounting for van der Waals and non-Γ-point effects.

DOI:10.1126/science.1254419

1 hartree = 27.2107 eV

When accuracy is very important, I recommend going instead to the NIST website: Fundamental Physical Constants from NIST

Energy Conversion Table								
	hartree	**eV**	**cm^{-1}**	**kcal/mol**	**kJ/mol**	**°K**	**J**	**Hz**
hartree	1	27.2107	219 474.63	627.503	2 625.5	315 777.	43.60×10^{-19}	$6.57966 \times 10^{+15}$
eV	0.0367502	1	8 065.73	23.060 9	96.486 9	11 604.9	$1.602\ 10 \times 10^{-19}$	$2.418\ 04 \times 10^{+14}$
cm^{-1}	$4.556\ 33 \times 10^{-6}$	$1.239\ 81 \times 10^{-4}$	1	0.002 859 11	0.011 962 7	1.428 79	$1.986\ 30 \times 10^{-23}$	$2.997\ 93 \times 10^{+10}$
kcal/mol	0.001 593 62	0.043 363 4	349.757	1	4.18400	503.228	6.95×10^{-21}	$1.048\ 54 \times 10^{+13}$
kJ/mol	0.000 380 88	0.010 364 10	83.593	0.239001	1	120.274	1.66×10^{-21}	$2.506\ 07 \times 10^{+12}$
°K	0.000 003 166 78	0.000 086 170 5	0.695 028	0.001 987 17	0.008 314 35	1	$1.380\ 54 \times 10^{-23}$	$2.083\ 64 \times 10^{+10}$
J	$2.294 \times 10^{+17}$	$6.241\ 81 \times 10^{+18}$	$5.034\ 45 \times 10^{+22}$	$1.44 \times 10^{+20}$	$6.02 \times 10^{+20}$	$7.243\ 54 \times 10^{+22}$	1	$1.509\ 30 \times 10^{+33}$
Hz	$1.519\ 83 \times 10^{-16}$	$4.135\ 58 \times 10^{-15}$	$3.335\ 65 \times 10^{-11}$	$9.537\ 02 \times 10^{-14}$		$4.799\ 30 \times 10^{-11}$	$6.625\ 61 \times 10^{-34}$	1

This table was taken from http://mccammon.ucsd.edu/~dzhang/energy-unit-conv-table.html.

MD algorithm: Verlet

$$\boldsymbol{r}(t+\Delta t) = \qquad (1)$$

Taylor expansion

$$\boldsymbol{r}(t-\Delta t) = \qquad (2)$$

Verlet, L.: Computer “experiments” on classical fluids. i. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.* **1967,** 159, 98–103

MD algorithm: Verlet

$$\boldsymbol{r}(t+\Delta t)=\boldsymbol{r}(t)+\boldsymbol{v}(t)\Delta t+\frac{\boldsymbol{F}(\boldsymbol{r}(t))}{2m}\Delta t^2+\frac{1}{6}\frac{\partial^3 \boldsymbol{r}}{\partial t^3}\bigg|_t\Delta t^3+O(\Delta t^4) \qquad (1)$$

Taylor expansion

$$\boldsymbol{r}(t-\Delta t)=\boldsymbol{r}(t)-\boldsymbol{v}(t)\Delta t+\frac{\boldsymbol{F}(\boldsymbol{r}(t))}{2m}\Delta t^2-\frac{1}{6}\frac{\partial^3 \boldsymbol{r}}{\partial t^3}\bigg|_t\Delta t^3+O(\Delta t^4) \qquad (2)$$

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

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

Verlet, L.: Computer “experiments” on classical fluids. i. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.* **1967,** 159, 98–103

MD algorithm: Verlet

$$\boldsymbol{r}(t+\Delta t)=\boldsymbol{r}(t)+\boldsymbol{v}(t)\Delta t+\frac{\boldsymbol{F}(\boldsymbol{r}(t))}{2m}\Delta t^2+\frac{1}{6}\frac{\partial^3 \boldsymbol{r}}{\partial t^3}\bigg|_t\Delta t^3+O(\Delta t^4) \qquad (1)$$

