РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

«7-th School-Conference on
Atomistic Simulation of Functional Materials (ASFM 2018)»

Predictive power of classical MD calculations for n-alkanes rheological properties

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JIHT RAS

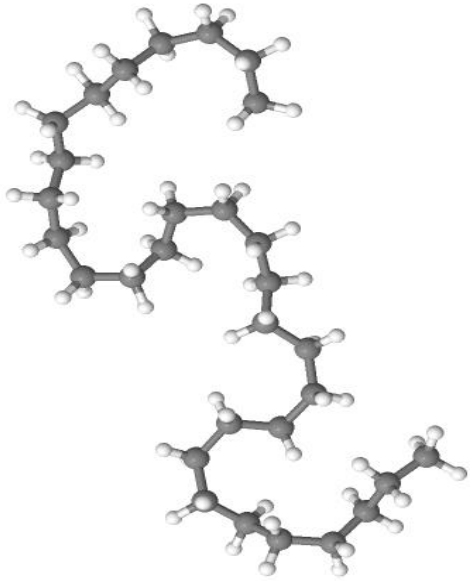
HIGHER SCHOOL OF ECONOMICS
NATIONAL RESEARCH UNIVERSITY

MIPT
MOSCOW INSTITUTE OF PHYSICS AND TECHNOLOGY

План доклада

n-$C_{30}H_{62}$

1. Самодиффузия в жидком н-триаконтане

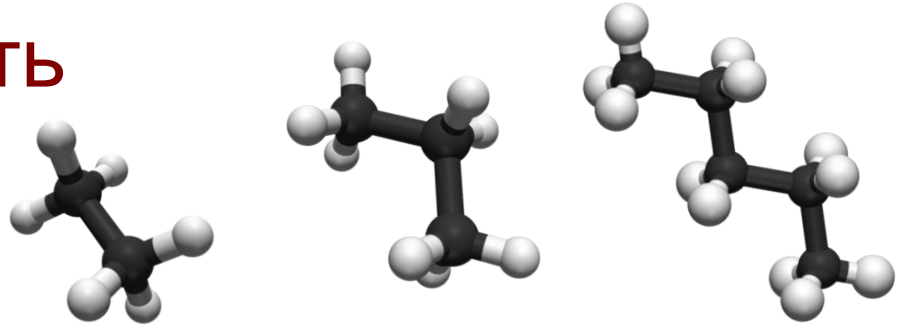


Молекула н-триаконтана

Потенциалы взаимодействия (+ COMPASS)

Предсказательная способность

2. Сдвиговая вязкость



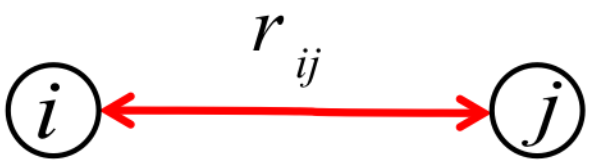
Сходимость Г-К

Неравновесная МД + эксперимент

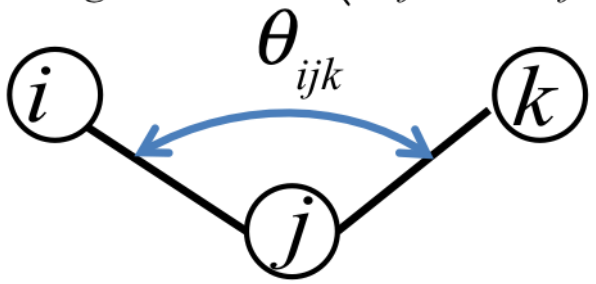
Модель класса I

$$E = E_{bond} + E_{angle} + E_{dihedral} + E_{LJ} + E_{Coul}$$

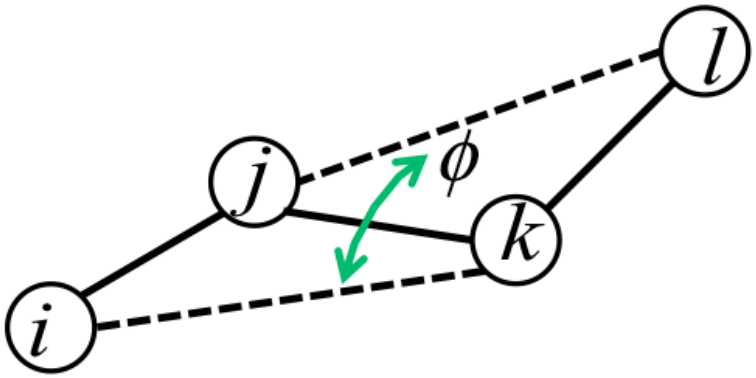
$$E_{bond} = K_b \left(r_{ij} - r_{ij}^{\,0} \right)^2$$



$$E_{angle} = K_a \left(\theta_{ijk} - \theta_{ijk}^{\,0} \right)^2$$

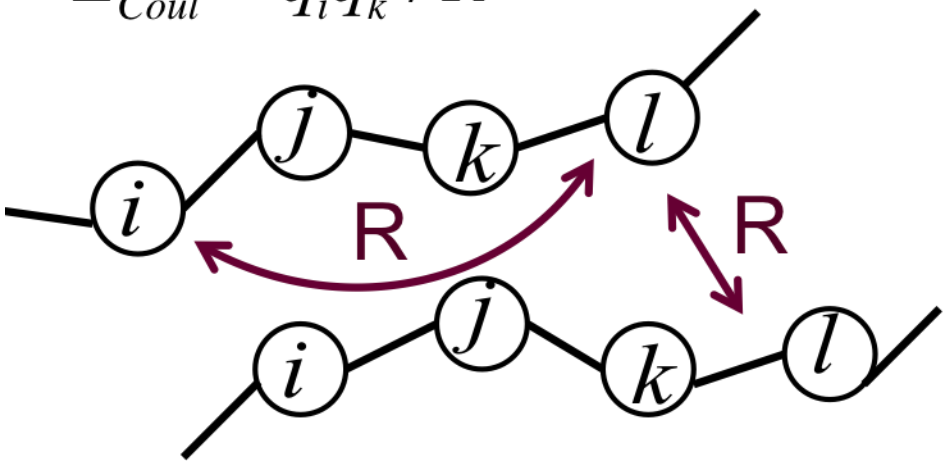


$$E_{dihedral} = \sum_i K_i [1 - \cos(i \cdot \phi)]$$



$$E_{LJ} = 4\varepsilon[(\sigma / R)^{12} - (\sigma / R)^6]$$

$$E_{Coul} = q_i q_k / R$$



Потенциалы

TraPPE-UA (1996)

Martin, M. G., Siepmann, J. I. **Tra**nsferable **P**otentials for **P**hase **E**quilibria. 1. **U**nited-**A**tom Description of n -Alkanes. // J. Phys. Chem. B. 1998. V. 102(14) P. 2569–2577

1766 citations

OPLS-AA (1996)

Open **P**otential for **L**iquid **S**imulations – **A**ll-**A**tom

Jorgensen W. L., Maxwell, D. S., Tirado-Rives J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids // J. Am. Chem. Soc. 1996. V. 118(45). P. 11225–11236.

8485 citations

L-OPLS-AA (2012)

Siu, S. W. I., Pluhackova, K., Bockmann, R. A. Optimization of the **OPLS-AA** Force Field for **L**ong Hydrocarbons // J. Chem. Theory Comput. 2012. V. 8. P. 1459.

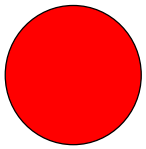
168 citations

Потенциалы

Number of molecules

United-atom approach

CH_2
CH_3

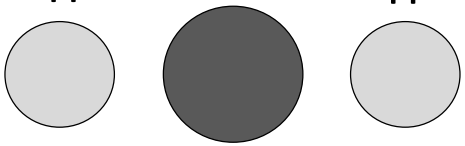


TraPPE-UA

- united-atom
- simple parameterization
- no charges

All-atom approach

H C H



L-, OPLS-AA

- all-atom
- charges

?

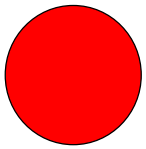
Computing costs

Потенциалы

Number of molecules

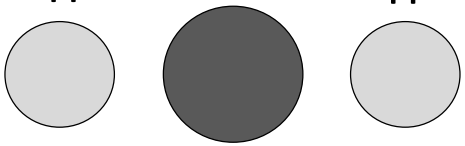
United-atom approach

CH_2
CH_3



All-atom approach

H C H



TraPPE-UA

- united-atom
- simple parameterization
- no charges

L-, OPLS-AA

- all-atom
- charges

COMPASS

- difficult parameterization

Computing costs

Модель класса II

COMPASS (1998)

Sun, H.

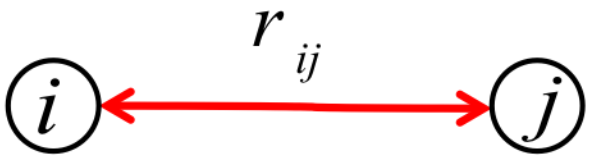
COMPASS: An ab Initio Force-Field Optimized for Condensed-Phase Applications s Overview with Details on Alkane and Benzene Compounds.

J. Phys. Chem., *5647*(98), 7338–7364

3285 citations

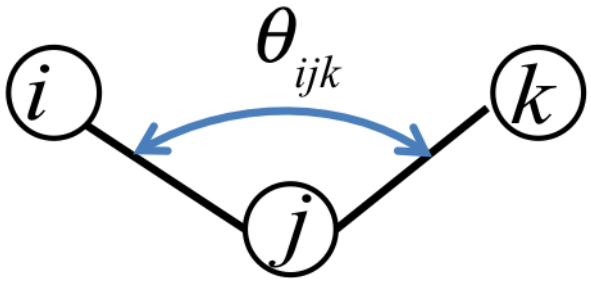
$$E = E_{bond} + E_{angle} + E_{dihedral} + E_{LJ} + E_{Coul}$$

$$E = K_2(r - r_0)^2 + K_3(r - r_0)^3 + K_4(r - r_0)^4$$



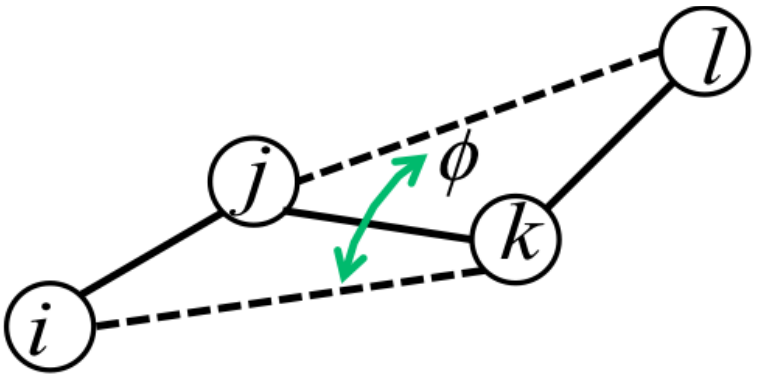
Модель класса II

$$
\begin{aligned}
E &= E_a + E_{bb} + E_{ba} \\
E_a &= K_2(\theta - \theta_0)^2 + K_3(\theta - \theta_0)^3 + K_4(\theta - \theta_0)^4 \\
E_{bb} &= M(r_{ij} - r_1)(r_{jk} - r_2) \\
E_{ba} &= N_1(r_{ij} - r_1)(\theta - \theta_0) + N_2(r_{jk} - r_2)(\theta - \theta_0)
\end{aligned}
$$



Модель класса II

$$
\begin{aligned}
E &= E_d + E_{mbt} + E_{ebt} + E_{at} + E_{aat} + E_{bb13} \\
E_d &= \sum_{n=1}^{3} K_n[1 - \cos(n\phi - \phi_n)] \\
E_{mbt} &= (r_{jk} - r_2)[A_1 \cos(\phi) + A_2 \cos(2\phi) + A_3 \cos(3\phi)] \\
E_{ebt} &= (r_{ij} - r_1)[B_1 \cos(\phi) + B_2 \cos(2\phi) + B_3 \cos(3\phi)] + \\
&\quad (r_{kl} - r_3)[C_1 \cos(\phi) + C_2 \cos(2\phi) + C_3 \cos(3\phi)] \\
E_{at} &= (\theta_{ijk} - \theta_1)[D_1 \cos(\phi) + D_2 \cos(2\phi) + D_3 \cos(3\phi)] + \\
&\quad (\theta_{jkl} - \theta_2)[E_1 \cos(\phi) + E_2 \cos(2\phi) + E_3 \cos(3\phi)] \\
E_{aat} &= M(\theta_{ijk} - \theta_1)(\theta_{jkl} - \theta_2) \cos(\phi) \\
E_{bb13} &= N(r_{ij} - r_1)(r_{kl} - r_3)
\end{aligned}
$$



+ Lennard-Jones **6-9** + Coulomb

```
set type 1 charge   -0.159000
set type 2 charge   0.000000
set type 3 charge   -0.053000
set type 4 charge   0.053000
set type 5 charge   -0.106000

pair_style      lj/class2/coul/long 12.0
pair_modify     tail yes mix sixthpower
kspace_style    pppm 0.00001
special_bonds   lj/coul 0.0 0.0 1.0 dihedral yes
pair_coeff 1   1   0.0620000000   3.8540000000 # c4
pair_coeff 2   2   0.0200000000   3.8540000000 # c44
pair_coeff 3   3   0.0400000000   3.8540000000 # c43
pair_coeff 4   4   0.0230000000   2.8780000000 # h1
pair_coeff 5   5   0.0620000000   3.8540000000 # c4

bond_style      class2
bond_coeff   1     1.5300   299.6700  -501.7700   679.8100 # c4-c44
bond_coeff   2     1.1010   345.0000  -691.8900   844.6000 # c4-h1
bond_coeff   3     1.5300   299.6700  -501.7700   679.8100 # c4-c43
bond_coeff   4     1.1010   345.0000  -691.8900   844.6000 # c43-h1

angle_style     class2
angle_coeff   1   110.7700    41.4530   -10.6040     5.1290 # c44-c4-h1
angle_coeff   2   107.6600    39.6410   -12.9210    -2.4318 # h1-c4-h1
angle_coeff   3   112.6700    39.5160    -7.4430    -9.5583 # c4-c44-c4
angle_coeff   4   112.6700    39.5160    -7.4430    -9.5583 # c44-c4-c43
angle_coeff   5   110.7700    41.4530   -10.6040     5.1290 # c43-c4-h1
angle_coeff   6   112.6700    39.5160    -7.4430    -9.5583 # c4-c43-c4
angle_coeff   7   110.7700    41.4530   -10.6040     5.1290 # c4-c43-h1

dihedral_style  class2
dihedral_coeff   1     0.0000     0.0000     0.0316     0.0000    -0.1681     0.0000# h1-c4-c44-c4
dihedral_coeff   2     0.0000     0.0000     0.0514     0.0000    -0.1430     0.0000# c43-c4-c44-c4
dihedral_coeff   3     0.0000     0.0000     0.0514     0.0000    -0.1430     0.0000# c44-c4-c43-c4
dihedral_coeff   4     0.0000     0.0000     0.0316     0.0000    -0.1681     0.0000# c44-c4-c43-h1
dihedral_coeff   5     0.0000     0.0000     0.0316     0.0000    -0.1681     0.0000# h1-c4-c43-c4
dihedral_coeff   6    -0.1432     0.0000     0.0617     0.0000    -0.1530     0.0000# h1-c4-c43-h1

improper_style  class2
improper_coeff  1     0.0000     0.0000
improper_coeff  2     0.0000     0.0000
improper_coeff  3     0.0000     0.0000
improper_coeff  4     0.0000     0.0000
improper_coeff  5     0.0000     0.0000
improper_coeff  6     0.0000     0.0000
improper_coeff  7     0.0000     0.0000

angle_coeff  1  bb       3.3872     1.5300     1.1010
angle_coeff  2  bb       5.3316     1.1010     1.1010
angle_coeff  3  bb       0.0000     1.5300     1.5300
angle_coeff  4  bb       0.0000     1.5300     1.5300
angle_coeff  5  bb       3.3872     1.5300     1.1010
angle_coeff  6  bb     0.0000     1.5300     1.5300
angle_coeff  7  bb     3.3872     1.5300     1.1010

angle_coeff  1  ba      20.7540    11.4210     1.5300     1.1010
angle_coeff  2  ba      18.1030    18.1030     1.1010     1.1010
angle_coeff  3  ba       8.0160     8.0160     1.5300     1.5300
angle_coeff  4  ba       8.0160     8.0160     1.5300     1.5300
angle_coeff  5  ba      20.7540    11.4210     1.5300     1.1010
```

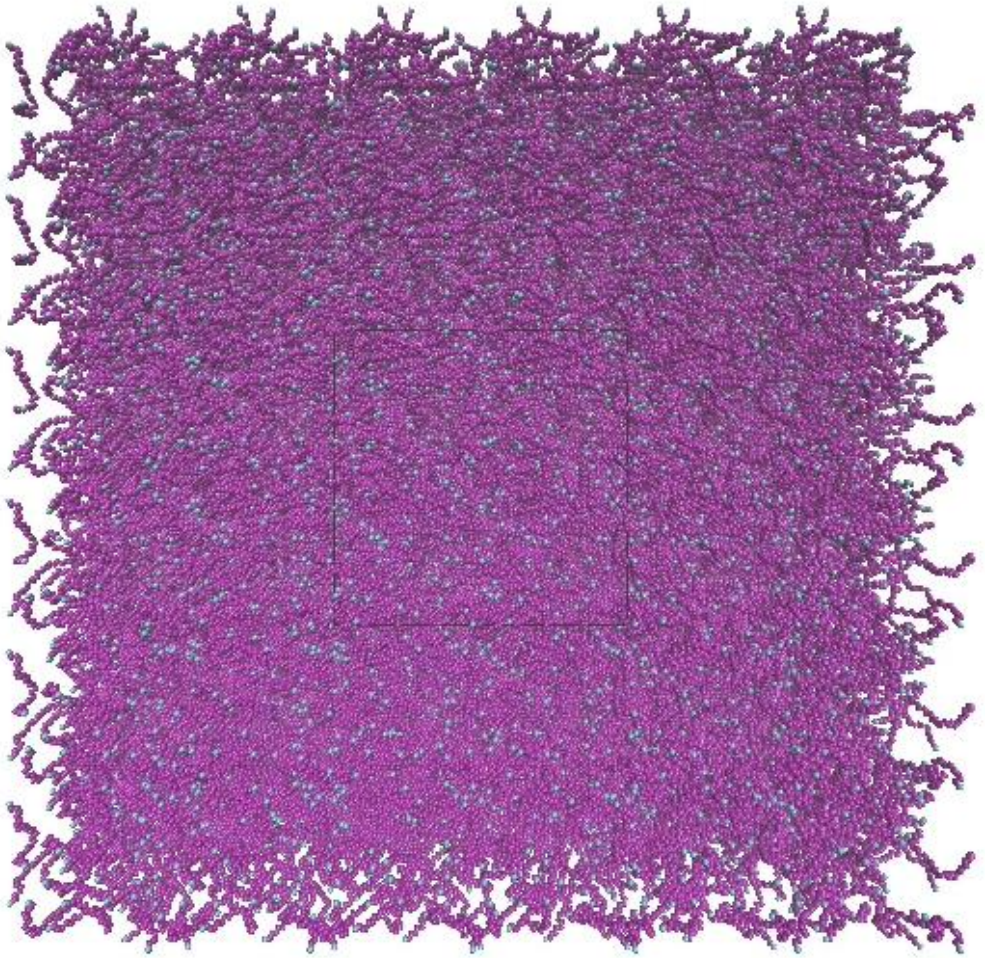
```
angle_coeff  4  ba       8.0160     8.0160     1.5300     1.5300
angle_coeff  5  ba      20.7540    11.4210     1.5300     1.1010
angle_coeff  6  ba       8.0160     8.0160     1.5300     1.5300
angle_coeff  7  ba      20.7540    11.4210     1.5300     1.1010

improper_coeff  1 aa       0.2738    -0.4825     0.2738   110.7700   107.6600   110.77
improper_coeff  2 aa      -0.3157    -0.3157    -0.3157   107.6600   107.6600   107.66
improper_coeff  3 aa      -0.1729    -0.1729    -0.1729   112.6700   112.6700   112.67
improper_coeff  4 aa      -1.3199    -1.3199     0.1184   112.6700   110.7700   110.77
improper_coeff  5 aa       0.2738    -0.4825     0.2738   110.7700   107.6600   110.77
improper_coeff  6 aa      -0.1729    -0.1729    -0.1729   112.6700   112.6700   112.67
improper_coeff  7 aa      -1.3199    -1.3199     0.1184   112.6700   110.7700   110.77

dihedral_coeff  1 aat    -16.1640   110.7700   112.6700
dihedral_coeff  2 aat    -22.0450   112.6700   112.6700
dihedral_coeff  3 aat    -22.0450   112.6700   112.6700
dihedral_coeff  4 aat    -16.1640   112.6700   110.7700
dihedral_coeff  5 aat    -16.1640   110.7700   112.6700
dihedral_coeff  6 aat    -12.5640   110.7700   110.7700

dihedral_coeff  1 ebt      0.0814     0.0591     0.2219     0.2486     0.2422    -0.09
dihedral_coeff  2 ebt     -0.0732     0.0000     0.0000    -0.0732     0.0000     0.00
dihedral_coeff  3 ebt     -0.0732     0.0000     0.0000    -0.0732     0.0000     0.00
dihedral_coeff  4 ebt      0.2486     0.2422    -0.0925     0.0814     0.0591     0.22
dihedral_coeff  5 ebt      0.0814     0.0591     0.2219     0.2486     0.2422    -0.09
dihedral_coeff  6 ebt      0.2130     0.3120     0.0777     0.2130     0.3120     0.07

dihedral_coeff  1 mbt    -14.8790    -3.6581    -0.3138     1.5300
dihedral_coeff  2 mbt    -17.7870    -7.1877     0.0000     1.5300
dihedral_coeff  3 mbt    -17.7870    -7.1877     0.0000     1.5300
dihedral_coeff  4 mbt    -14.8790    -3.6581    -0.3138     1.5300
dihedral_coeff  5 mbt    -14.8790    -3.6581    -0.3138     1.5300
dihedral_coeff  6 mbt    -14.2610    -0.5322    -0.4864     1.5300

dihedral_coeff  1  bb13      0.0000     1.1010     1.5300
dihedral_coeff  2  bb13      0.0000     1.5300     1.5300
dihedral_coeff  3  bb13      0.0000     1.5300     1.5300
dihedral_coeff  4  bb13      0.0000     1.5300     1.1010
dihedral_coeff  5  bb13      0.0000     1.1010     1.5300
dihedral_coeff  6  bb13      0.0000     1.1010     1.1010

dihedral_coeff  1 at      0.3113     0.4516    -0.1988    -0.2454     0.0000    -0.11
dihedral_coeff  2 at      0.3886    -0.3139     0.1389     0.3886    -0.3139     0.13
dihedral_coeff  3 at      0.3886    -0.3139     0.1389     0.3886    -0.3139     0.13
dihedral_coeff  4 at     -0.2454     0.0000    -0.1136     0.3113     0.4516    -0.19
dihedral_coeff  5 at      0.3113     0.4516    -0.1988    -0.2454     0.0000    -0.11
dihedral_coeff  6 at     -0.8085     0.5569    -0.2466    -0.8085     0.5569    -0.24
```

Система

Потенциал объединенного атома

- CH_3
- CH_2
- Центры масс

$\langle \Delta r^2 \rangle$ $\langle v(0)v(t) \rangle$



P ~ 1 atm T = 360 ÷ 500 K

L = 19.2 nm N = 800k

*LAMMPS

Среднеквадратичные смещения

Ballistic regime

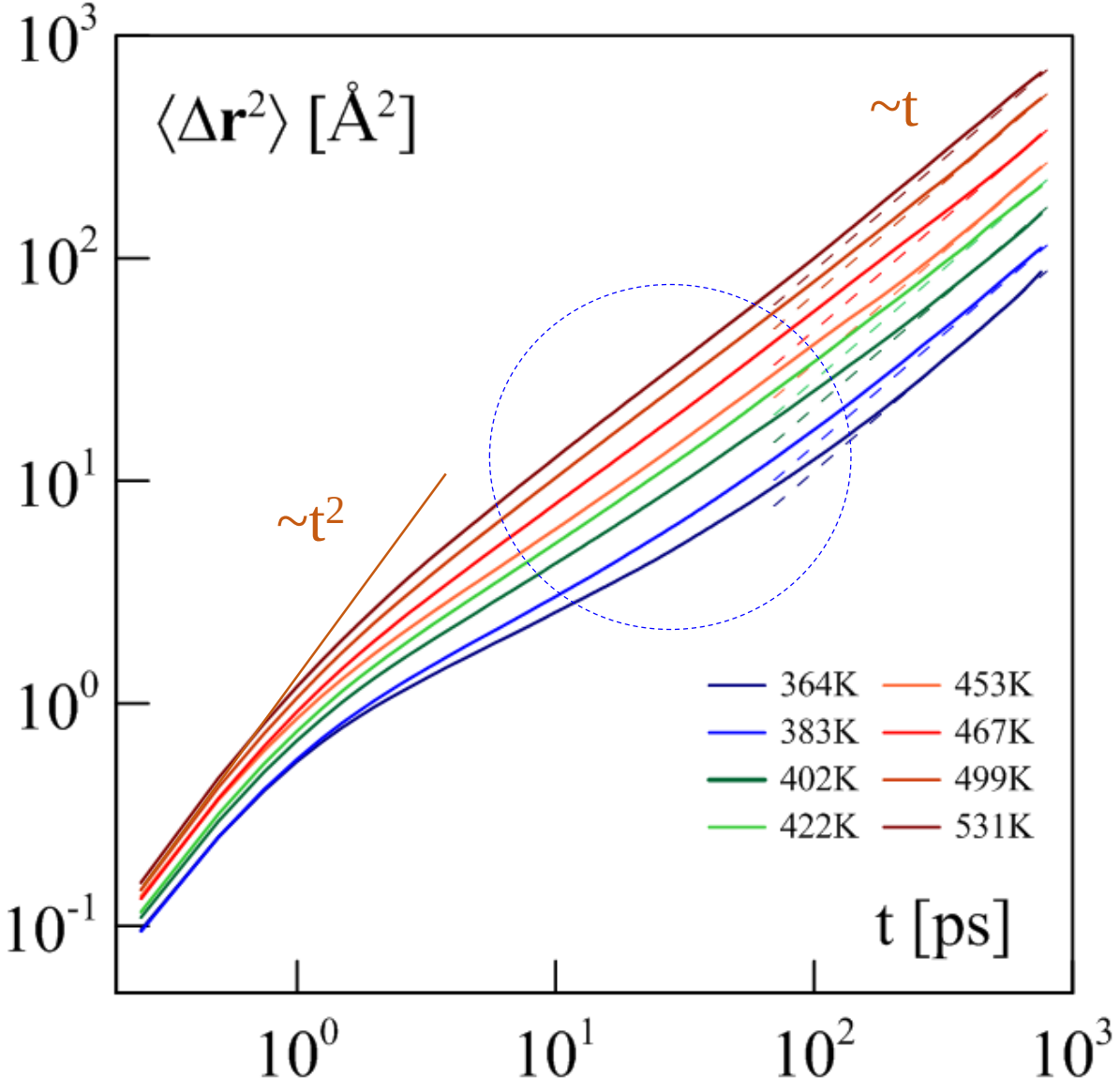
$$\langle \Delta r^2 \rangle = v^2 t^2$$

Subdiffusive regime

$$\langle \Delta r^2 \rangle \sim t^{\alpha},\ \alpha < 1$$

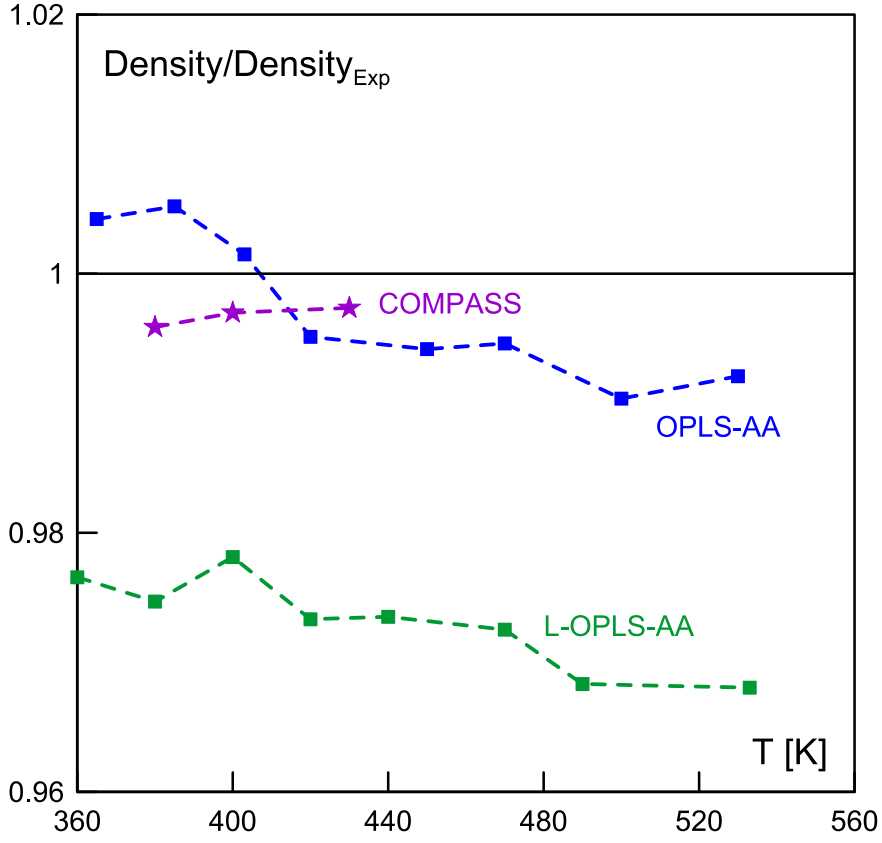
Diffusive regime

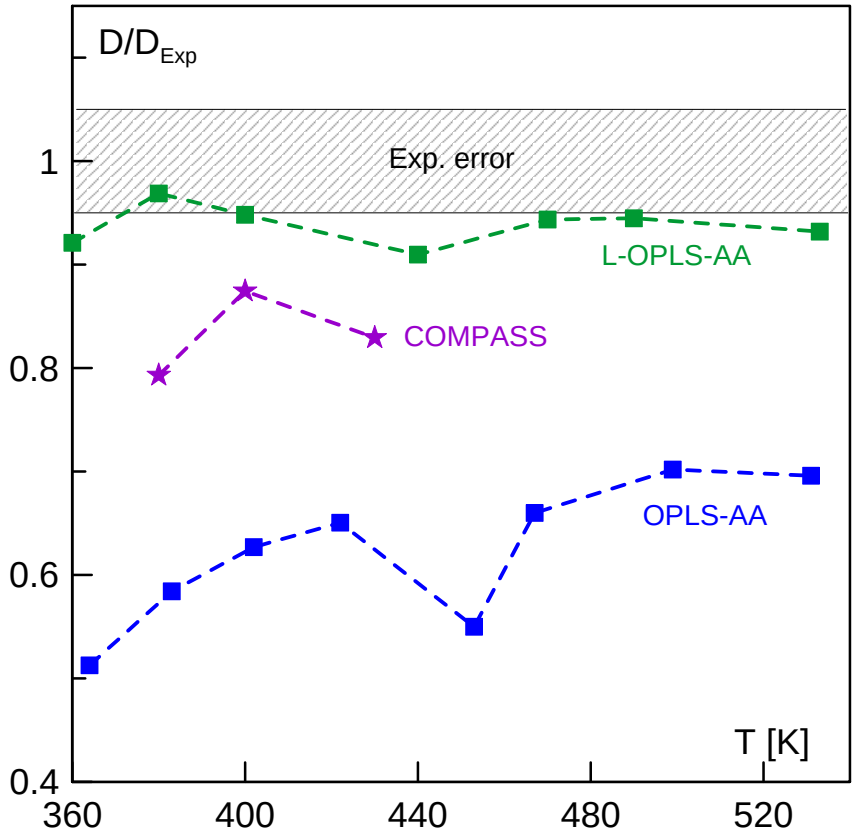
$$\langle \Delta r^2 \rangle = 6Dt$$



Предсказательная способность

Kondratyuk N., Norman G. and Stegailov V. *J. Chem. Phys.*, 2016, **145**, 204504.





COMPASS (модель класса 2): **корректные** плотность и диффузия

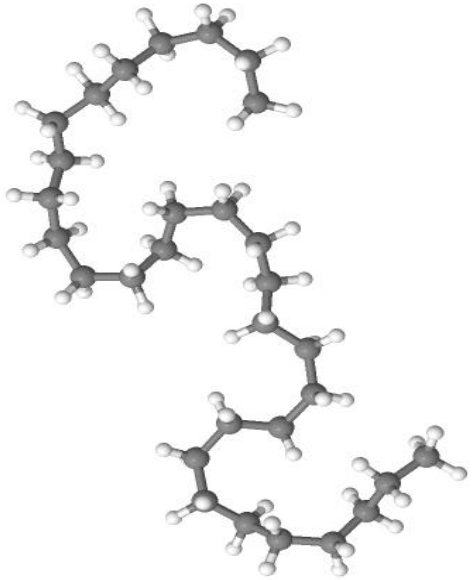
* В.М. Татаевский. Физико-химические свойства индивидуальных углеводородов. Москва: ГОСТТОПТЕХИЗДАТ, 1960. 413 с.

**T. Vardag, N. Karger, H.D. Lüdemann // Ber. Bunsenges. Phys. Chem. 1991. V. 95. N. 8. P. 859.

План доклада

n-$C_{30}H_{62}$

1. Самодиффузия в жидком н-триаконтане



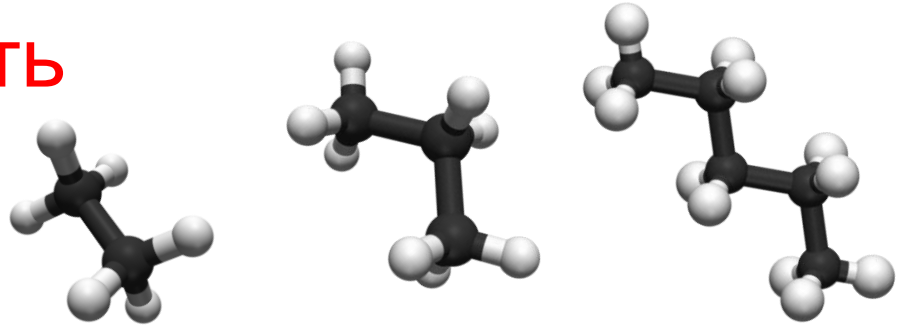
Молекула н-триаконтана

Потенциалы взаимодействия (+ COMPASS)

Сходимость Г-К

Предсказательная способность

2. Сдвиговая вязкость



Сходимость Г-К

Неравновесная МД + эксперимент

Мотивация

1. РНФ 17-79-20391 (В.В. Писарев)

Атомистическое и многомасштабное моделирование фильтрации флюидов в пористой среде

2. “Старые счеты”: проблемы со сходимостью Г-К

Table 1. Physical properties for the different models at 353 K and 0.775 g/cm^3.

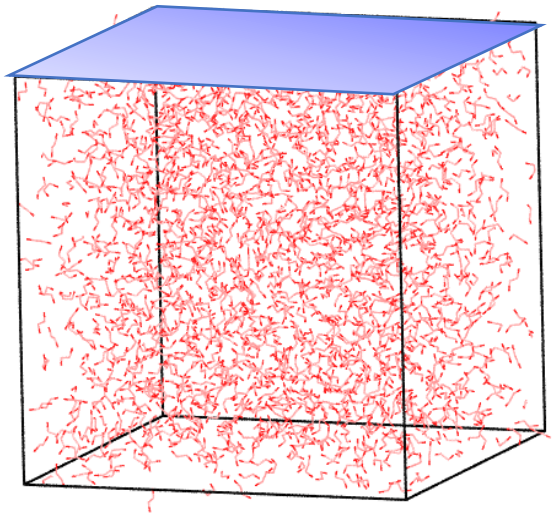
Model	TraPPE	DREIDING	OPLS	Exp
Pressure, bar	1	4200	1	1
Shear viscosity, mPa s	0.96	4.33	—	4.87 [22]

Kondratyuk, N. D., Lankin, A. V, Norman, G. E. and Stegailov, V. V. (**2015**). J. Phys. Conf. Ser. *653.* 12107.

Метод Грина-Кубо для вязкости

$$\eta_{\alpha\beta} = \frac{V}{k_B T} \int_0^\infty C_\sigma(t) dt$$

$\sigma_{\alpha\beta}$



$$C_\sigma(t) = \langle \sigma_{\alpha\beta}(0) \sigma_{\alpha\beta}(t) \rangle$$

$$\sigma_{\alpha\beta} V = \sum_{i=1}^{N} m_i v_{i_\alpha} v_{i_\beta} + \sum_{i=1}^{N} r_{i_\alpha} f_{i_\beta}$$

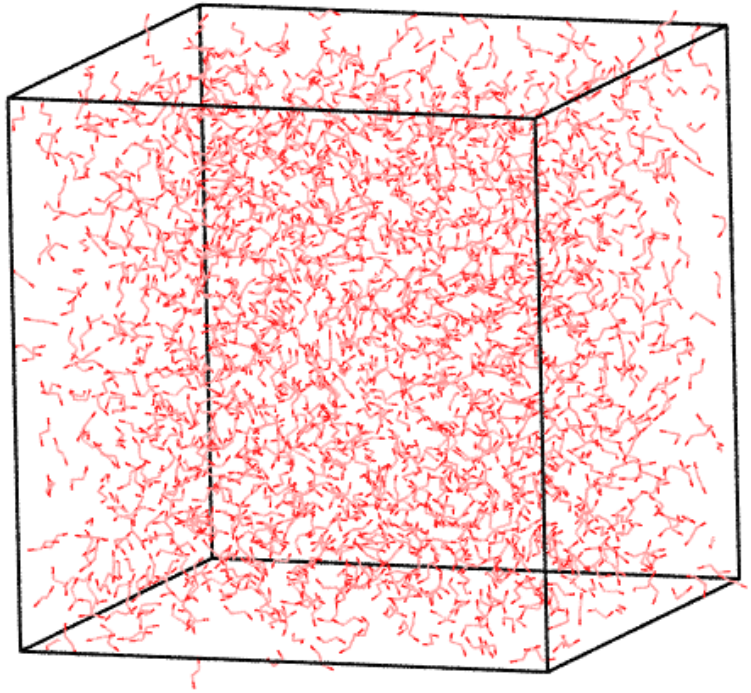
Рассматриваемые системы

Этан, пропан, бутан, пентан

Потенциал OPLS-AA (полноатомный)

NVE, интегратор rRESPA
(1 фс – шаг для электростатики и LJ)

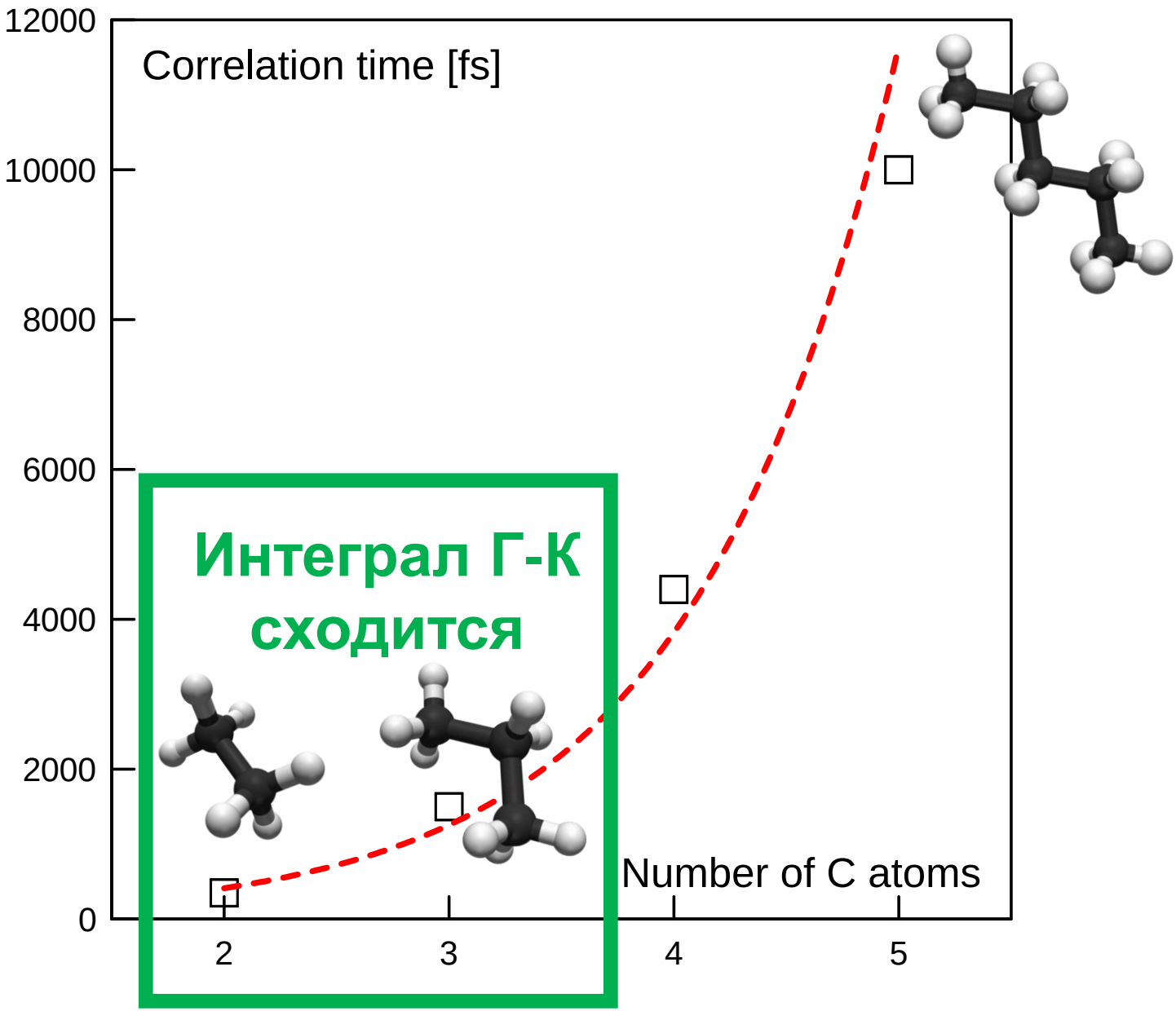
Длины траекторий - 6 нс



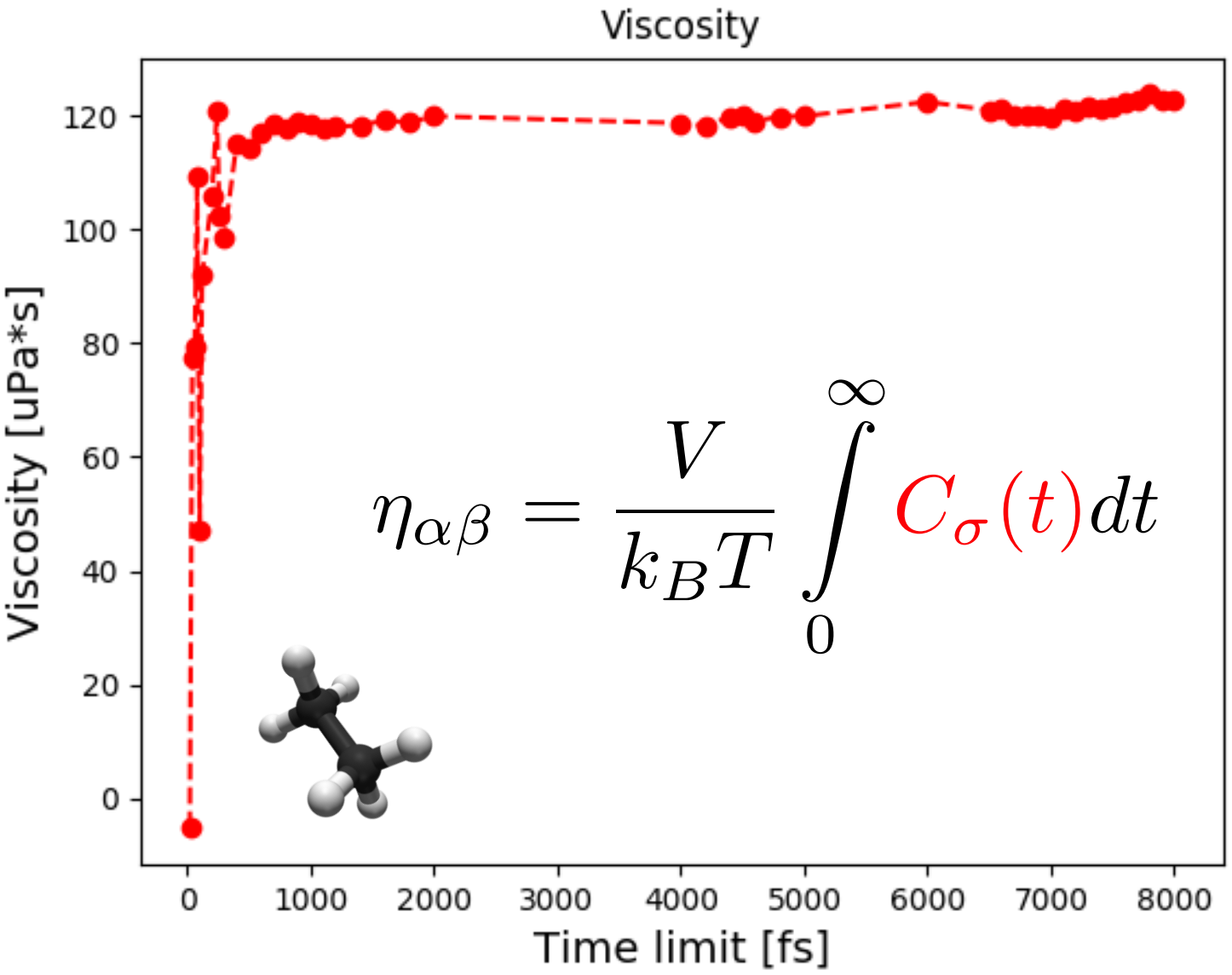
T = 330 K ρ = 0.5 g/cm^3

L ~ 6 nm N = 80k

Время затухания АКФ



Сходимость интеграла Грина-Кубо



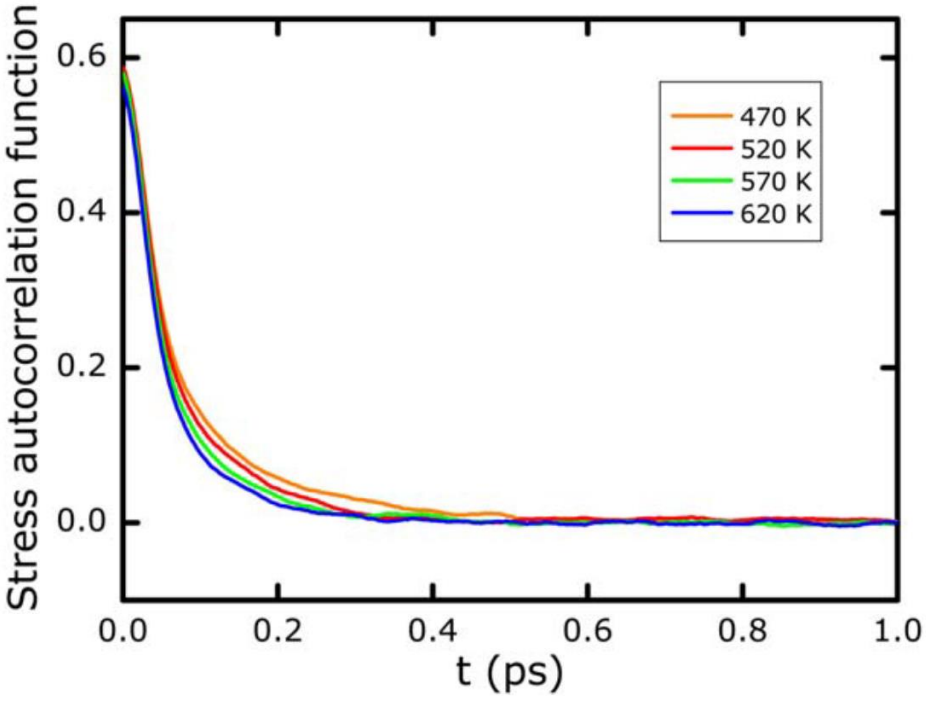
$$\eta_{\alpha\beta} = \frac{V}{k_B T} \int_0^\infty C_\sigma(t) dt$$