Taylor expansion

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

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

Verlet, L.: Computer “experiments” on classical fluids. i. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.* **1967,** 159, 98–103

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Taylor expansion

$$\boldsymbol{r}(t-\Delta t)=\boldsymbol{r}(t)-\boldsymbol{v}(t)\Delta t+\frac{\boldsymbol{F}(\boldsymbol{r}(t))}{2m}\Delta t^2-\frac{1}{6}\frac{\partial^3 \boldsymbol{r}}{\partial t^3}\bigg|_t\Delta t^3+O(\Delta t^4) \qquad (2)$$

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

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

Verlet, L.: Computer “experiments” on classical fluids. i. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.* **1967,** 159, 98–103

MD algorithm: Verlet

$$\boldsymbol{r}(t+\Delta t)=\boldsymbol{r}(t)+\boldsymbol{v}(t)\Delta t+\frac{\boldsymbol{F}(\boldsymbol{r}(t))}{2m}\Delta t^2+\frac{1}{6}\frac{\partial^3 \boldsymbol{r}}{\partial t^3}\bigg|_t\Delta t^3+O(\Delta t^4) \qquad (1)$$

Taylor expansion

$$\boldsymbol{r}(t-\Delta t)=\boldsymbol{r}(t)-\boldsymbol{v}(t)\Delta t+\frac{\boldsymbol{F}(\boldsymbol{r}(t))}{2m}\Delta t^2-\frac{1}{6}\frac{\partial^3 \boldsymbol{r}}{\partial t^3}\bigg|_t\Delta t^3+O(\Delta t^4) \qquad (2)$$

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

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

Verlet, L.: Computer “experiments” on classical fluids. i. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.* **1967,** 159, 98–103

MD algorithm: velocity Verlet

$$\boldsymbol{v}(t+\Delta t/2)=\boldsymbol{v}(t)-\left(\frac{\partial V}{\partial \boldsymbol{r}(t)}\right)\frac{\Delta t}{2m}+O(\Delta t^3)$$

$$\boldsymbol{r}(t+\Delta t)=\boldsymbol{r}(t)+\boldsymbol{v}(t+\Delta t/2)\Delta t+O(\Delta t^4);$$

$$\boldsymbol{v}(t+\Delta t)=\boldsymbol{v}(t+\Delta t/2)-\left(\frac{\partial V}{\partial \boldsymbol{r}(t+\Delta t)}\right)\frac{\Delta t}{2m}+O(\Delta t^2)$$

William C. Swope, Hans C. Andersen
Peter H. Berens, Kent R. Wilson
A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters
Journal of Chemical Physics, 76, 637-649

Why velocity Verlet so powerful?

Classical Liouville theorem

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + i\hat{L}\{\rho\} = 0, \quad \frac{\mathrm{d}\rho}{\mathrm{d}t} = i\hat{L}\{\rho\}$$

Density does not contain time explicitly

$$\rho = \frac{e^{-H/(kT)}}{Z}$$

$$i\hat{L}\{\rho\} = [H,\rho] = \sum_{i=1}^{3N} \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i}$$

Classical operator

Classical propagator

$$\rho(\boldsymbol{p},\boldsymbol{q};t) = e^{i\hat{L}\{\rho\}t}\rho(\boldsymbol{p},\boldsymbol{q};t=0)$$

Trotter expansion[a]

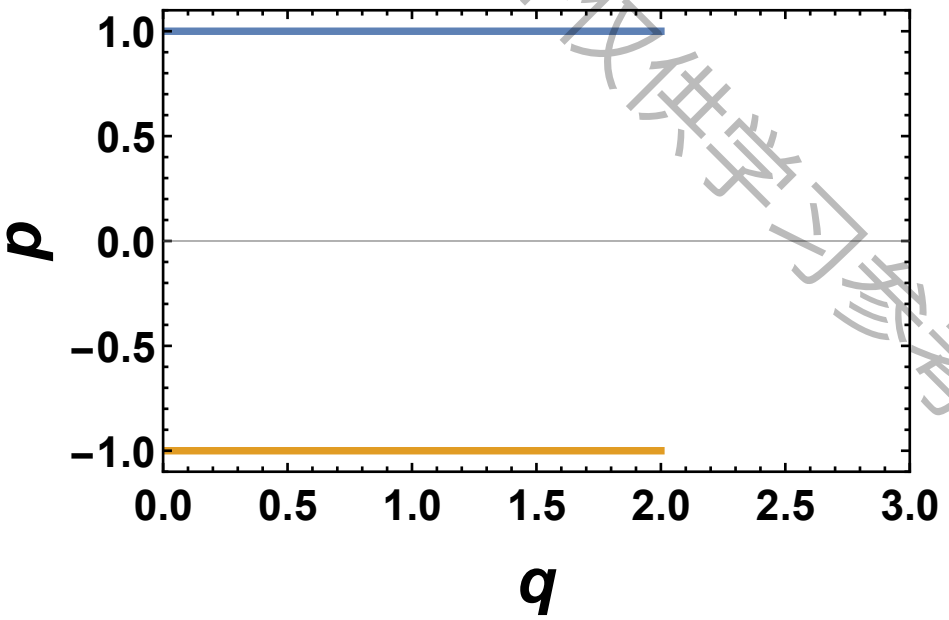
$$\approx e^{i\hat{L}_2\{\rho\}t/2} e^{i\hat{L}_1\{\rho\}t} e^{i\hat{L}_2\{\rho\}t/2} \rho(\boldsymbol{p},\boldsymbol{q};t=0) \quad O(t^3)$$

A. Pérez, M. E. Tuckerman, and M. H. Müser, *J. Chem. Phys.* **130**, 184105 (2009).
M. E. Tuckerman, *Statistical Mechanics*, Oxford University Press, 2010

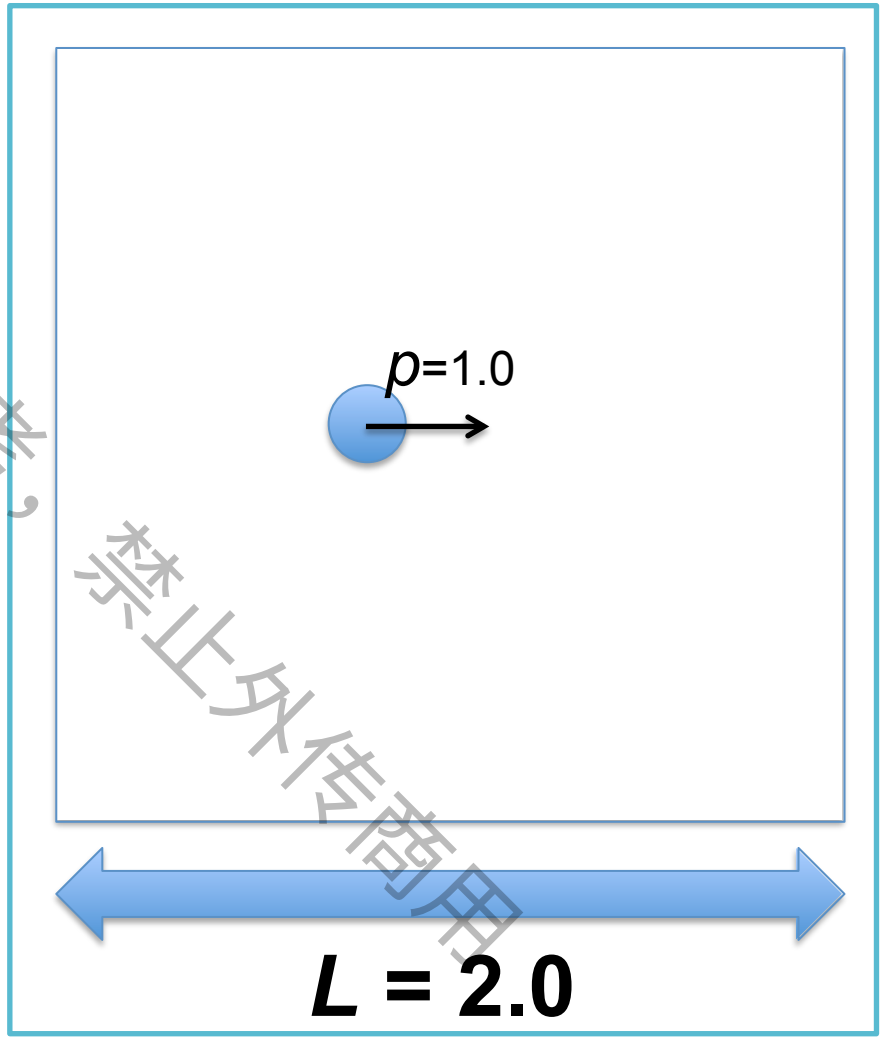
[a]: 1) Trotter, H., On the product of semi-groups of operators. *Proceedings of the American Mathematical Society* **10**, 545–551 (1959).
2) M. Suzuki, Generalized Trotter's formula and systematic approximants of exponential operators and inner derivations with applications to many-body problems, *Comm. Math. Phys.* **51**, 183-190 (1976)