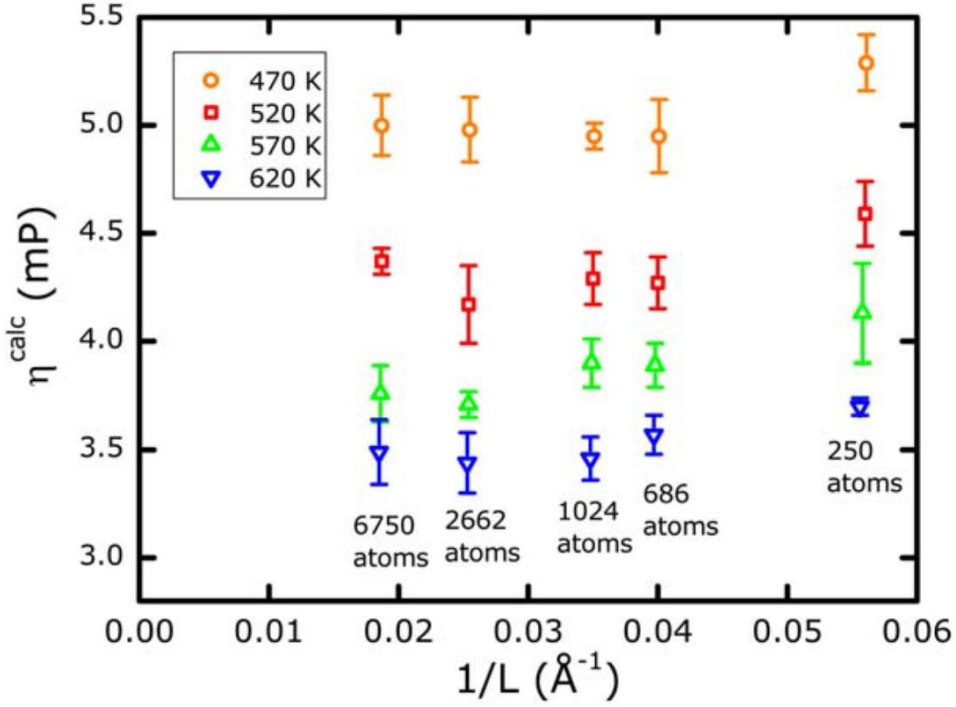
Сходимость интеграла Грина-Кубо

Chen, M. , Vella, J. R., Panagiotopoulos, A. Z., Debenedetti, P. G., Stillinger, F. H. and Carter, E. A.

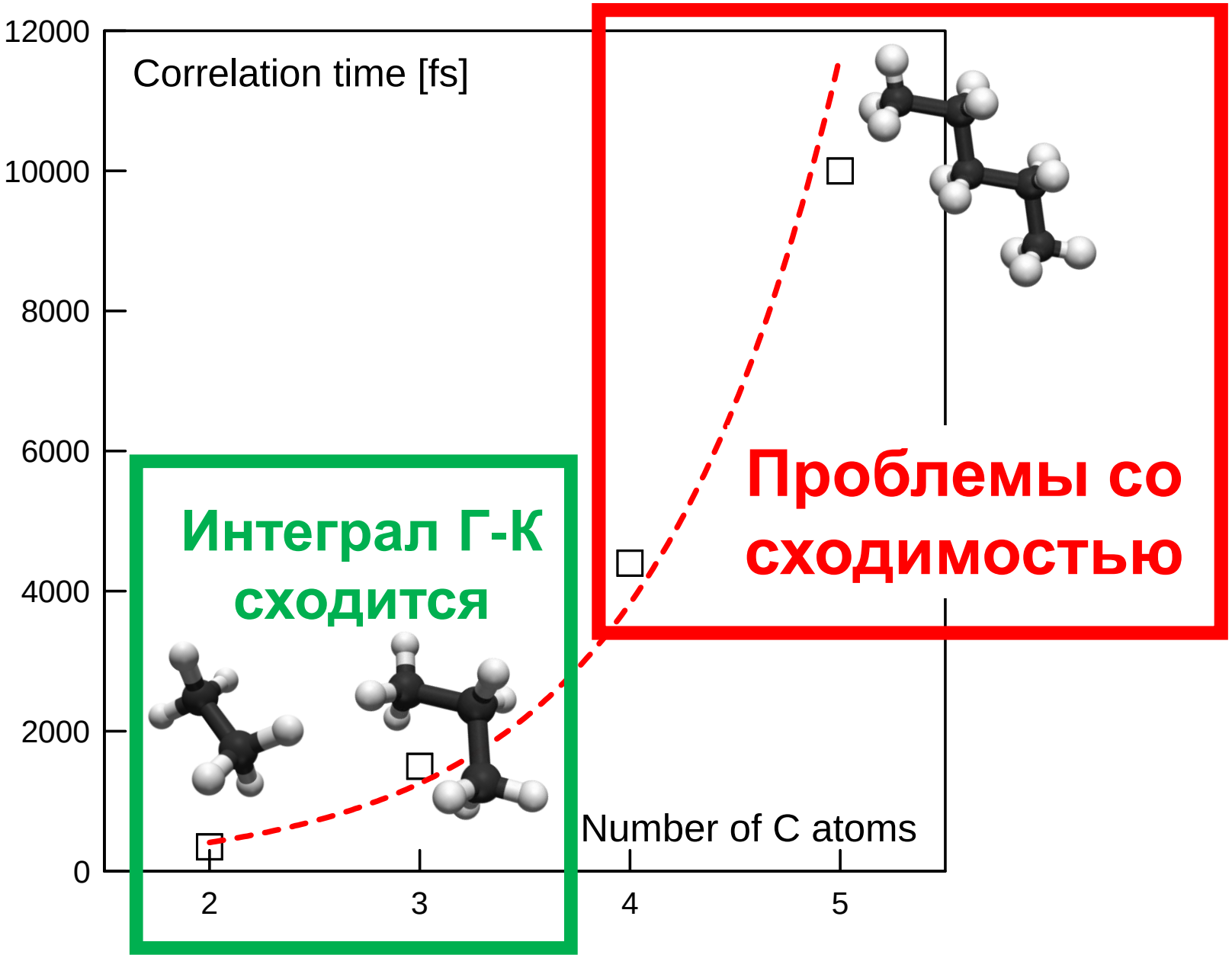
Liquid Li structure and dynamics: A comparison between OFDFT and second nearest-neighbor embedded-atom method.

AIChE J., (**2015**), 61: 2841-2853

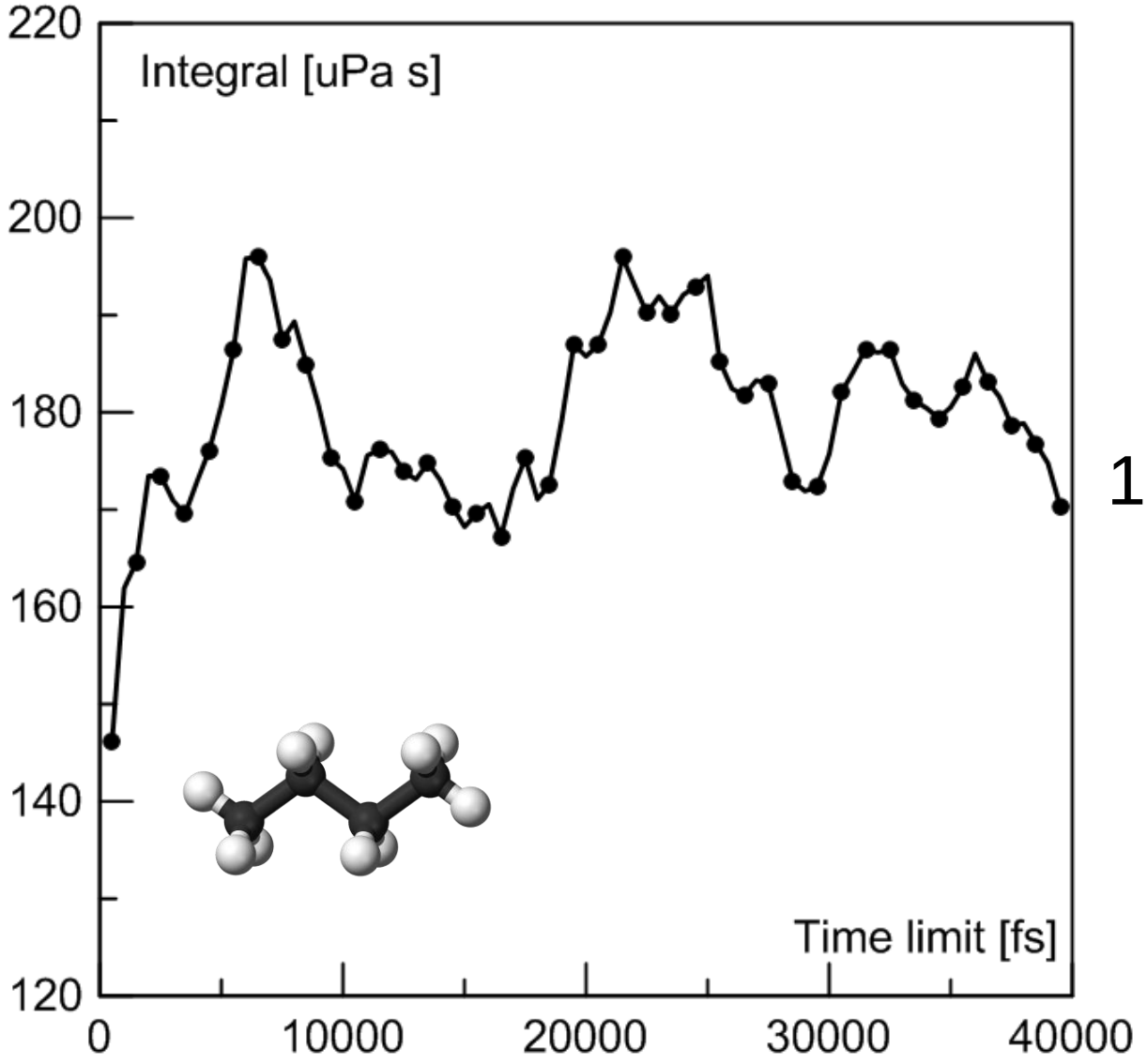




Время затухания АКФ

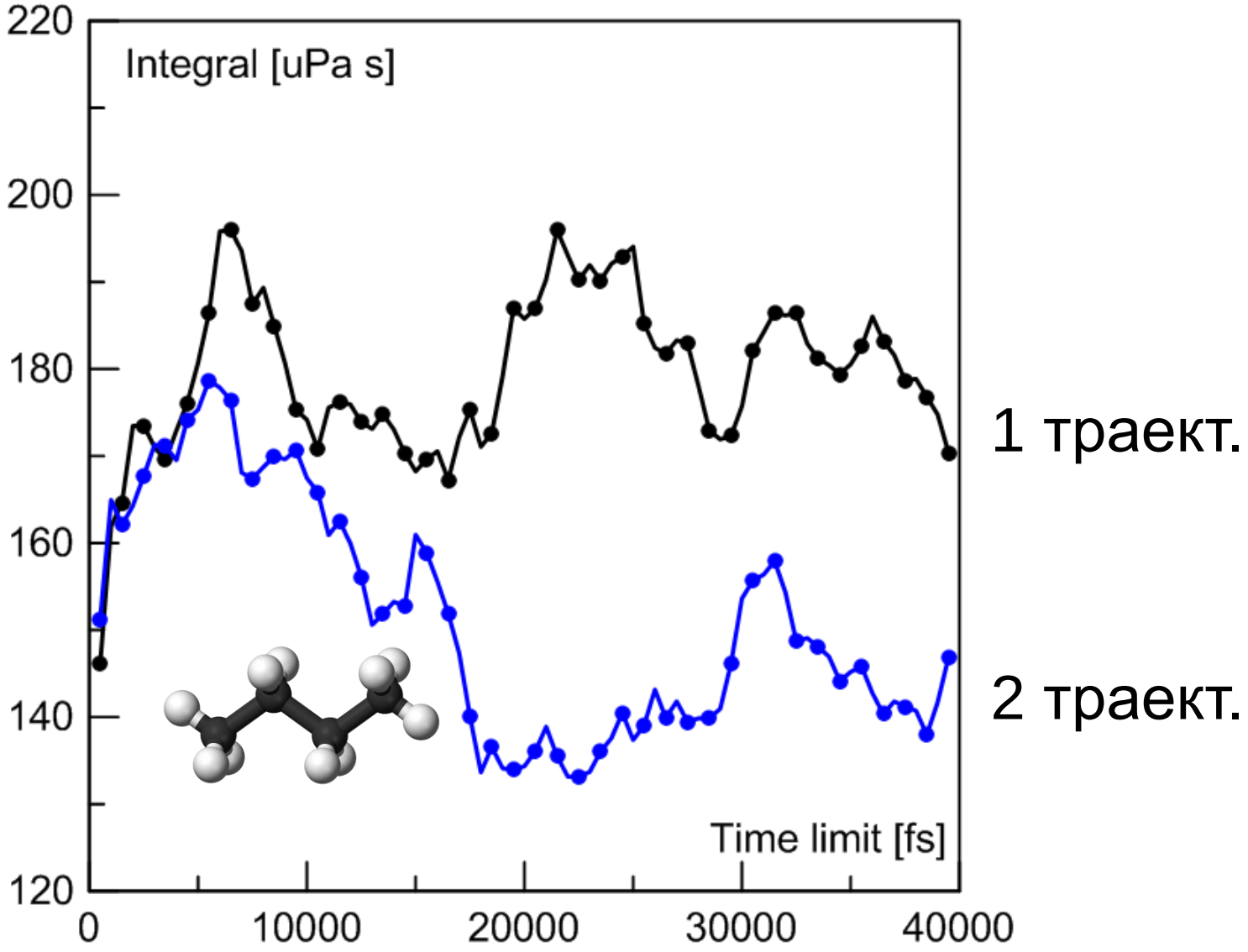


Сходимость интеграла Грина-Кубо

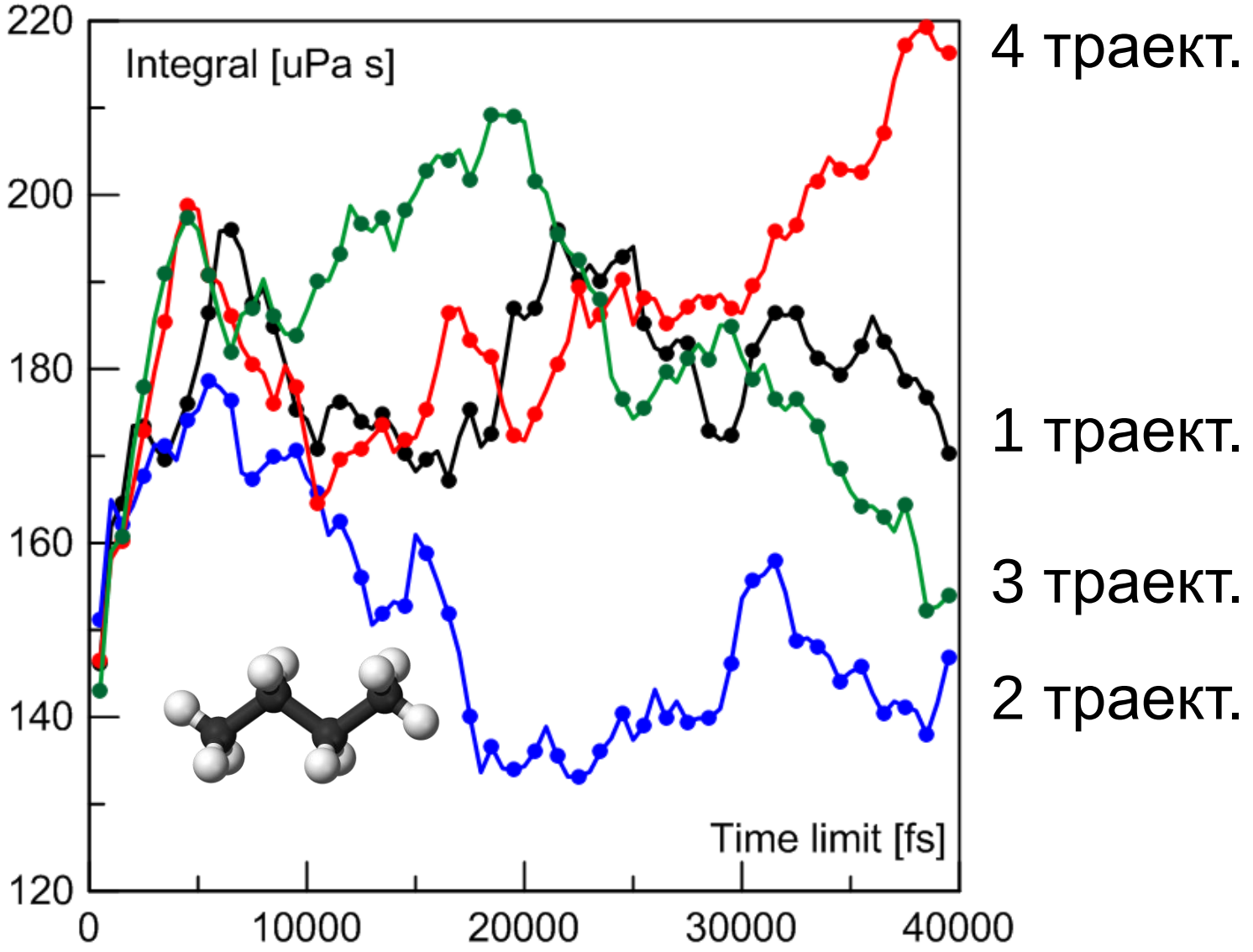


1 траект.

Сходимость интеграла Грина-Кубо

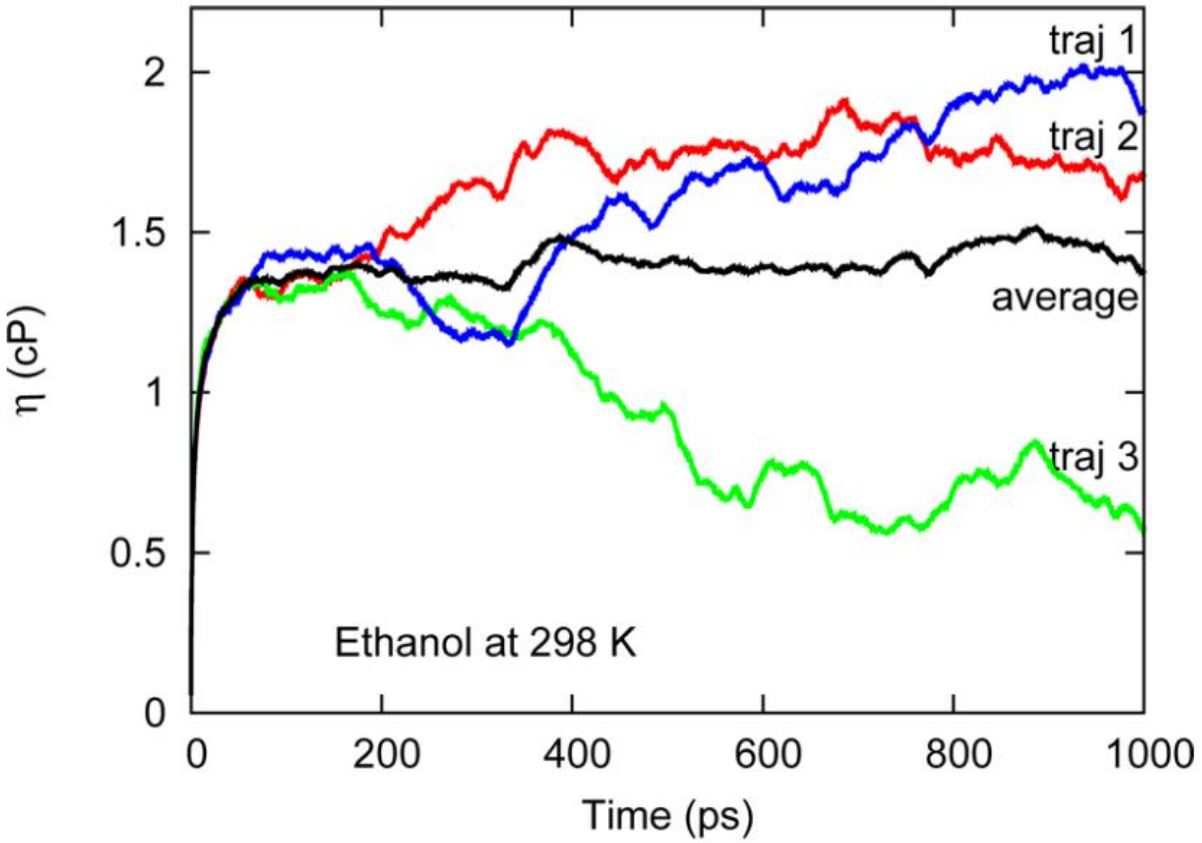


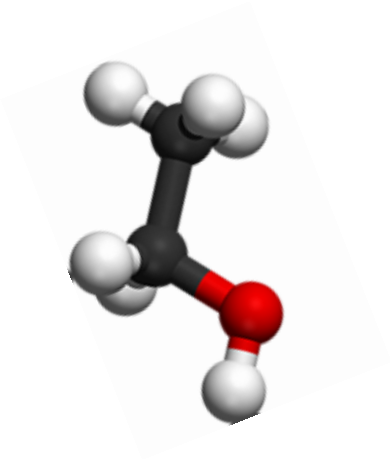
Сходимость интеграла Грина-Кубо



Сходимость интеграла Грина-Кубо

Zhang, Y., Otani, A. and Maginn, E. J.
Reliable Viscosity Calculation from Equilibrium Molecular Dynamics Simulations: A Time Decomposition Method.
J. Chem. Theory Comput., (**2015**), *11*(8), 3537–3546.





Time decomposition method

(1) Generate N independent NVT trajectories at a given temperature;

(2) For each trajectory, calculate the shear viscosity based on the Green−Kubo relation (eq 1);

(3) Calculate the average of the running integrals over N trajectories $\langle \eta(t) \rangle$ and the standard deviation, which is a function of time:

$$\sigma(t) = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (\eta(t)_i - \langle \eta(t) \rangle)^2}$$

Zhang, Y., Otani, A. and Maginn, E. J. (**2015**). *J. Chem. Theory Comput.*, *11*(8), 3537.

Time decomposition method

(4) Fit the standard deviation to a power law function

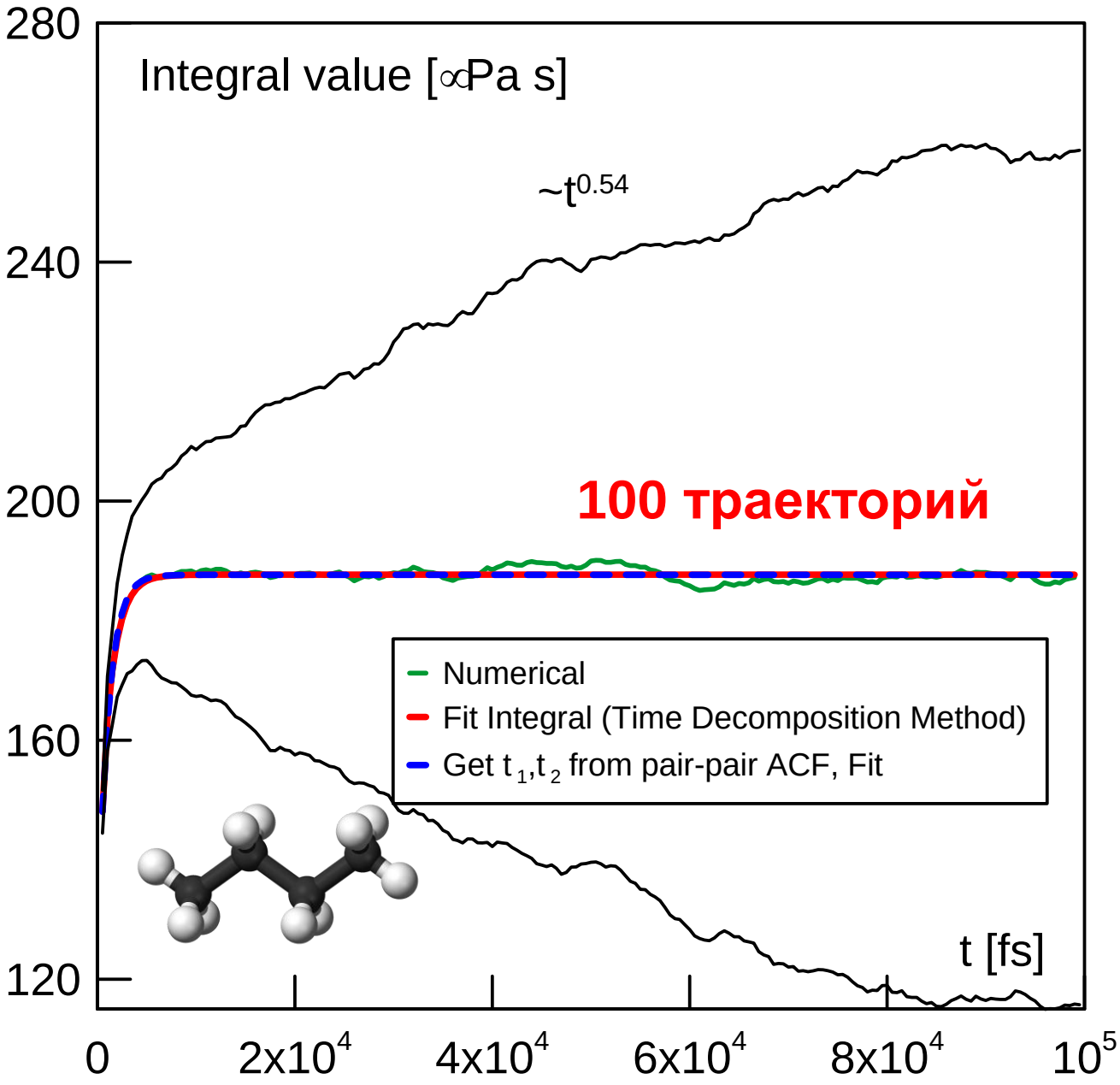
$$\sigma(t) = At^b \tag{4}$$

(5) Fit the averaged running integral by the double-exponential function (eq 2) for the time period up to t_{cut} with the weight $1/t^b$, where b is the fitting result from step (4) and t_{cut} can be decided from the relation between η and $\sigma(t)$. We found that the time when $\sigma(t)$ is about 40% of $\langle\eta(t)\rangle$ is a good choice. Take the long time limit of the fitted double-exponential function as the calculated viscosity;

$$\eta(t) = A\alpha\tau_1(1 - e^{-t/\tau_1}) + A(1 - \alpha)\tau_2(1 - e^{-t/\tau_2})$$

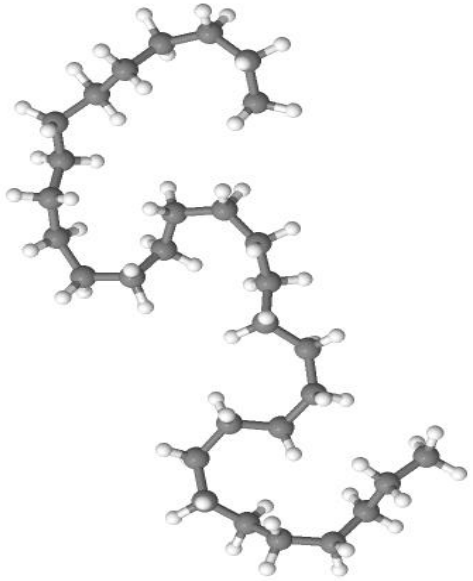
Zhang, Y., Otani, A. and Maginn, E. J. (**2015**). *J. Chem. Theory Comput.*, *11*(8), 3537.

Time decomposition method



План доклада

n-$C_{30}H_{62}$



Молекула н-триаконтана

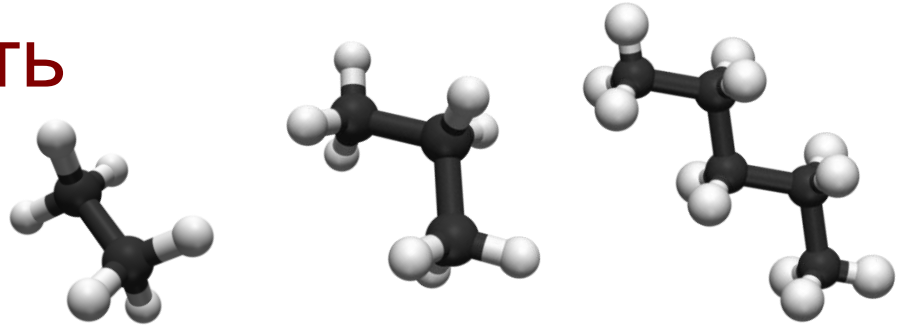
1. Самодиффузия в жидком н-триаконтане

Потенциалы взаимодействия (+ COMPASS)

Сходимость Г-К

Предсказательная способность

2. Сдвиговая вязкость



Сходимость Г-К

Неравновесная МД + эксперимент

Метод неравновесной МД

Поток импульса

$$\eta = \frac{j_z(p_x)}{\partial v_x / \partial z}$$

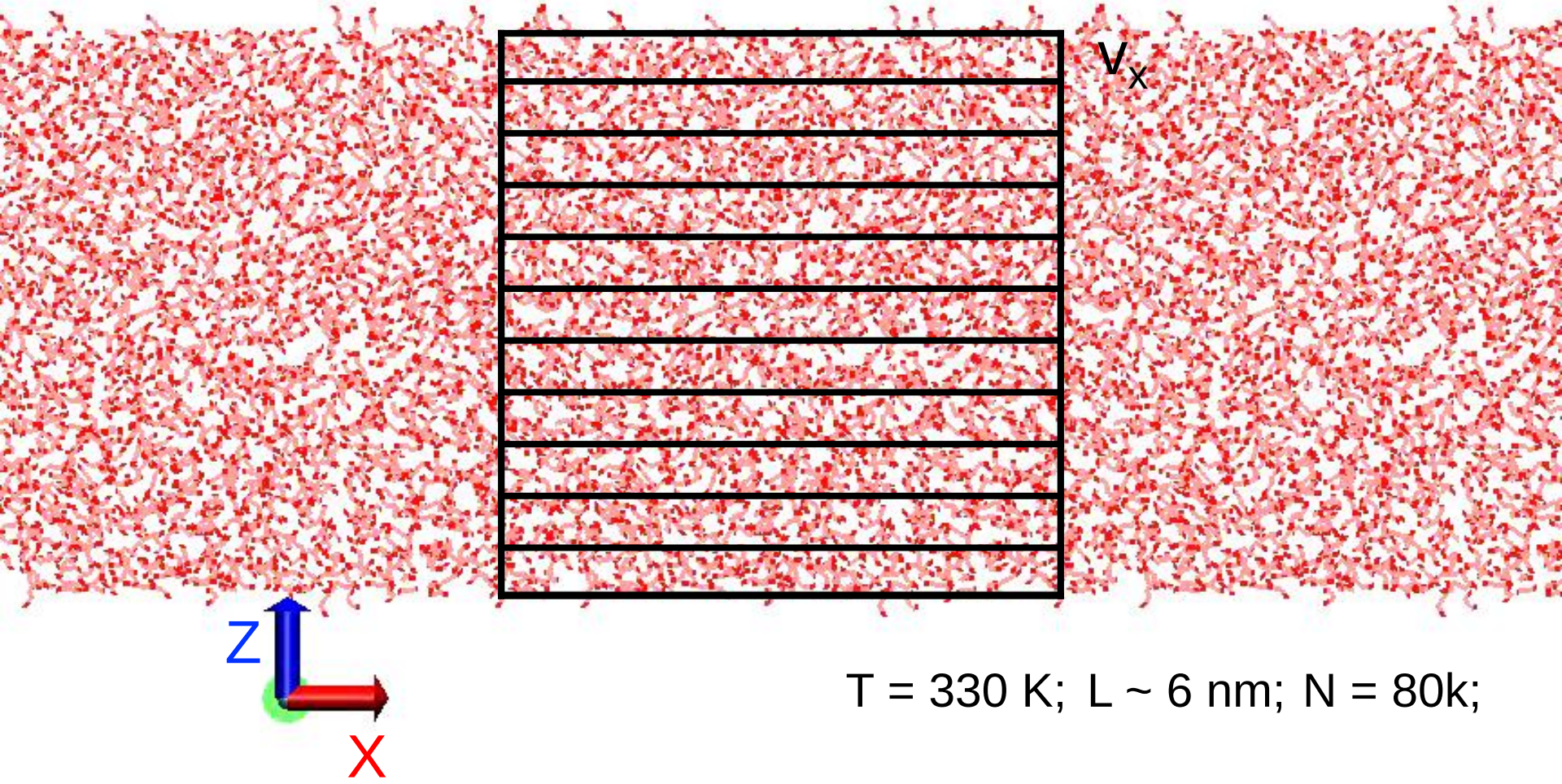
Профиль скорости

На практике: обмен скоростями V_x каждые N шагов

(Muller-Plathe) Muller-Plathe, Phys Rev E, 59, 4894-4898 (**1999**).

Метод неравновесной МД

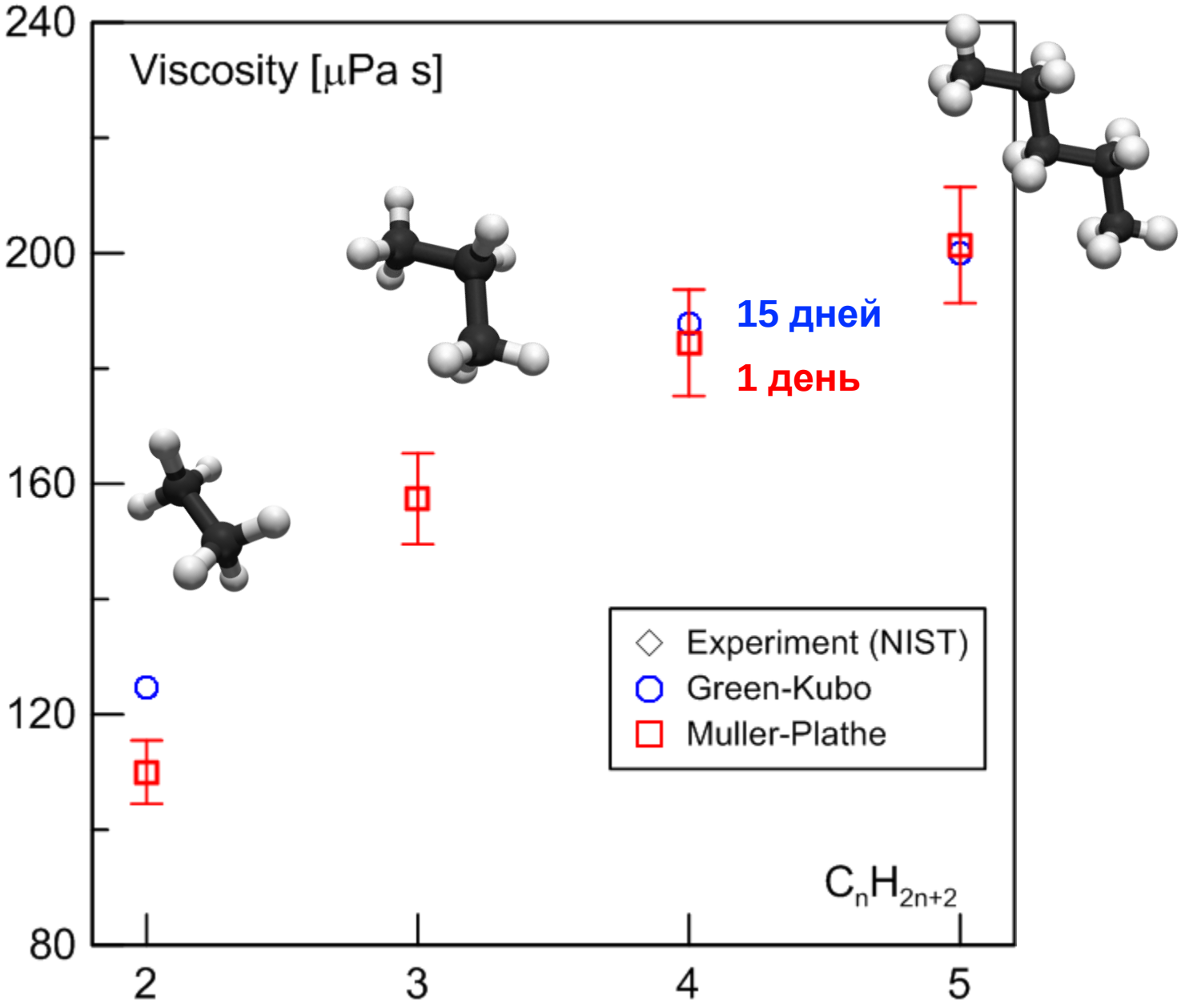
1 расчет = 1 день на узле Desmos (Intel Xeon E5-1650 v3 + NVIDIA GTX 1070)



T = 330 K; L ~ 6 nm; N = 80k;

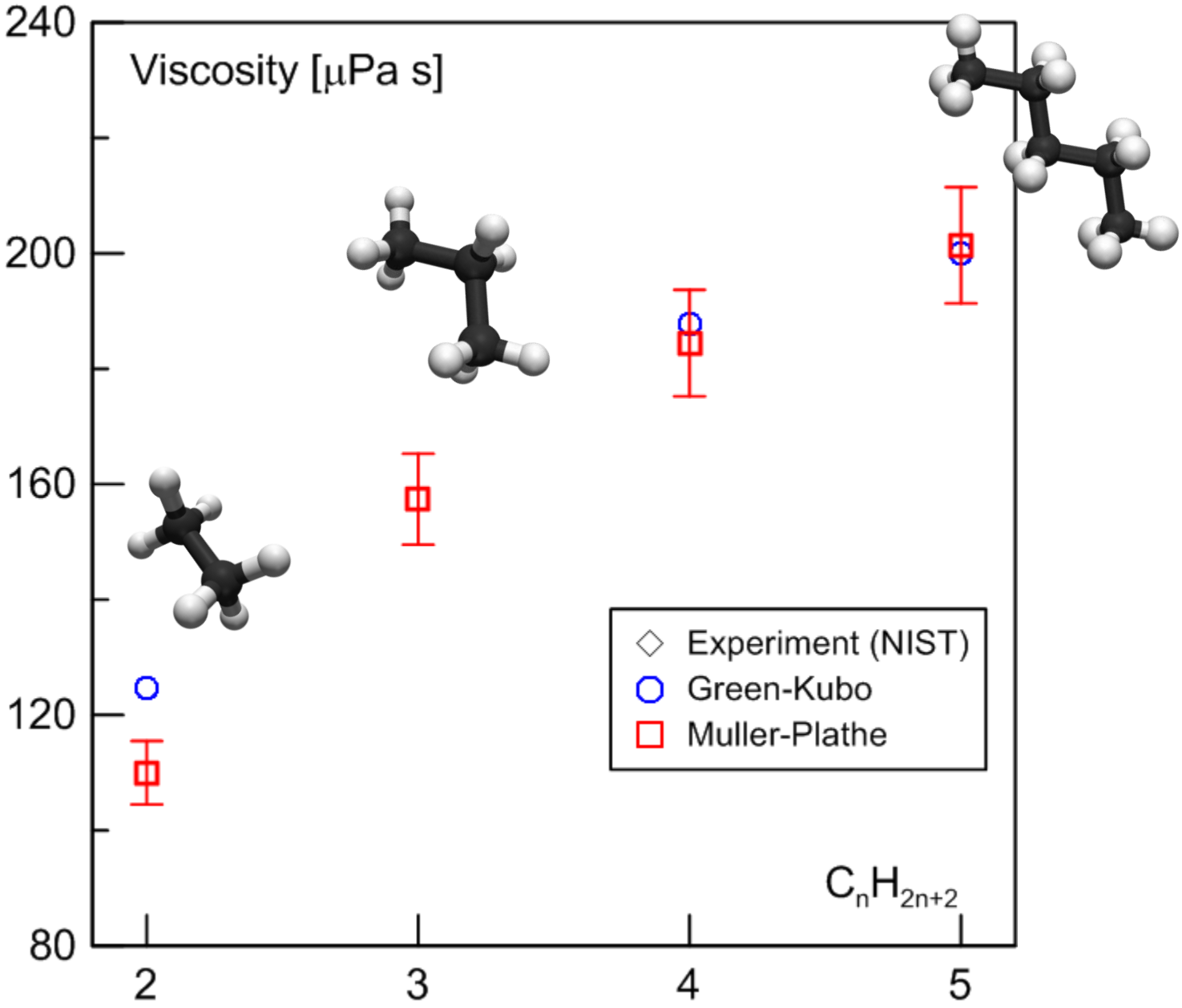
(Muller-Plathe) Muller-Plathe, Phys Rev E, 59, 4894-4898 (**1999**).

Результаты расчета

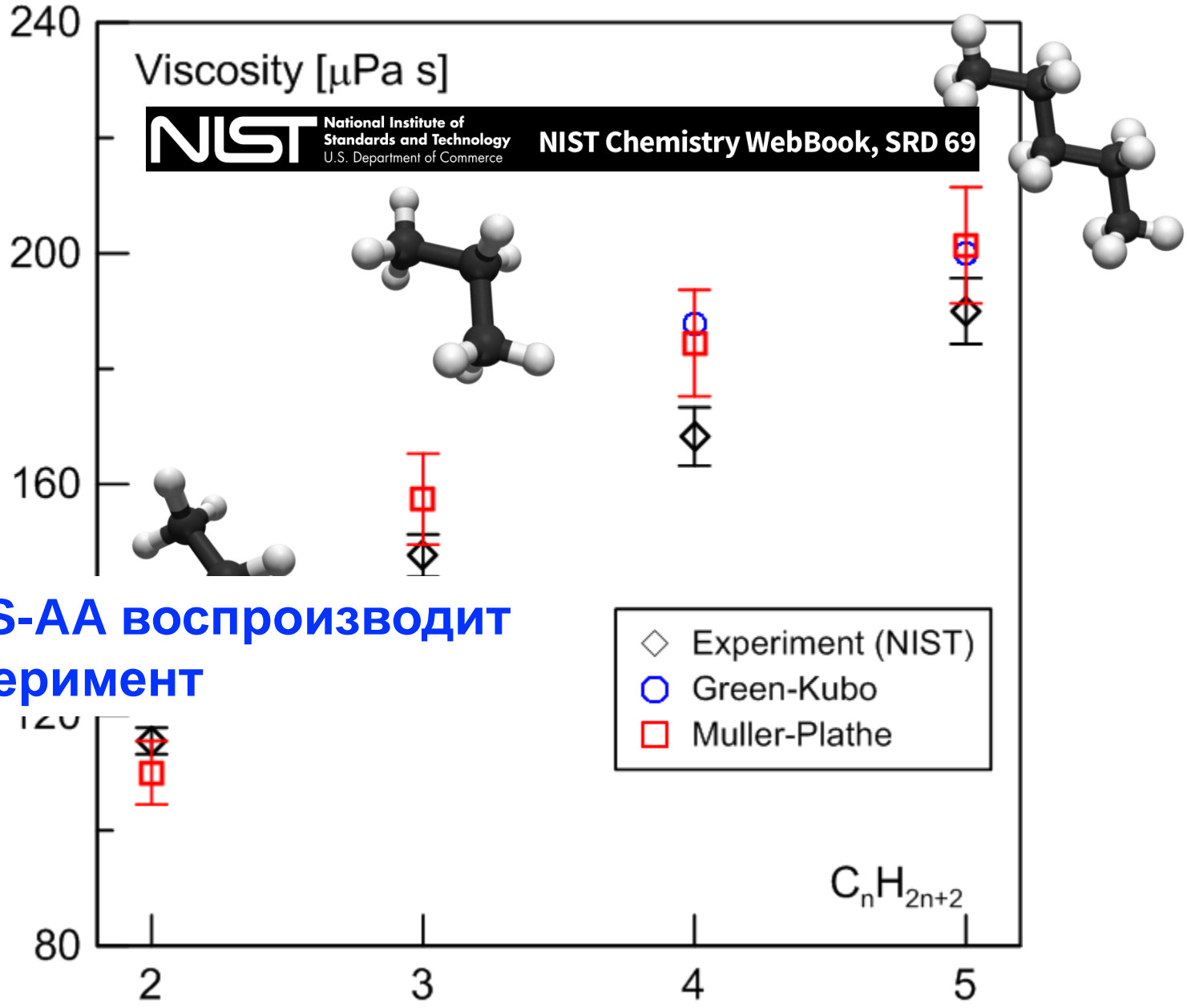


Сравнение с экспериментом

Результаты расчета



Результаты расчета



OPLS-AA воспроизводит эксперимент

Выводы

Степень скорелированности **определяет сложность** расчета транспортных коэффициентов