DISTRACTION: PHASE SPACE AND LIOUVILLE DYNAMICS

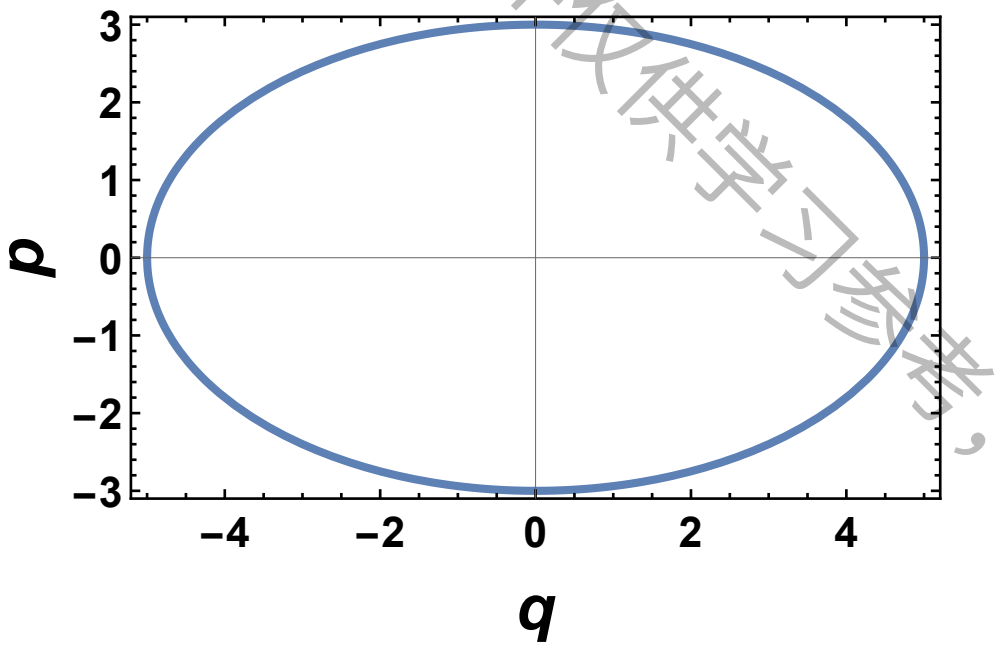
Phase space

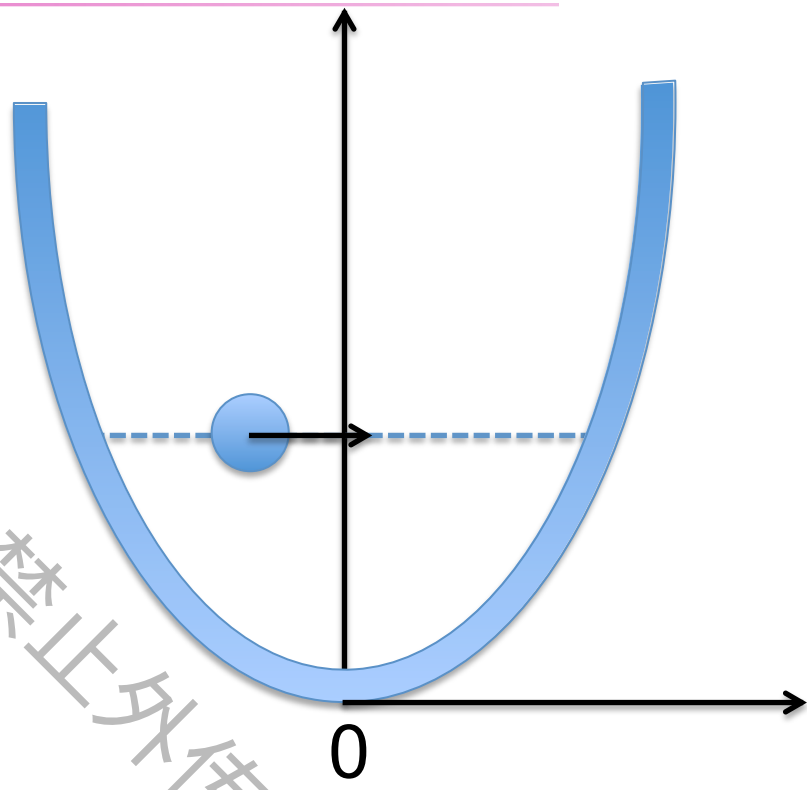


$$\rho = \frac{e^{-H/(kT)}}{Z} = \frac{e^{-p^2/(2mkT)}}{Z}$$



Phase space





Quiz (1)：What's Liouville theorem?
Quiz (2)：Difference between dρ and $\partial\rho$?

If A is a ***dynamical variable***, (*A* does not explicitly contain time)

$$\frac{\mathrm{d}A}{\mathrm{d}t}=\frac{\partial A}{\partial t}+i\hat{L}\{A\}=i\hat{L}\{A\}\quad(A=A(\vec{q},\vec{p}))$$

Classical Poisson bracket

$$i\hat{L}\{A\}=[H,A]=\sum_{i=1}^{3N}\frac{\partial H}{\partial p_i}\frac{\partial A}{\partial q_i}-\frac{\partial H}{\partial q_i}\frac{\partial A}{\partial p_i}$$

$$i\hat{L}=\sum_{i=1}^{3N}\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i}-\frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i}=\sum_{i=1}^{3N}\dot{q}_i\frac{\partial}{\partial q_i}+\dot{p}_i\frac{\partial}{\partial p_i}$$

Hamilton equation

$$e^{i\hat{L}\{A\}t} = e^{i\hat{L}\{A\}(N\Delta t)} = \left[e^{i\hat{L}\{A\}\Delta t} \right]^N$$

$$\boldsymbol{x}(t) = (\boldsymbol{p},\boldsymbol{q}) = e^{i\hat{L}\{\boldsymbol{x}\}N\Delta t}\boldsymbol{x}(0)$$

The perturbation of $\boldsymbol{x}$=($\boldsymbol{q}$,$\boldsymbol{p}$) under the perturbation of $\boldsymbol{L}$ should be small enough to guarantee the phase trajectory stable.

$$\hat{L} \to \hat{L} + \Delta\hat{L}$$

$$\Rightarrow \boldsymbol{x} \to \boldsymbol{x} + \Delta\boldsymbol{x}$$

$$i\hat{L} = \sum_{i=1}^{3N}\left[\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i}\right] = \sum_{i=1}^{3N}\dot{q}_i\frac{\partial}{\partial q_i} + \dot{p}_i\frac{\partial}{\partial p_i}$$

$$= i\hat{L}_1 + i\hat{L}_2$$

$$i\hat{L}_1 = \sum_{i=1}^{3N}\dot{x}_i\frac{\partial}{\partial x_i} = \sum_{i=1}^{3N}\frac{\partial H}{\partial p_i}\frac{\partial}{\partial x_i}$$

$$i\hat{L}_2 = \sum_{i=1}^{3N}\dot{p}_i\frac{\partial}{\partial p_i} = -\sum_{i=1}^{3N}\frac{\partial H}{\partial x_i}\frac{\partial}{\partial p_i}$$