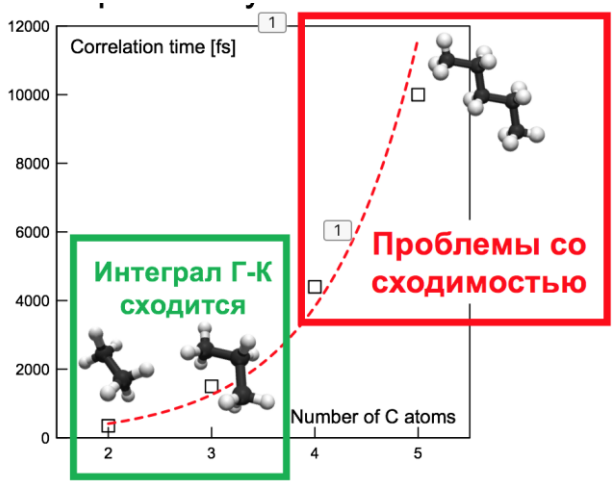
$$\int_{t=0}^{2ps} C_V(t)\,dt/3$$

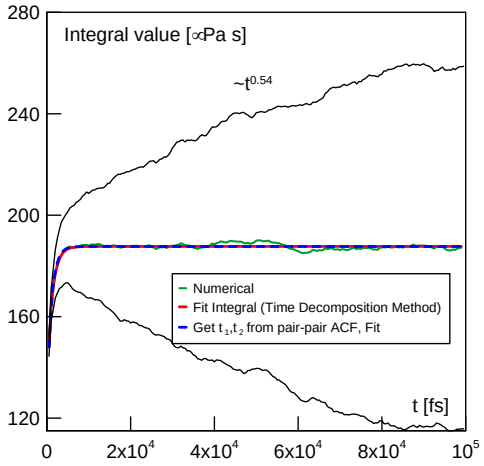
$$=$$

$$D=D_n+D_a$$

$$=$$

$$\int_{t=2ps}^{\infty} At^{-\beta}\,dt$$

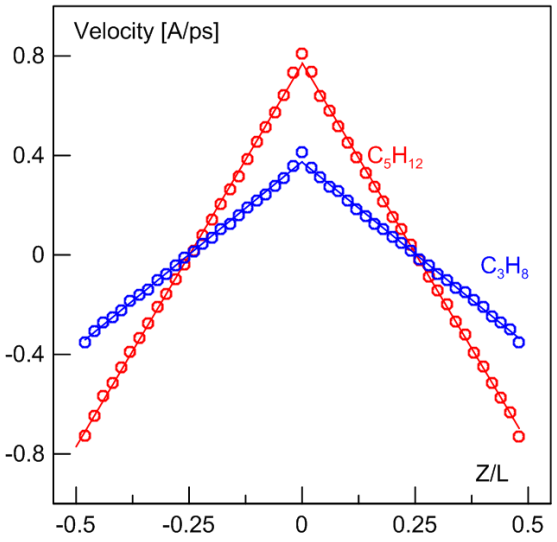


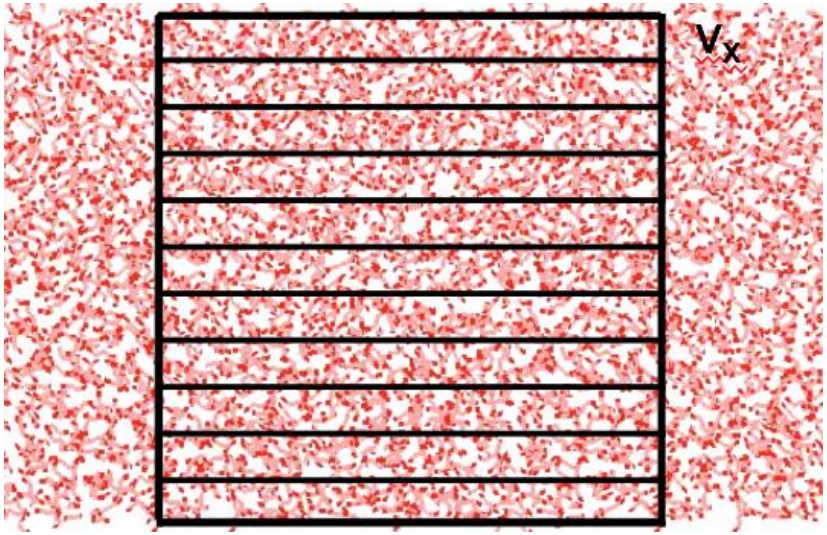


Выводы

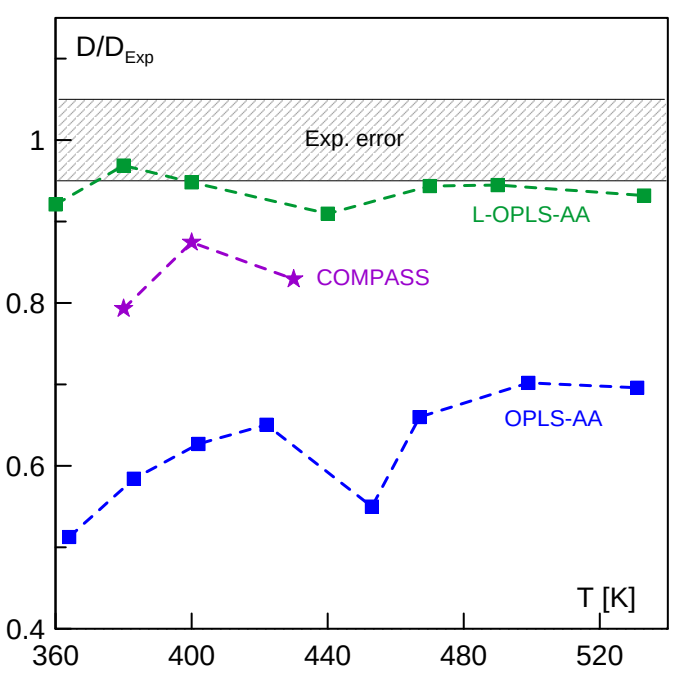
Степень скореллированости **определяет сложность** расчета транспортных коэффициентов

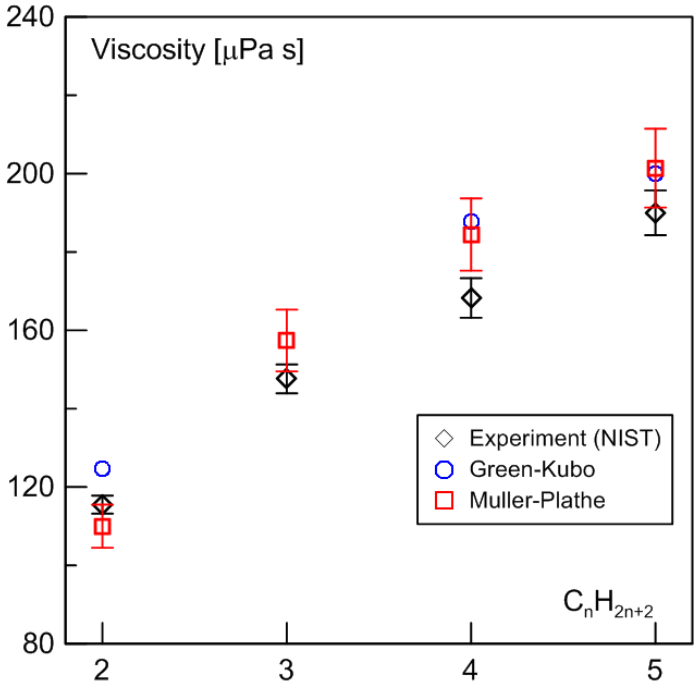
Методы **неравновесной МД** требуют на порядок меньших времен расчета





Выводы





Полноатомные модели позволяют рассчитывать диффузию и вязкость с **хорошей точностью**

Выводы

Степень корреляции **определяет сложность** расчета транспортных коэффициентов

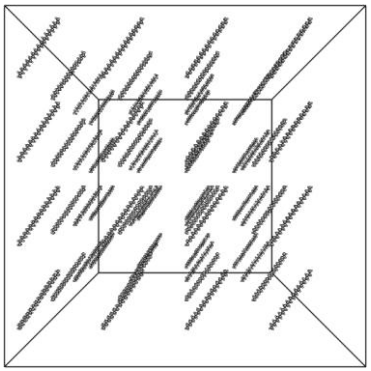
Методы **неравновесной МД** требуют на порядок меньших времен расчета

Полноатомные модели позволяют рассчитывать диффузию и вязкость с **хорошей точностью**

Работа выполнена при поддержке грантов РНФ 14-50-00124 и 17-79-20391, а также программы «5-100» НИУ ВШЭ.

Preparing the system

Initial configuration*



$r_{intermolec} > r_{cut}$ (12 A)

1.

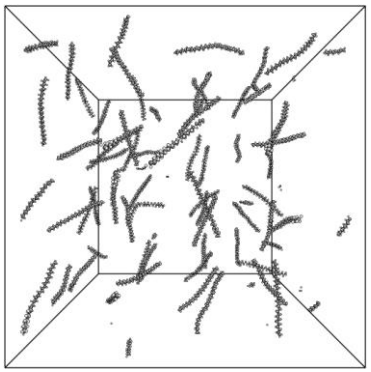
NVE

T = 500 K

100 ps

Δt = 1 fs

Gas



2.

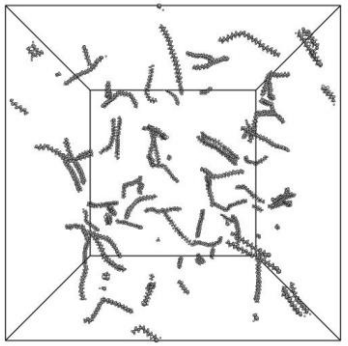
NVE

compression

0.25 x L

100 ps

Liquid



Liquid relaxation:

→ 3. NPT (2 ns) P~1 atm, T~360 K, ρ_{ave} (0.5 ns)

4. NVT (2 ns) ρ_{ave}, T~360 K

5. NVE, Warming-up (0.5 ns), T~700 K

6. NVT, Cooling back to T~360 K, NVT

Parameters:

ρ, T, P~1 atm

$\langle \kappa^2 \rangle$ - the relative shape anisotropy parameter

*LAMMPS

The linear momentum is zeroed in the end of the relaxation process.

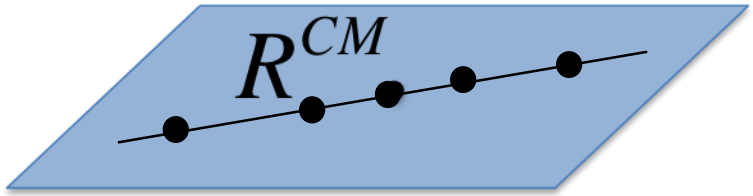
The relative shape anisotropy κ^2

Gyration tensor

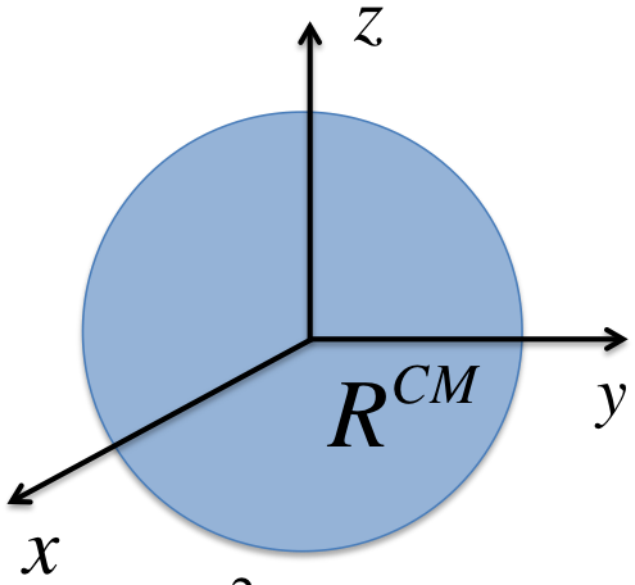
$$MS_{mn} = \sum_{i=1}^{N} m_i (r^i{}_m - R^{CM})(r^i{}_n - R^{CM})$$

$$\begin{bmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{zy} \\ S_{zx} & S_{zy} & S_{zz} \end{bmatrix} \rightarrow (\lambda_x, \lambda_y, \lambda_z) \rightarrow \kappa^2 = \frac{3}{2} \frac{\lambda^4{}_x + \lambda^4{}_y + \lambda^4{}_z}{(\lambda^2{}_x + \lambda^2{}_y + \lambda^2{}_z)^2} - \frac{1}{2}$$

eigenvalues

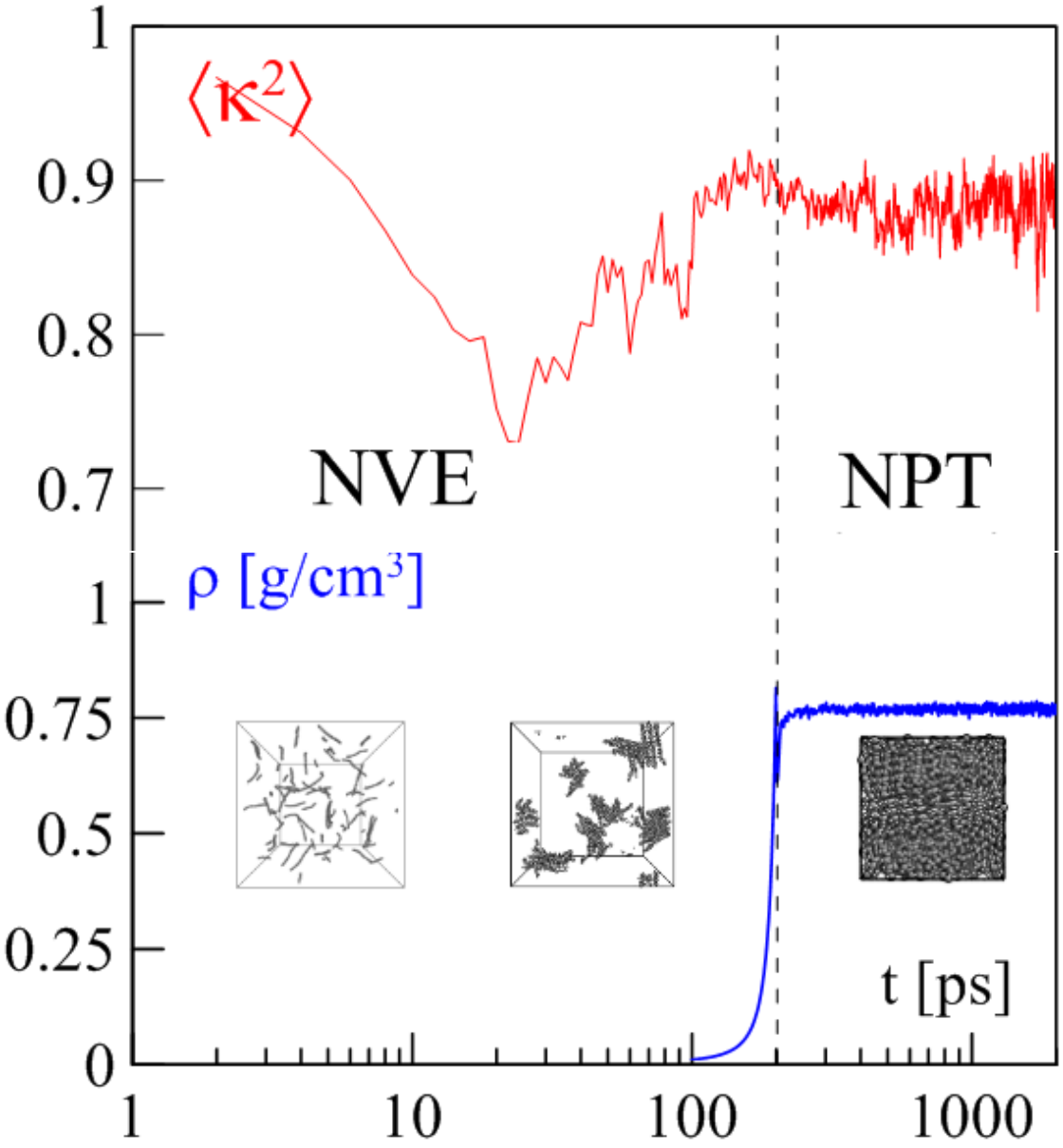


$\kappa^2 = 1$



$\kappa^2 = 0$

The relaxation parameters

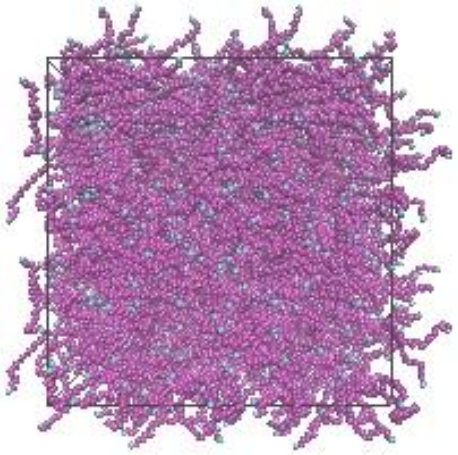


P~1 atm

T=360 K

Replication

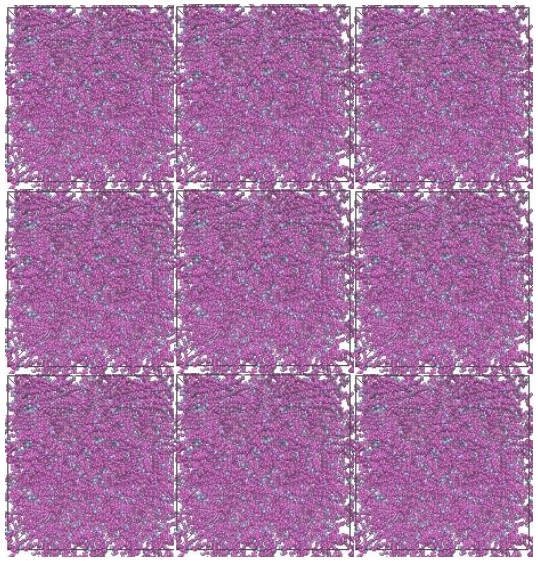
125 molecules



3x3x3 AA

4x4x4 UA

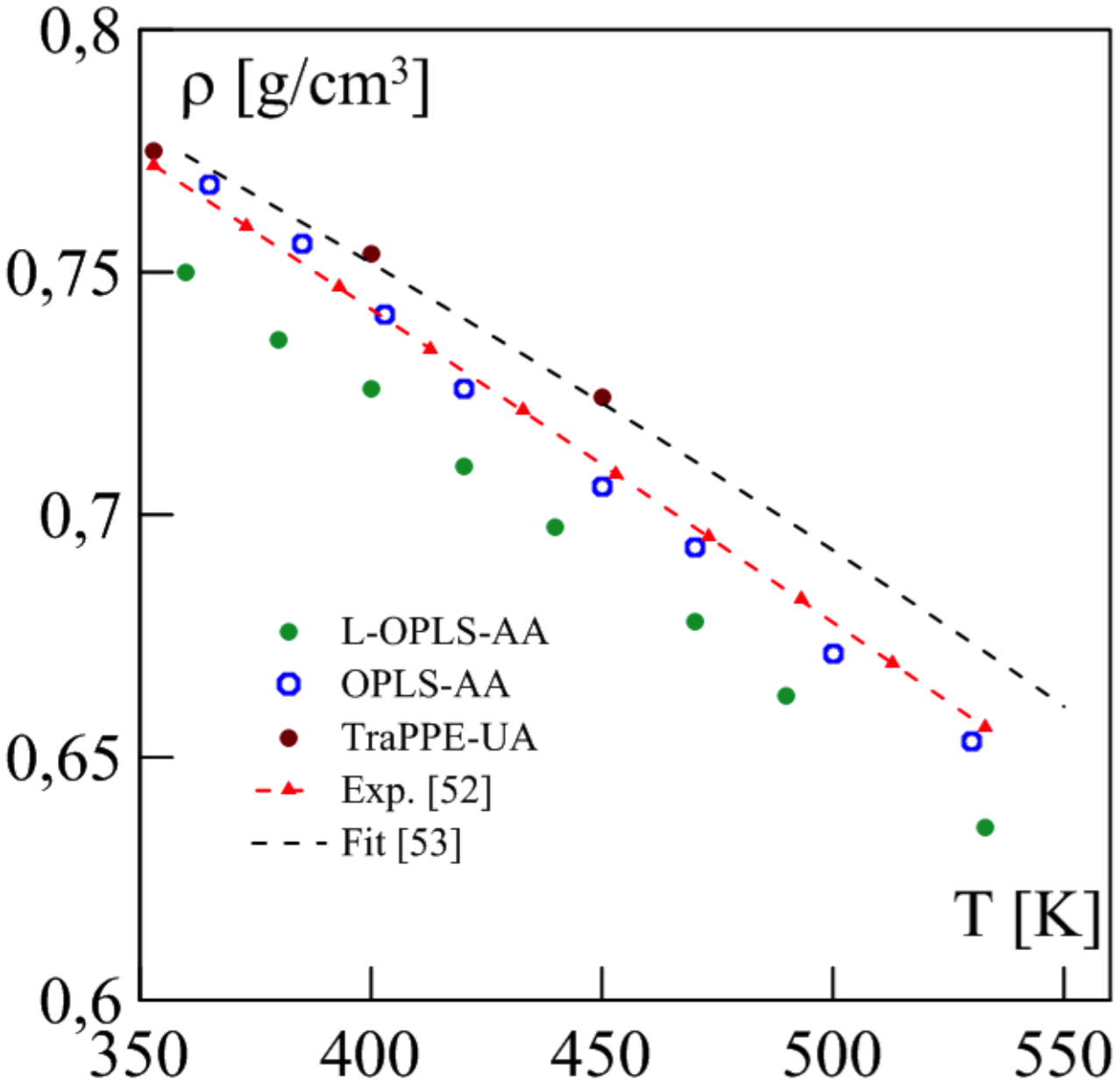
3375 molecules



125-3375 molecules – AA (330000 atoms)

125-8000 molecules – UA (240000 atoms)