Example 1: Free particle

$$H = \frac{p^2}{2m} \qquad \rho = e^{-\frac{\beta p^2}{2m}}$$

$$\frac{\partial H}{\partial p} = \frac{p}{m} \qquad \frac{\partial H}{\partial x} = 0$$

$$\frac{\partial \rho}{\partial p} = -\frac{\beta p}{m}\rho \qquad \frac{\partial \rho}{\partial x} = 0$$

$$i\hat{L}_1\rho = i\hat{L}_2\rho = 0$$

Example 2: Harmonic Oscillator (1)

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \qquad \rho = \frac{1}{Z} e^{-\frac{\beta p^2}{2m} - \frac{\beta m\omega^2}{2}x^2}$$

Omit *Z* below

$$\frac{\partial H}{\partial p} = \frac{p}{m} \qquad \frac{\partial H}{\partial x} = m\omega^2 x$$

$$\frac{\partial \rho}{\partial p} = -\frac{\beta p}{m}\rho \qquad \frac{\partial \rho}{\partial x} = -\beta m\omega^2 x\rho$$

Example 2: Harmonic Oscillator (2)

$$i\hat{L}_1\rho = \frac{\partial H}{\partial p}\frac{\partial \rho}{\partial x} = \frac{p}{m}\left(-\beta m\omega^2 x\rho\right)$$

$$= -\beta\omega^2 px\rho$$

$$i\hat{L}_2\rho = -\frac{\partial H}{\partial x}\frac{\partial \rho}{\partial p} = -m\omega^2 x\left(-\frac{\beta p}{m}\rho\right)$$

$$= \beta\omega^2 xp\rho$$

Example 2: Harmonic Oscillator (3)

$$i\hat{L}_2\left(i\hat{L}_1\rho\right) = -\frac{\partial H}{\partial x}\frac{\partial\left[-\beta\omega^2 px\rho\right]}{\partial p}$$

$$= \beta\omega^2\left(m\omega^2 x\right)\left[-x\rho - \frac{\beta px}{m}\rho\right] = -\beta m\omega^4 x^2\rho\left(1-\frac{\beta p^2}{m}\right)$$

$$i\hat{L}_1\left(i\hat{L}_2\rho\right) = \frac{\partial H}{\partial p}\frac{\partial\left[\beta\omega^2 xp\rho\right]}{\partial x}$$

$$= \beta\omega^2\left(\frac{p^2}{m}\right)\left[\rho + x\left(-\beta m\omega^2 x\rho\right)\right] = \beta\omega^2\frac{p^2}{m}\rho\left(1-\beta m\omega^2 x^2\right)$$

COME BACK TO THE VERLET ALGORITHM

From theory to algorithm (1)

$$(\boldsymbol{p}(t),\boldsymbol{q}(t)) = e^{i\hat{L}\{\boldsymbol{x}\}t}(\boldsymbol{p}(0),\boldsymbol{q}(0))$$

$$\approx e^{i\hat{L}_2\{\boldsymbol{x}\}t/2} e^{i\hat{L}_1\{\boldsymbol{x}\}t} e^{i\hat{L}_2\{\boldsymbol{x}\}t/2}\boldsymbol{x}(0)$$

$$e^{i\hat{L}_2\{\boldsymbol{x}\}\Delta t/2}\boldsymbol{x}(t_0) = \left[1 + i\hat{L}_2\frac{\Delta t}{2} + \frac{1}{2!}\left(i\hat{L}_2\right)^2\left(\frac{\Delta t}{2}\right)^2 + \cdots\right]\boldsymbol{x}(t_0) \approx \left(1 + i\hat{L}_2\frac{\Delta t}{2}\right)\boldsymbol{x}(t_0)$$

$$= \boldsymbol{x}(t_0) + \frac{\Delta t}{2}\sum_{i=1}^{3N}\dot{p}_i\frac{\partial \boldsymbol{x}(t_0)}{\partial p_i}$$