Systems for calculation



How the other systems are obtained at T

1. System at 360 K

2. Calculating density (Yaws approximation)

3. Deforming the unit cell to the approximation density (700 K, NVE, 100 ps)

4. NVT (T, ρ_{approx}, 500 ps)

5. NPT (T, P ~ 1 atm, 500 ps)

6. Calculating the average density during the process

7. Deforming the unit cell to the average density (T, NVE, 100 ps)

8. Zeroing the linear momentum of the system

9. Scaling the velocity distribution to T

Size effects in the E-S method

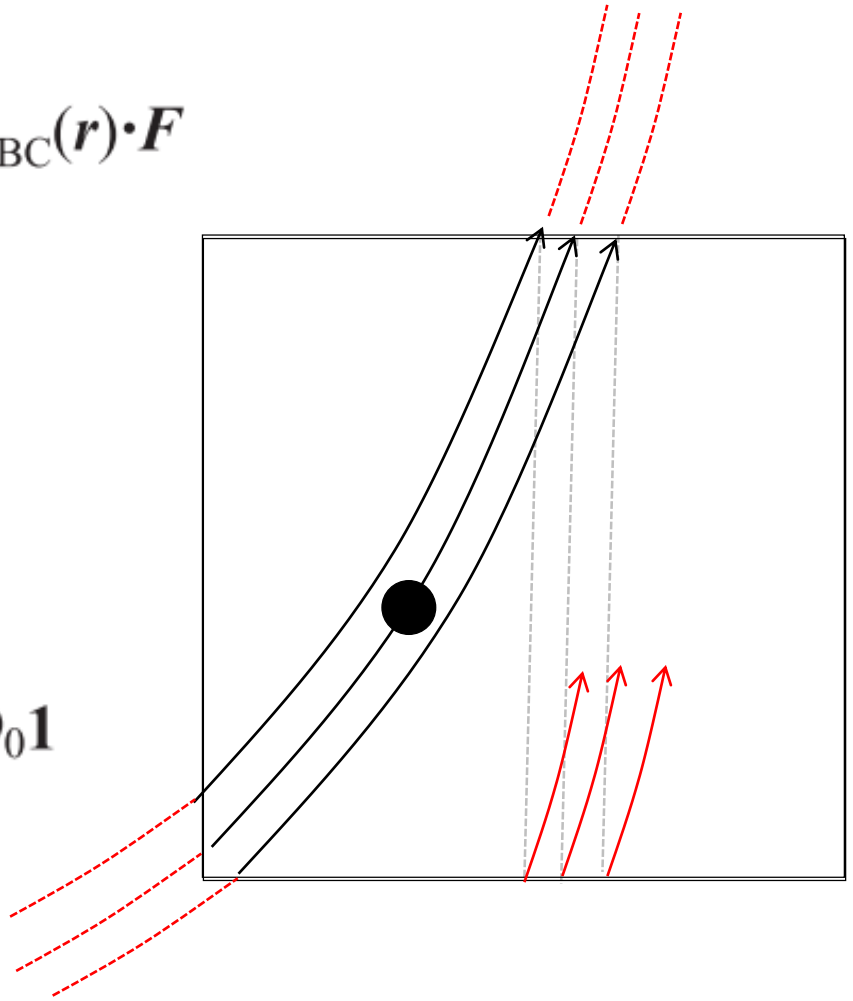
$$\boldsymbol{v}(\boldsymbol{r}) = \boldsymbol{T}_{\mathrm{PBC}}(\boldsymbol{r})\cdot\boldsymbol{F}$$

For **P**eriodic **B**oundary **C**onditions:

$$\boldsymbol{T}_{\mathrm{PBC}}(\boldsymbol{r}) = \sum_{\substack{\boldsymbol{k} \\ k\neq 0}} \frac{\exp(-i\boldsymbol{k}\cdot\boldsymbol{r})}{\eta k^2 V}\left(\mathbf{1} - \frac{\boldsymbol{kk}}{k^2}\right)$$

For infinite system:

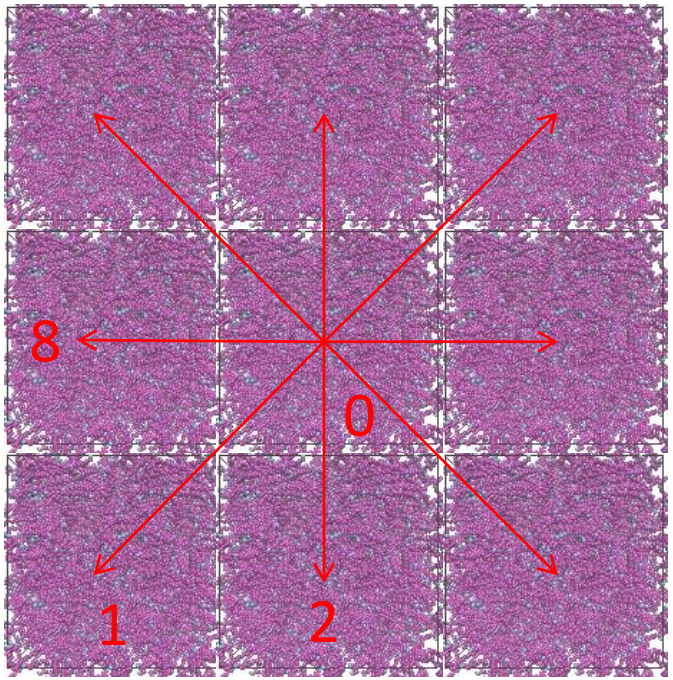
$$\boldsymbol{T}_0(\boldsymbol{r}) = \frac{1}{8\pi\eta r}\left(\mathbf{1} + \frac{\boldsymbol{rr}}{r^2}\right) = (k_{\mathrm{B}}T)^{-1}D_0\mathbf{1}$$



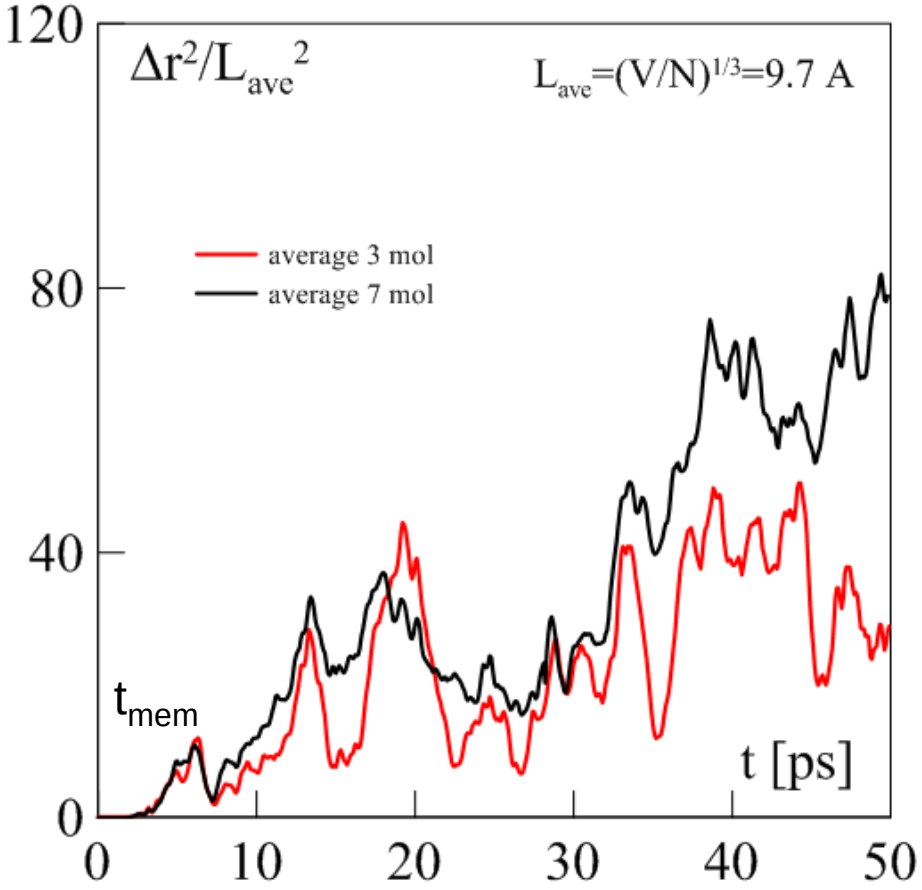
$$\boldsymbol{D}_{\mathrm{PBC}} = D_0\mathbf{1} + k_{\mathrm{B}}T\lim_{r\to 0}[\boldsymbol{T}_{\mathrm{PBC}}(\boldsymbol{r}) - \boldsymbol{T}_0(\boldsymbol{r})]$$

*I. Yeh and G. Hummer // J. Phys. Chem. B. 2004. V. 108. N. 40. P. 15873

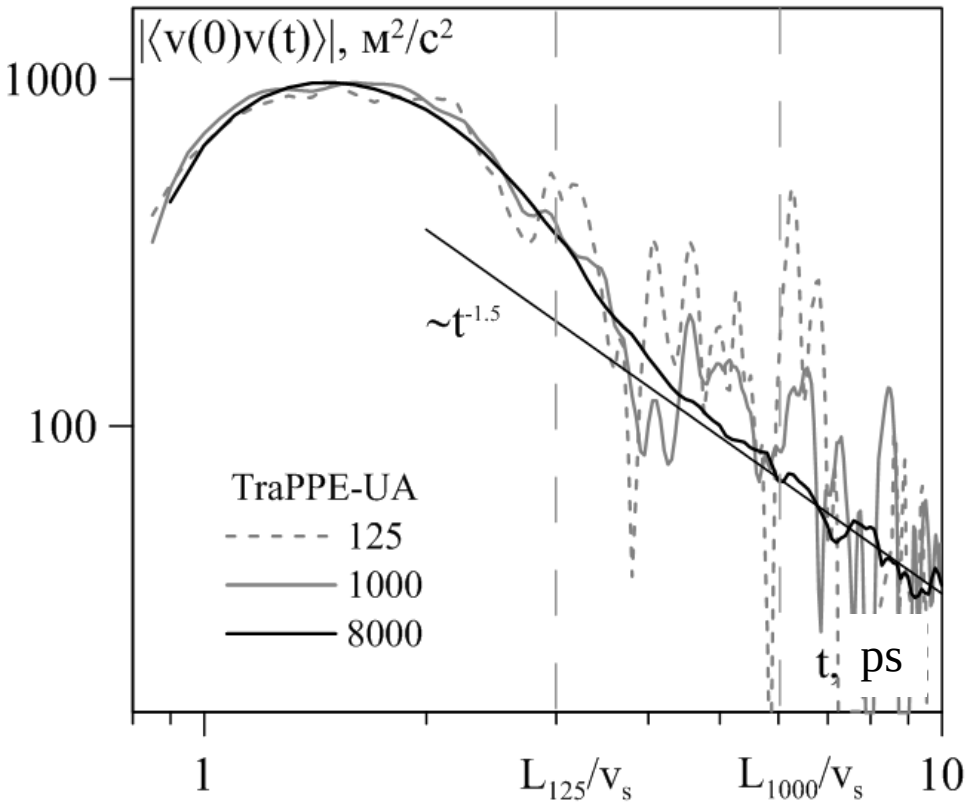
Replication independency

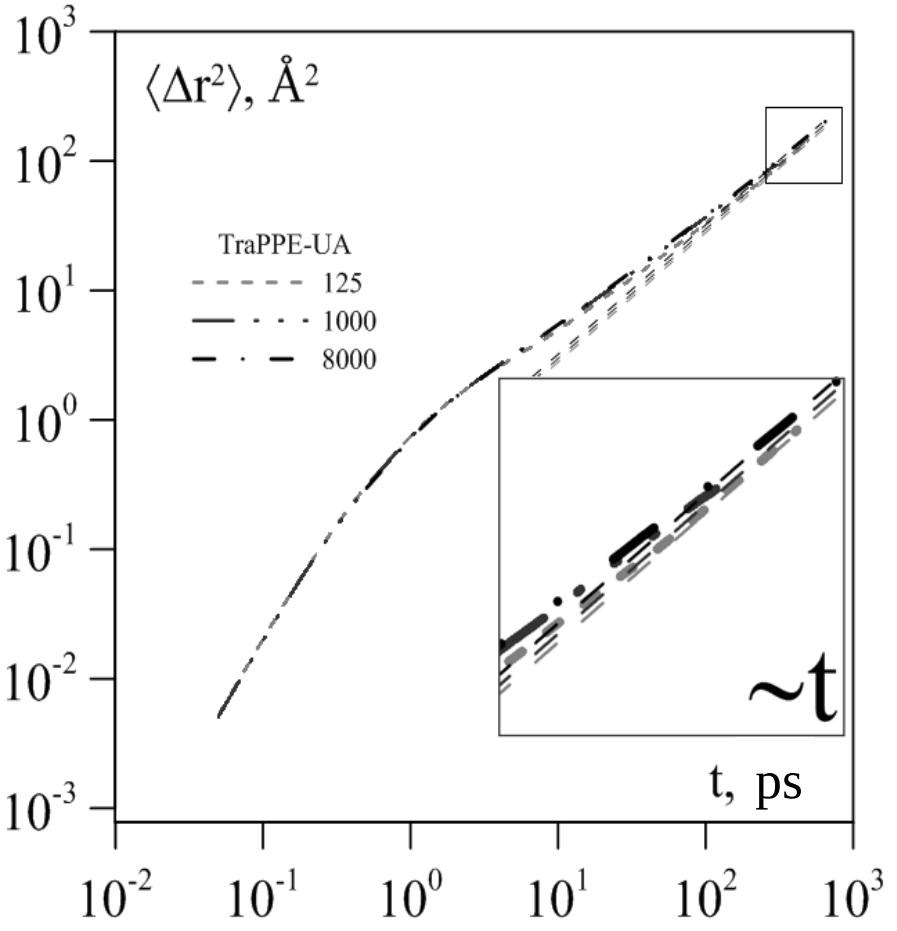


$$\Delta r^2_{mol} = \sum_{k=1}^{26} (r^k_{mol} - r^0_{mol})^2$$

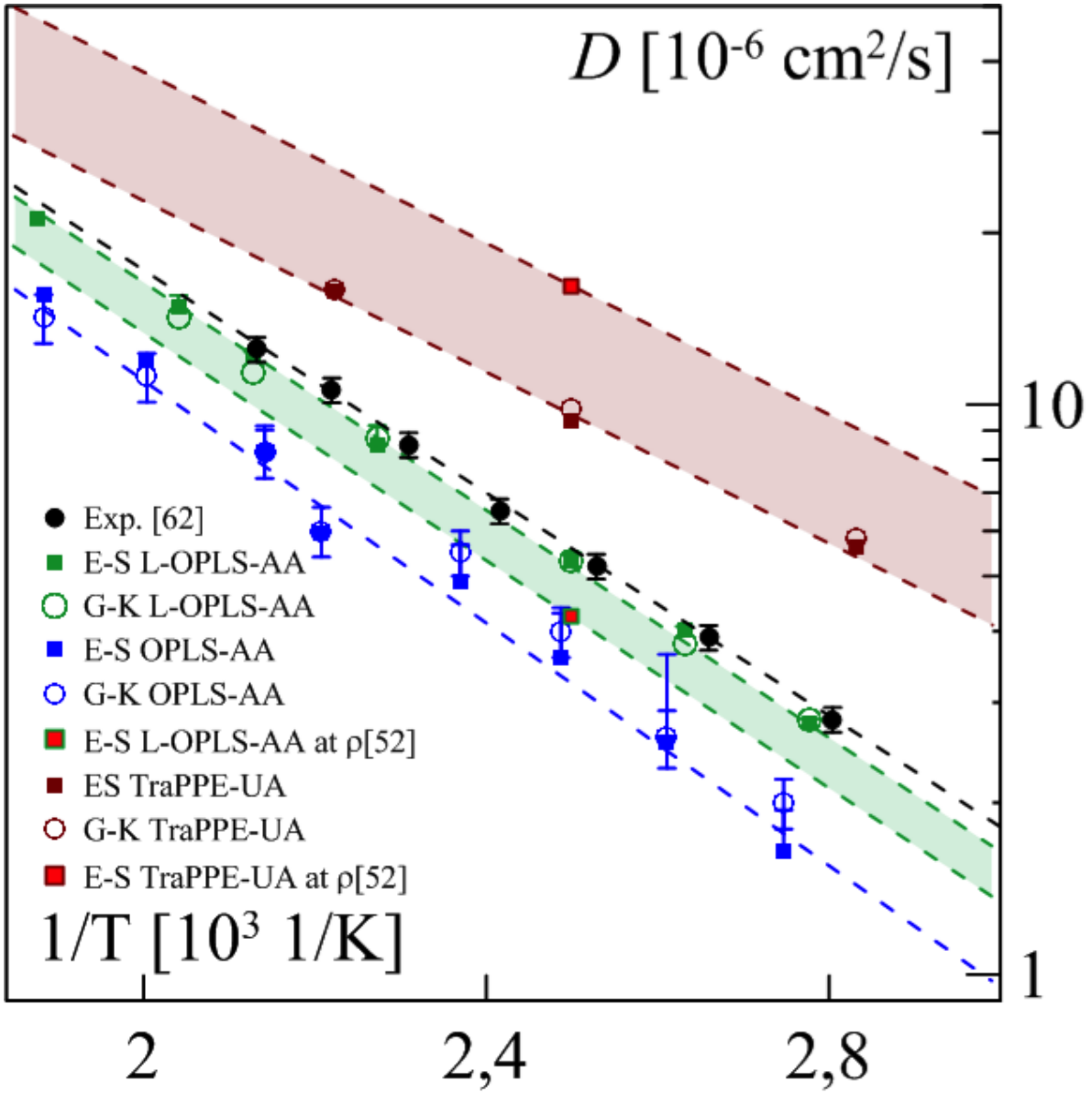


The dependence on the number of molecules



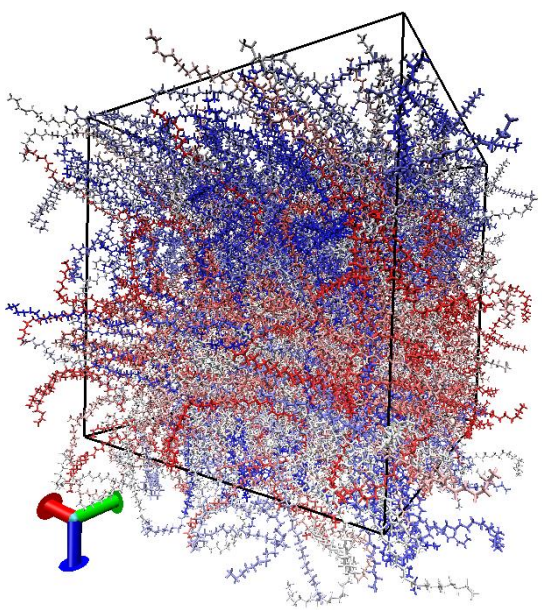


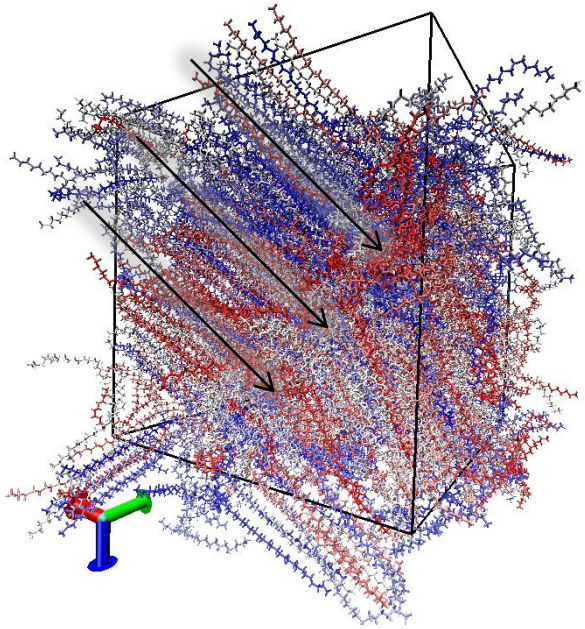
Simulation results vs experimental data



*T. Vardag, N. Karger, H.D. Lüdemann // Ber. Bunsenges. Phys. Chem. 1991. V. 95. N. 8. P. 859.

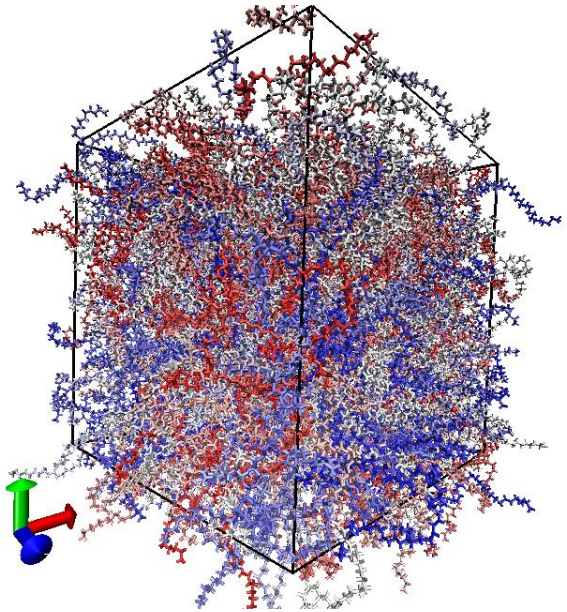
Metastable liquid in OPLS-AA

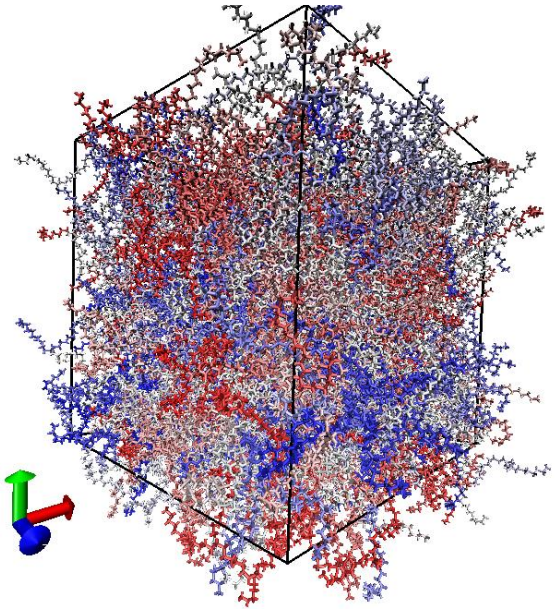




OPLS-AA

solidifies after 1.5 ns

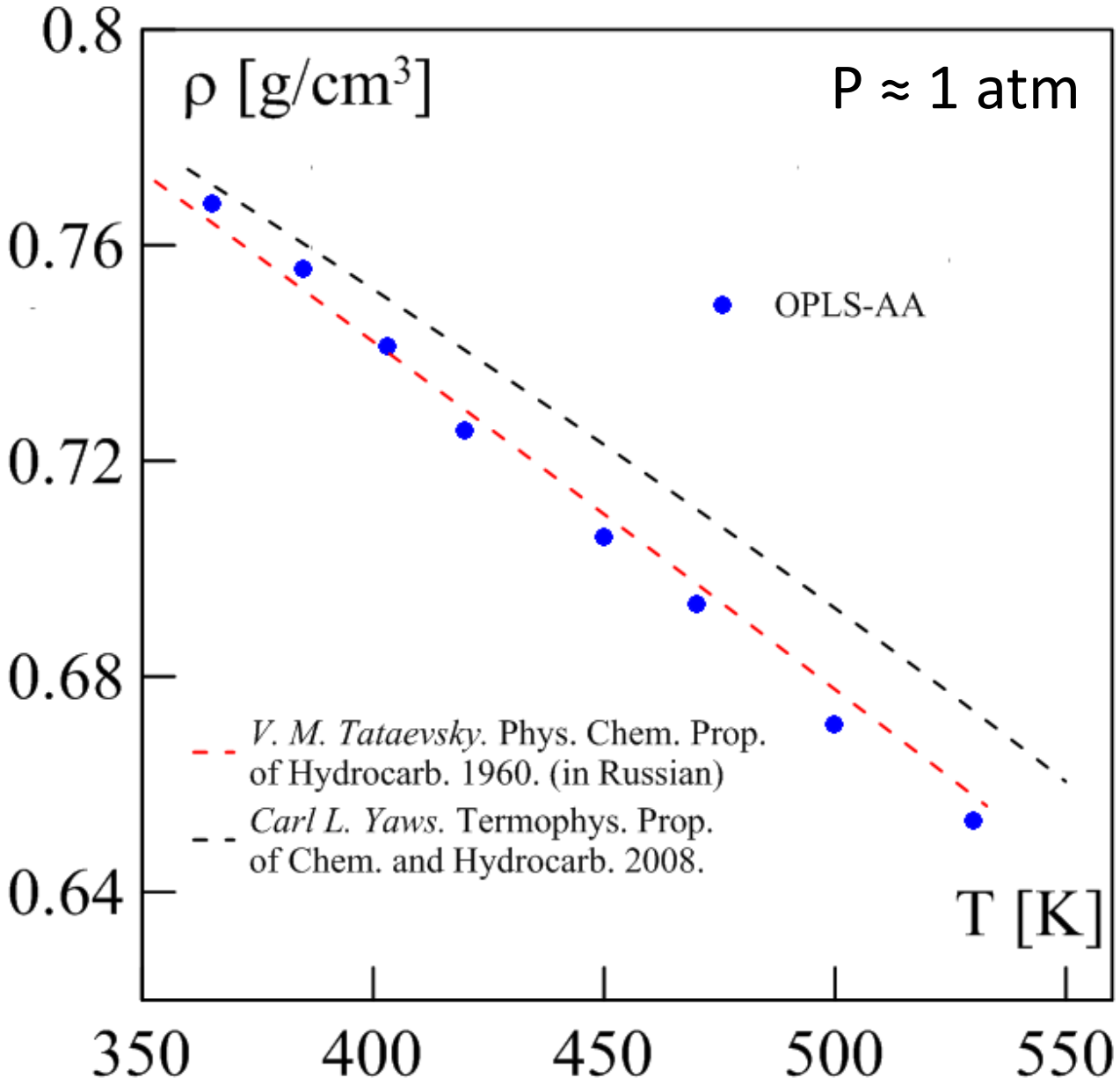




L-OPLS-AA

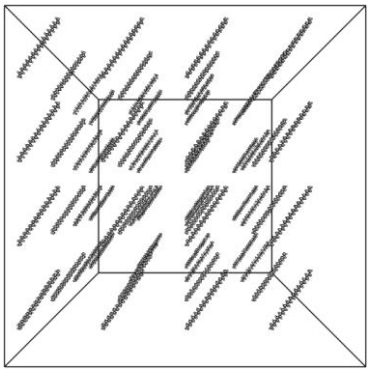
no solidification after 1.5 ns

Systems for calculation



Preparing the system

Initial configuration*



$r_{intermolec} > r_{cut}$ (12 A)

1.