From theory to algorithm (2)

$$\boldsymbol{x}_0 = \left\{x_1^0, x_2^0, \cdots, x_{3N}^0, p_1^0, p_2^0, \cdots, p_{3N}^0\right\}$$

$$\frac{\partial \boldsymbol{x}_0}{\partial p_i} = \left\{0, 0, \cdots, 0, 0, \cdots, 1, \cdots, 0\right\}$$

$\boldsymbol{p}$ does not related to $\boldsymbol{x}$

i_{th} momentum

$$e^{i\hat{L}_2\{\boldsymbol{x}\}\Delta t/2}\boldsymbol{x}(t_0) = \boldsymbol{x}(t_0) + \frac{\Delta t}{2}\sum_{i=1}^{3N}\dot{p}_i\frac{\partial \boldsymbol{x}(t_0)}{\partial p_i}$$

From theory to algorithm (3)

$$e^{i\hat{L}_2\Delta t/2}\boldsymbol{x}_0 = \left\{ x_1^0, x_2^0, \cdots, x_{3N}^0; \left\{ p_i + \frac{\Delta t}{2}\dot{p}_i \right\}_{i=1}^{3N} \right\} \qquad i\hat{L}_2 = -\sum_{i=1}^{3N} \frac{\partial H}{\partial x_i}\frac{\partial}{\partial p_i}$$

$$= \left\{ x_1^0, x_2^0, \cdots, x_{3N}^0; \left\{ p_i - \frac{\partial V}{\partial x_i}\frac{\Delta t}{2} \right\}_{i=1}^{3N} \right\}$$

$$= \boldsymbol{x}_0(\vec{q}(t_0); \vec{p}(t_0 + \frac{\Delta t}{2}))$$

x part is still unchanged, only *p* part propagated half delta *t*.

This is the first step of velocity Verlet algorithm!

From theory to algorithm (4)

$$\boldsymbol{x}(t_0;t_0+\frac{\Delta t}{2})=\left\{x_1^0,x_2^0,\cdots,x_{3N}^0,p_1^{t_0+\frac{\Delta t}{2}},p_2^{t_0+\frac{\Delta t}{2}},\cdots,p_{3N}^{t_0+\frac{\Delta t}{2}}\right\}$$

$$\frac{\partial}{\partial x_i}\boldsymbol{x}(t_0;t_0+\frac{\Delta t}{2})=\left\{0,0,\cdots,1,\cdots,0,0,\cdots,0\right\}$$

After propagating half delta t, the position is still unchanged.

i_{th} position

p does not related to *x*

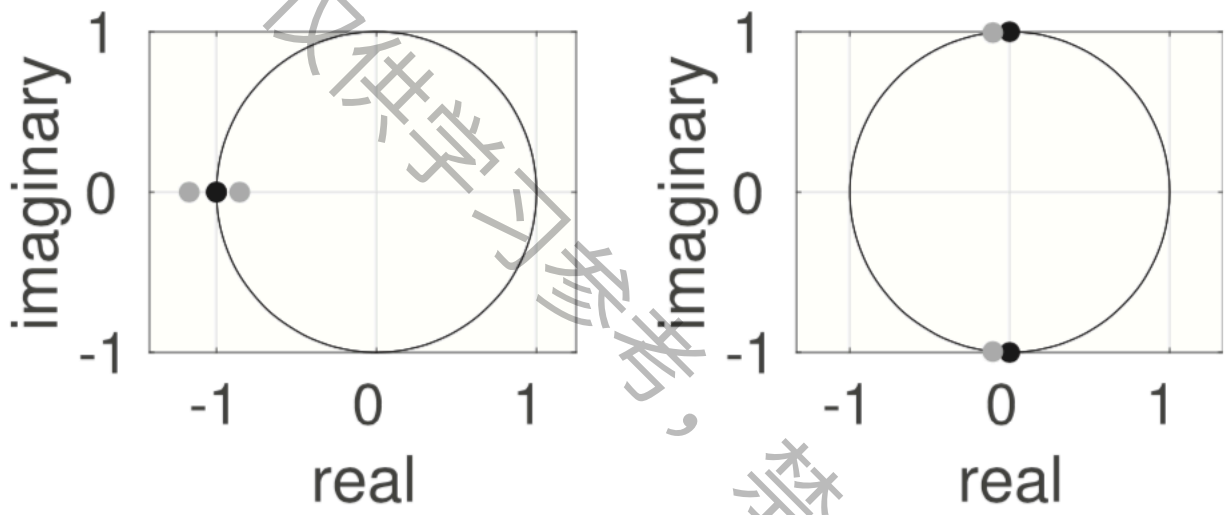
$$e^{i\hat{L}_1\Delta t}\boldsymbol{x}(t_0+\frac{\Delta t}{2})=\left\{\left\{x_i+\Delta t\dot{x}_i\right\}_{i=1}^{3N};p_1^{t_0+\frac{\Delta t}{2}},p_2^{t_0+\frac{\Delta t}{2}},\cdots,p_{3N}^{t_0+\frac{\Delta t}{2}}\right\}$$

$$=\left\{\left\{x_i+\frac{p_i}{m}\Delta t\right\}_{i=1}^{3N};p_1^{t_0+\frac{\Delta t}{2}},p_2^{t_0+\frac{\Delta t}{2}},\cdots,p_{3N}^{t_0+\frac{\Delta t}{2}}\right\}=\boldsymbol{x}(\vec{q}(t_0+\Delta t);\vec{p}(t_0+\frac{\Delta t}{2}))$$

From theory to algorithm (5)

$$e^{i\hat{L}_2\Delta t/2}\boldsymbol{x}(\vec{q}(t_0+\Delta t);\vec{p}(t_0+\frac{\Delta t}{2}))=\boldsymbol{x}(\vec{q}(t_0+\Delta t);\vec{p}(t_0+\Delta t))$$

How to measure the stability?



R. Korol et al. *J. Chem. Phys*. **151**, 124103 (2019)

MD algorithms

Runge-Kutta,
Runge-Kutta-Gill,
Runge-Kutta-Adams-Moulton-Hamming

Highly stable

Gear predictor-correction Velocity is more accurate.

Symplectic algorithm

Properties, Dynamics, and Electronic Structure of Atoms and Molecules

High-order symplectic integration in quasi-classical trajectory simulation: Case study for $O(^1D) + H_2$

Xin Zhang, Ke-Li Han

How to choose?

1. Stability;
2. Accuracy;
3. Speed;
4. Memory;
5. Symmetry of time reversion;
6. **Simplicity** $dp \times dr$ Long time stability in NVT ensemble, match Boltzmann distribution, and time reverse symmetry

Detailed balance

The rate of transitions from state *i* to state *j* is the same as from *j* to *i*, on average.

The flux of probability from state *i* to state *j* is exactly balanced by the probability flux from *j* to *i*:

$$p_i \rightarrow \pi_i \rho_{ij}^{eq} = p_j \rightarrow \pi_j \rho_{ji}^{eq}$$

Flux

Probability

Distribution

Probability depends on the ensemble:

Microcanonical ensemble:

$$\rho_i^{eq} = \rho = \frac{1}{\Omega}$$

Canonical ensemble:

$$\rho_i^{eq} \propto e^{-\beta E_i}$$

The Nobel Prize in Chemistry 2013

Photo: A. Mahmoud

Martin Karplus

Prize share: 1/3

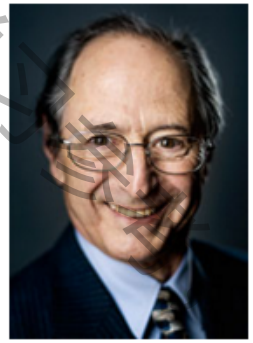


Photo: A. Mahmoud

Michael Levitt

Prize share: 1/3

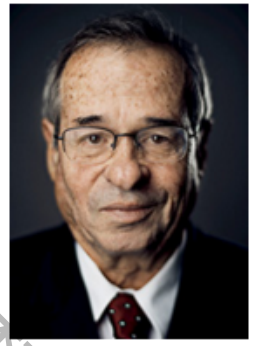


Photo: A. Mahmoud

Arieh Warshel

Prize share: 1/3

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems"*.