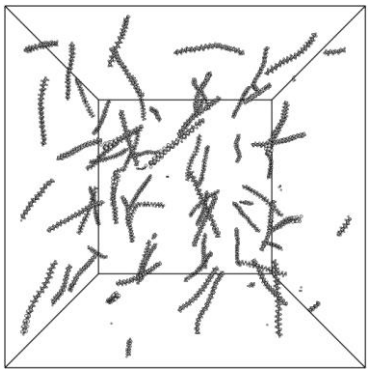
NVE

T = 500 K

100 ps

Δt = 1 fs

Gas



2.

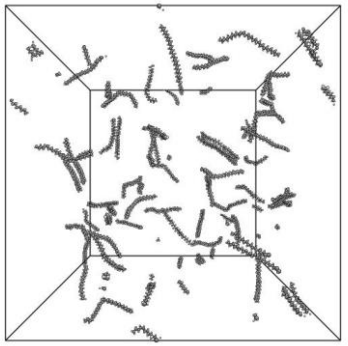
NVE

compression

0.25 x L

100 ps

Liquid



Liquid relaxation:

→ 3. NPT (2 ns) P~1 atm, T~360 K, ρ_{ave} (0.5 ns)

4. NVT (2 ns) ρ_{ave}, T~360 K

5. NVE, Warming-up (0.5 ns), T~700 K

6. NVT, Cooling back to T~360 K, NVT

Parameters:

ρ, T, P~1 atm

$\langle \kappa^2 \rangle$ - the relative shape anisotropy parameter

*LAMMPS

The linear momentum is zeroed in the end of the relaxation process.

How the other systems are obtained at T

1. System at 360 K

2. Calculating density (Yaws approximation)

3. Deforming the unit cell to the approximation density (700 K, NVE, 100 ps)

4. NVT (T, ρ_{approx}, 500 ps)

5. NPT (T, P ~ 1 atm, 500 ps)

6. Calculating the average density during the process

7. Deforming the unit cell to the average density (T, NVE, 100 ps)

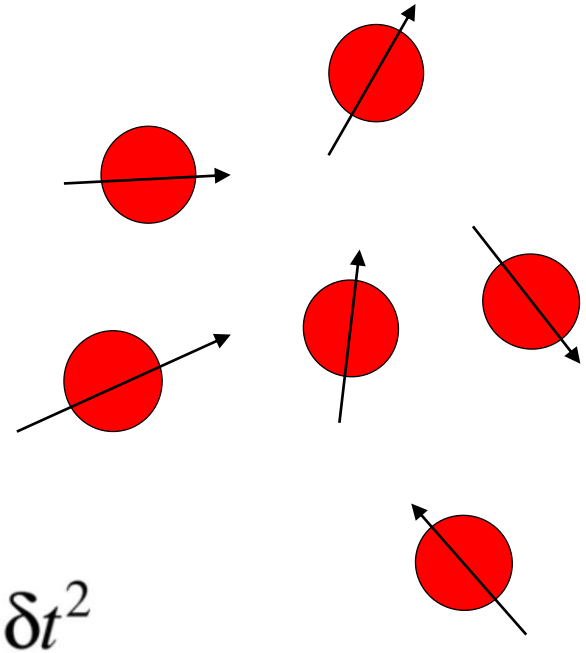
8. Zeroing the linear momentum of the system

9. Scaling the velocity distribution to T

The idea of molecular dynamics

Forces between different particles are derived from some analytical force model,

$$\mathbf{F} = -\nabla V(r) \qquad \mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij}$$



Equations of motion are solved with a finite difference algorithm,

$$\vec{r}_i(t+\delta t) = \vec{r}_i(t) + \vec{v}_i(t)\delta t + \frac{1}{2}\vec{a}_i(t)\delta t^2$$

T [K]	ρ [g/cm^3]	Diffusion coefficient, 10^{-6} cm^2/s		β, Δβ=0.1
		E-S	G-K	
364	0.768	1.7 ± 0.3	2.0 ± 0.2	2.05
383	0.756	2.5 ± 1.1	2.6 ± 0.3	2.0
402	0.741	3.6 ± 0.7	4.0 ± 0.4	1.97
422	0.726	4.9 ± 0.8	5.5 ± 0.5	1.97
453	0.706	5.9	6.0 ± 0.6	1.7
467	0.693	8.3 ± 0.9	8.2 ± 0.8	1.6
499	0.671	12.0	11.2 ± 1.1	1.5
530	0.653	15.6	14.2 ± 1.4	1.45

1. The difference between G-K and E-S is removed
2. β values are validated

What is the nature of the β values?

PHYSICAL REVIEW A VOLUME 1, NUMBER 1 JANUARY 1970

Decay of the Velocity Autocorrelation Function*

B. J. Alder and T. E. Wainwright
Lawrence Radiation Laboratory, University of California, Livermore, California 94550

(Received 10 July 1969)

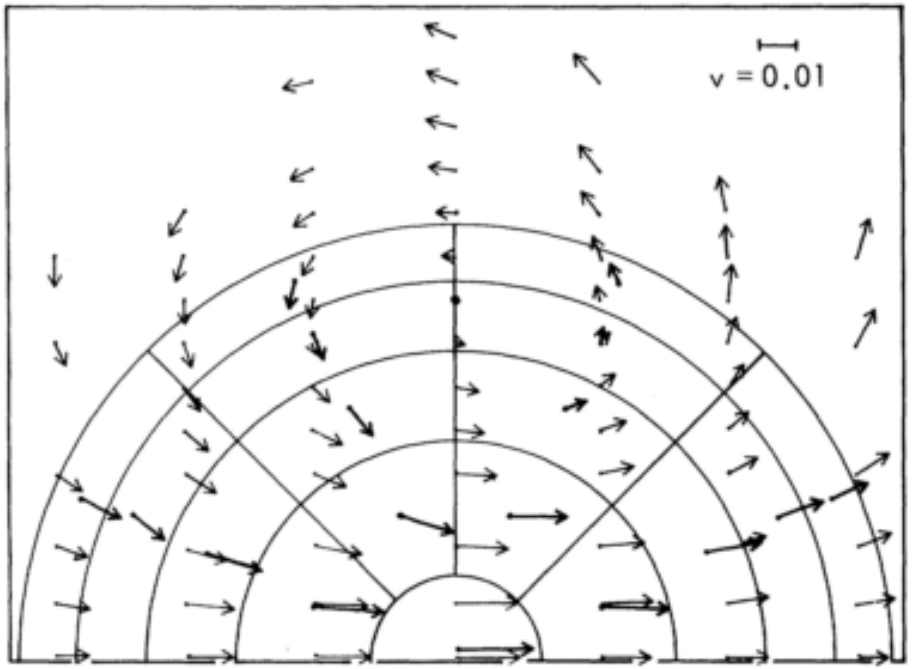


FIG. 1. Statistically averaged velocity field around a central disk from molecular dynamics (heavy arrows) compared to that given by the hydrodynamic model (light arrows). Because of symmetry only half the plane is shown. The scale of distance is indicated by the size of the central disk as shown by the smallest half-circle.

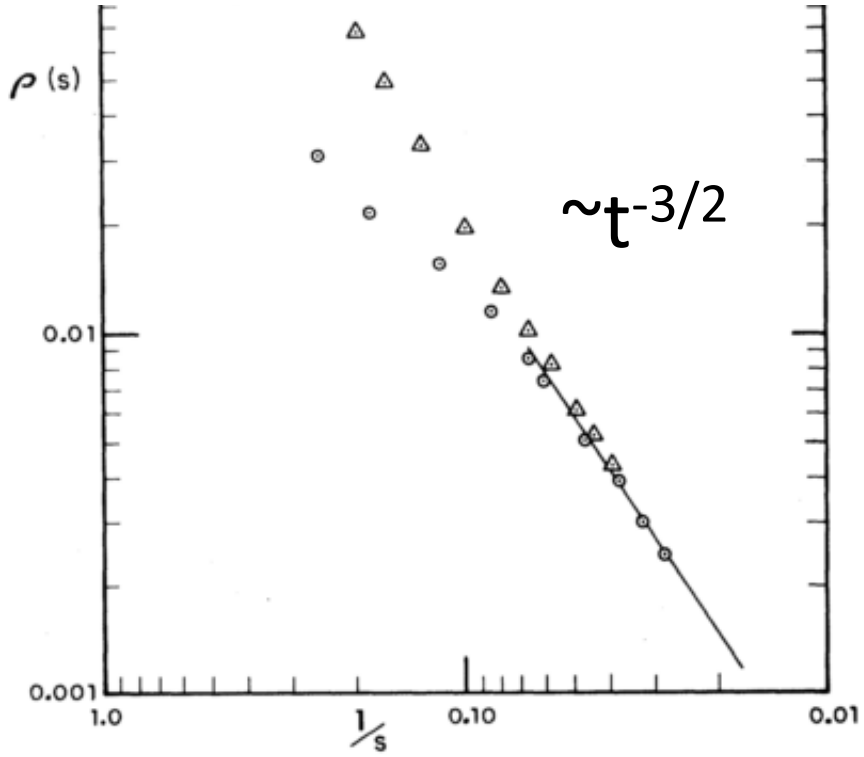
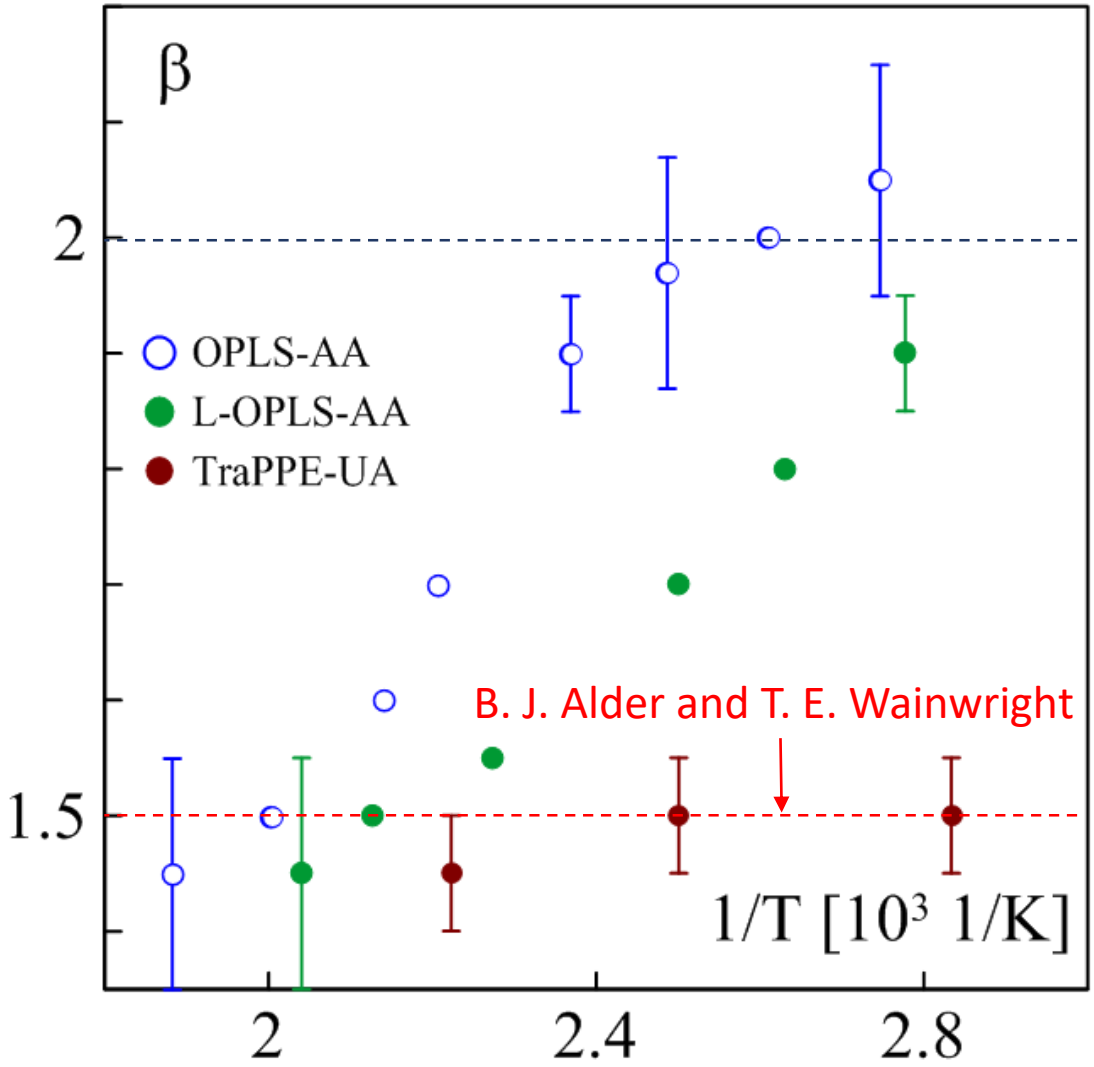


FIG. 2. Comparison of the velocity autocorrelation function $\rho(s)$ as a function of time (in terms of mean collision times s) between the hydrodynamic model (circles) and a 500-hard-sphere molecular-dynamic calculation (triangles) at a volume relative to close packing of 3 on a log-log plot. The straight line is drawn with a slope corresponding to $s^{-3/2}$. To the molecular dynamics $\rho(s)$

Pomeau VACF series expansion*

$$C_v(t) \simeq \sum_{n=1}^{\infty} b_n t^{1/2^n - 2}$$



$n \to \infty$

$b_\infty t^{-2}$

$n \to 1$

$b_1 t^{-3/2}$

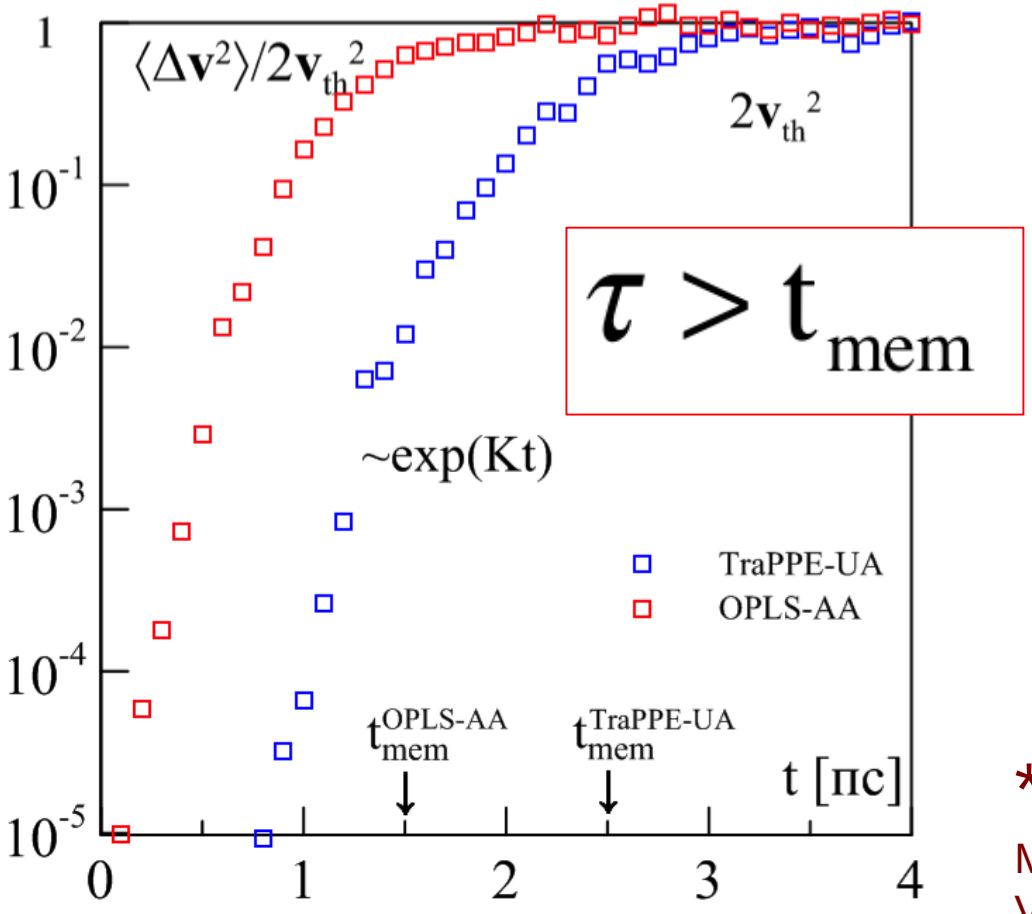
*Pomeau Y. // Phys. Rev. A. 1973. V. 7. № 3. P. 1134-1147.

Determination of τ^*

The same initial conditions

(r', v') - MD trajectory integrated with 1 fs;

(r'', v'') - MD trajectory integrated with 0.1 fs;



Lyapunov instability:

$$\langle \Delta v^2 \rangle = \sum_{mol} (v_i' - v_i'')^2 / N$$

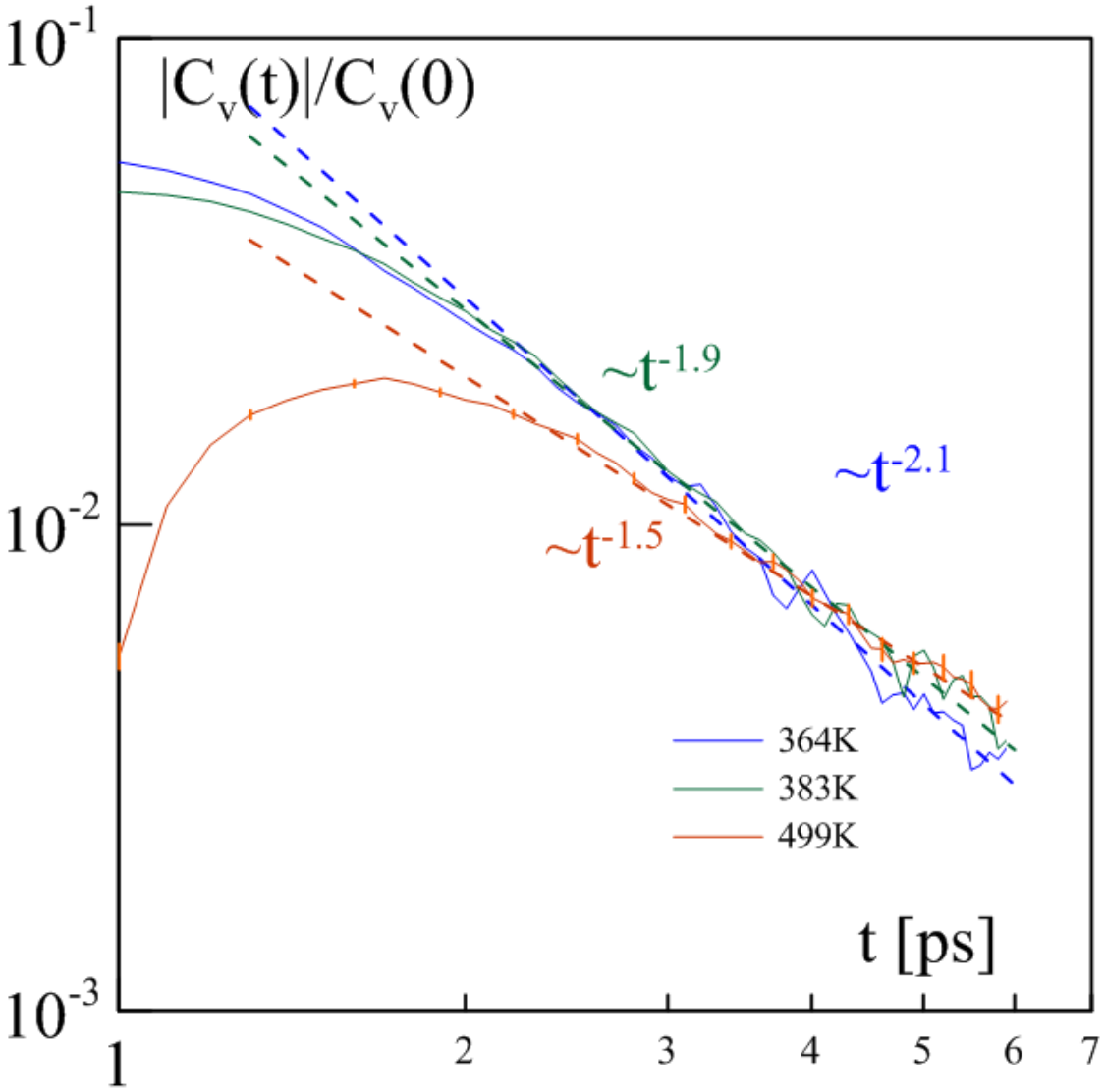
$$\langle \Delta v^2 \rangle \sim \exp(Kt),\ t < t_{mem}$$

$$\langle \Delta v^2 \rangle = 2v_{th}^2,\ t > t_{mem}$$

$$v_{th}^2 = 3k_B T / m$$

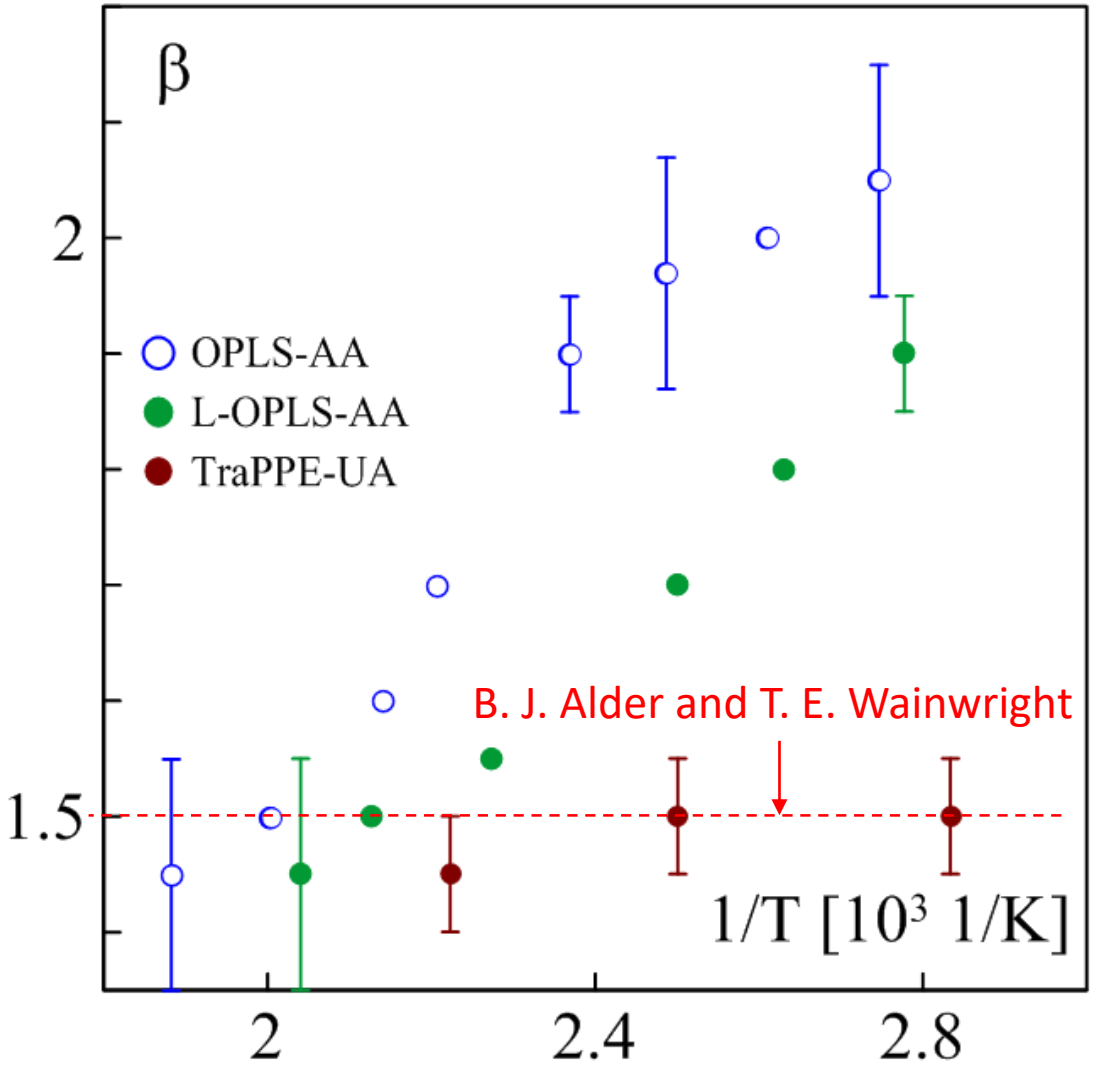
*G. E. Norman, V. V. Stegailov // Math. Mod. Comput. Simulat. 2013, Vol. 5, No. 4, pp. 305–333.

The C_v asymptotes for n-triacontane

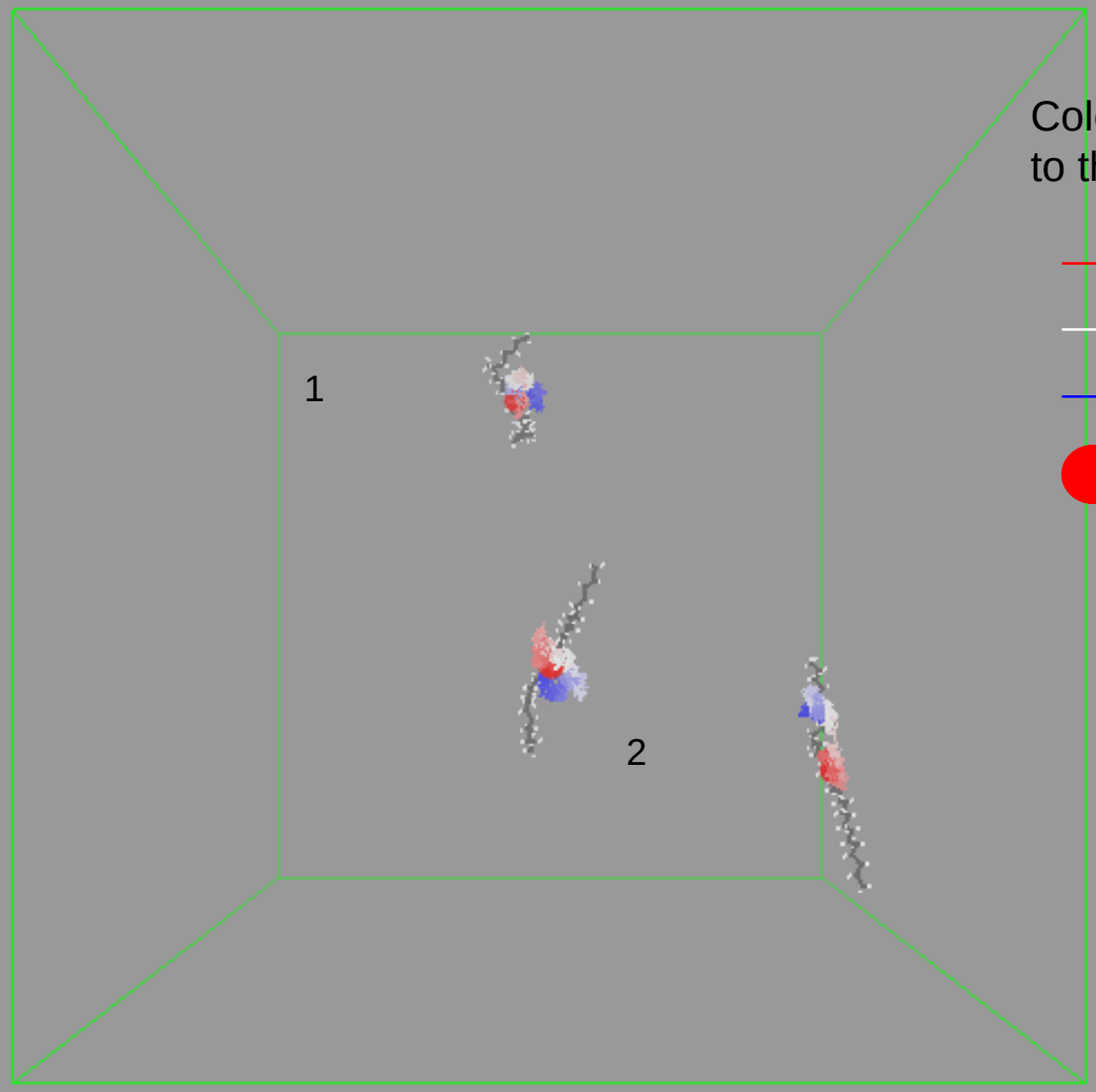


β dependence on temperature

$$C_V \sim t^{-\beta}$$

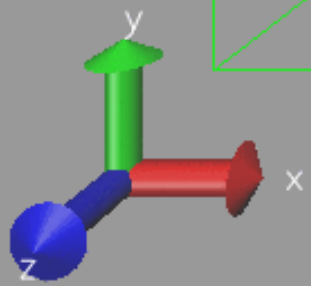


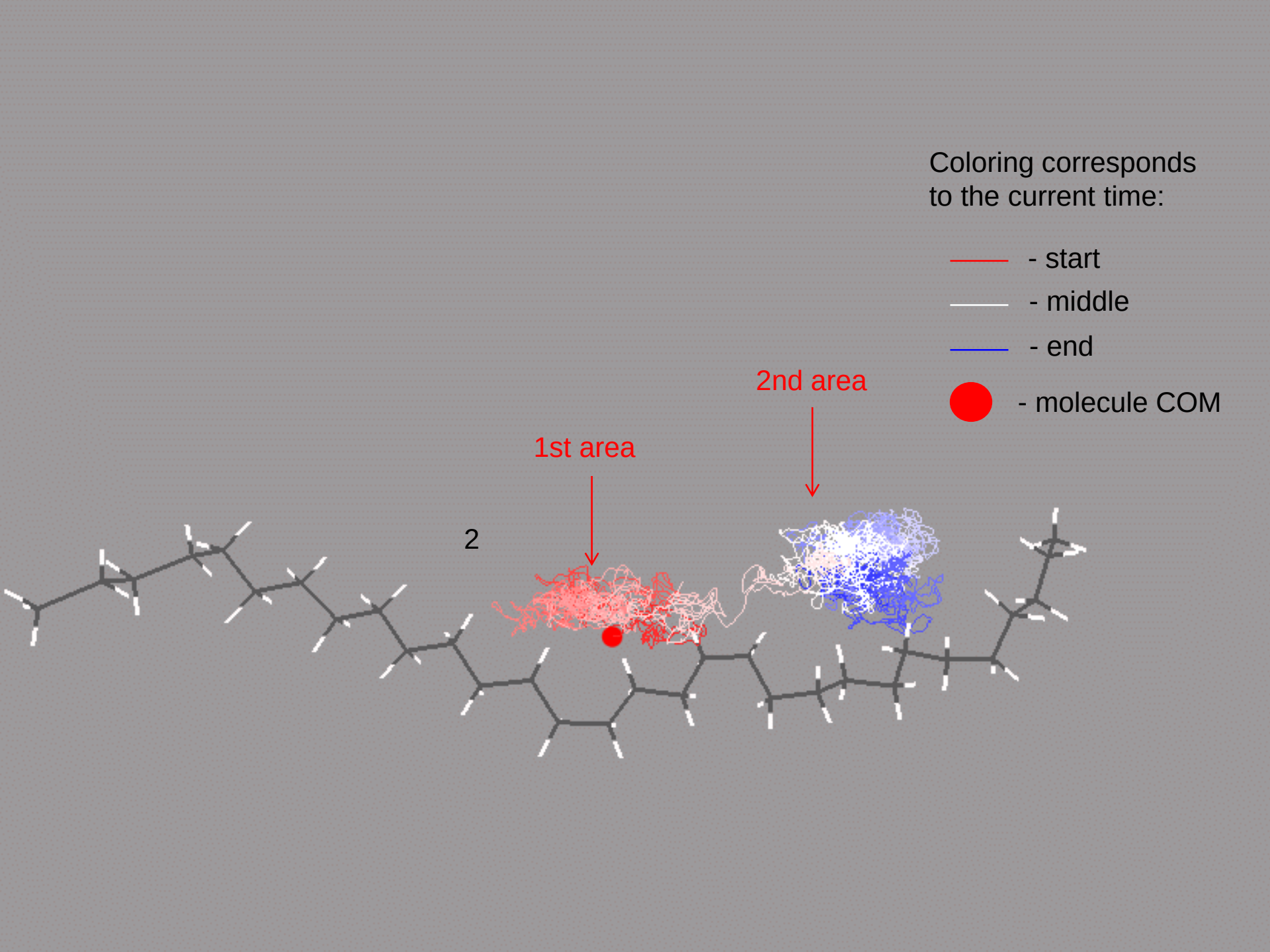
1 ns MD trajectory

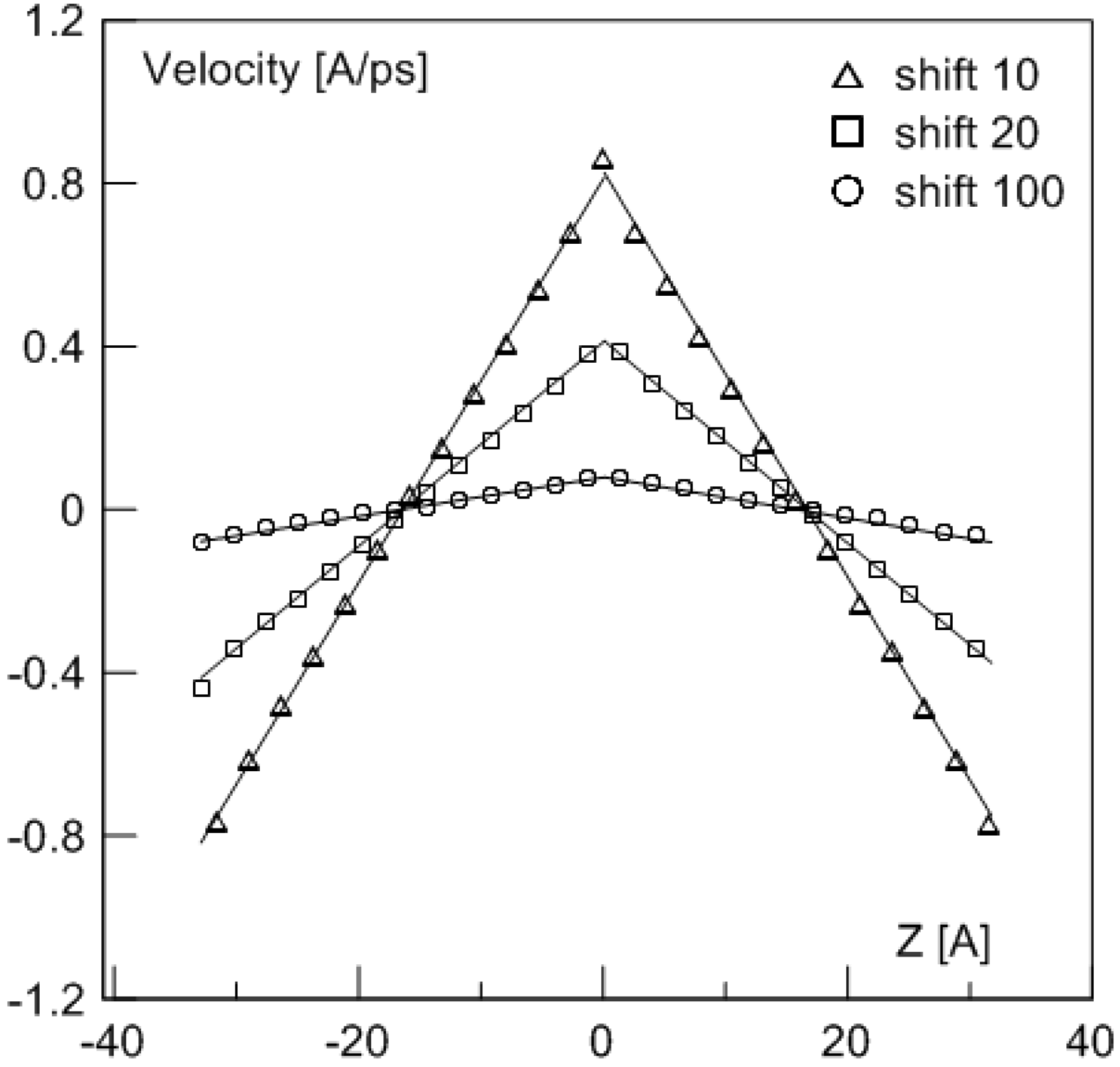


Coloring corresponds to the current time:

- start
- middle
- end
- molecule COM




Coloring corresponds
to the current time:
- start
- middle
- end
- molecule COM
2nd area
1st area
2


Velocity [A/ps]
shift 10
shift 20
shift 100
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-40
-20
0
20
40
Z [A]

Техника усреднения

$$\left\langle \Delta r^2 \right\rangle = 6Dt$$

The 1st stage of the averaging:

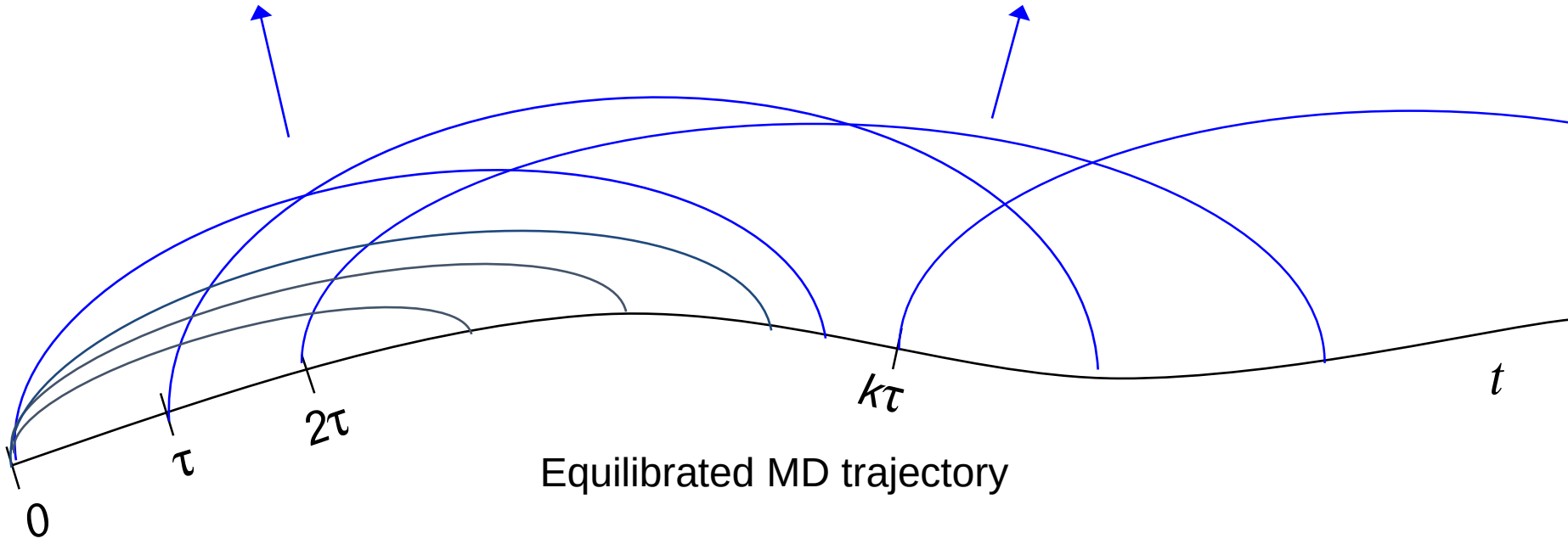
$$\left\langle \Delta r^2 \right\rangle = \sum_N \left(r_i^{CM}(t) - r_i^{CM}(0) \right)^2 / N$$

N - Number of the molecules (8000)

The 2nd stage of the averaging:

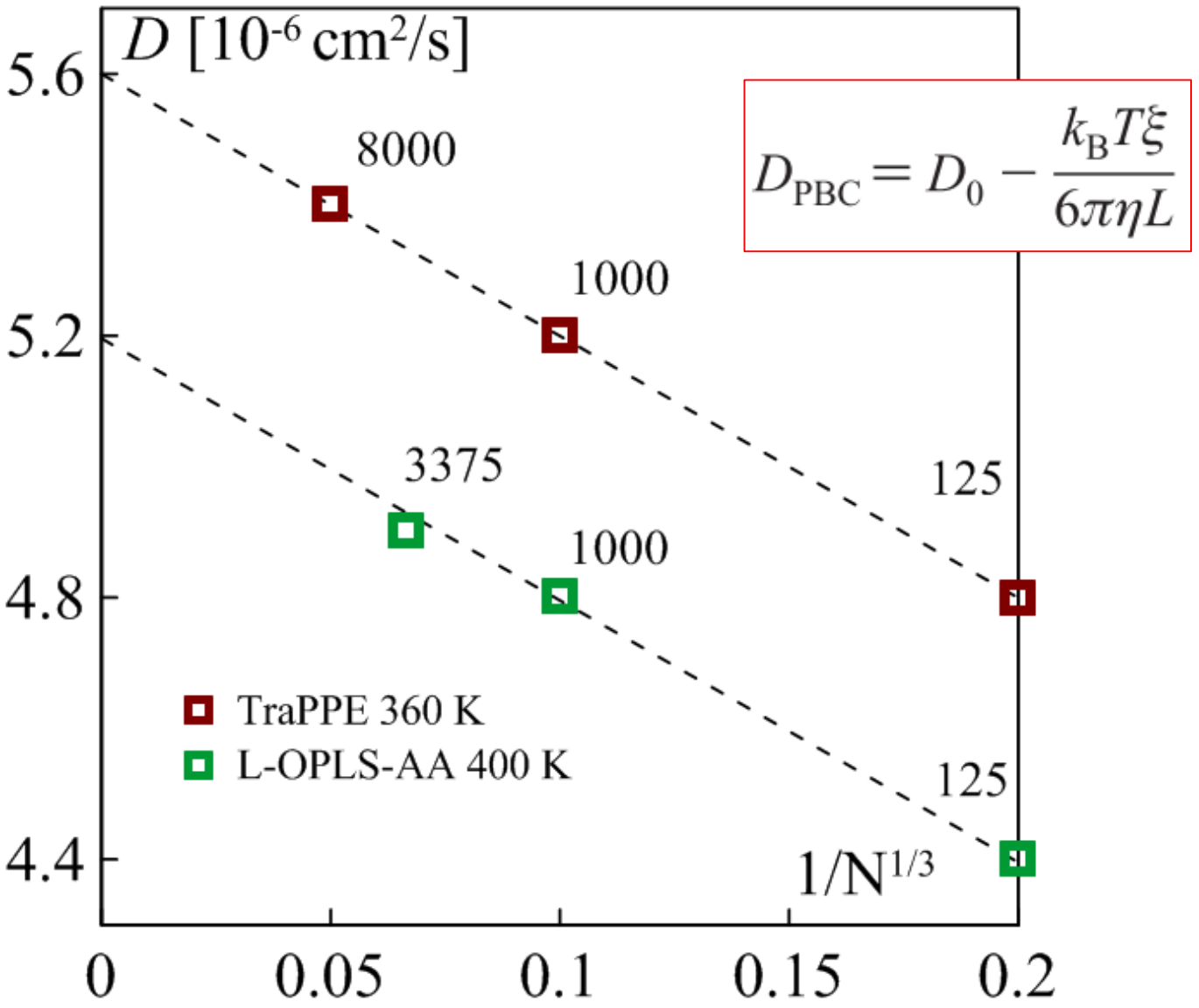
$$\left\langle \Delta r^2 \right\rangle = \sum_k^M \left\langle \Delta r^2 \right\rangle_{k\tau} / M$$

M - Number of the zero shifts (~60)



Equilibrated MD trajectory

Размерные эффекты



$$D_{PBC} = D_0 - \frac{k_B T \xi}{6\pi\eta L}$$

*I. Yeh and G. Hummer // J. Phys. Chem. B. 2004. V. 108. N. 40. P. 15873

Техника усреднения

$$C_v(t) = \langle \vec{v}(0)\, \vec{v}(t) \rangle$$

The 1st stage of the averaging:

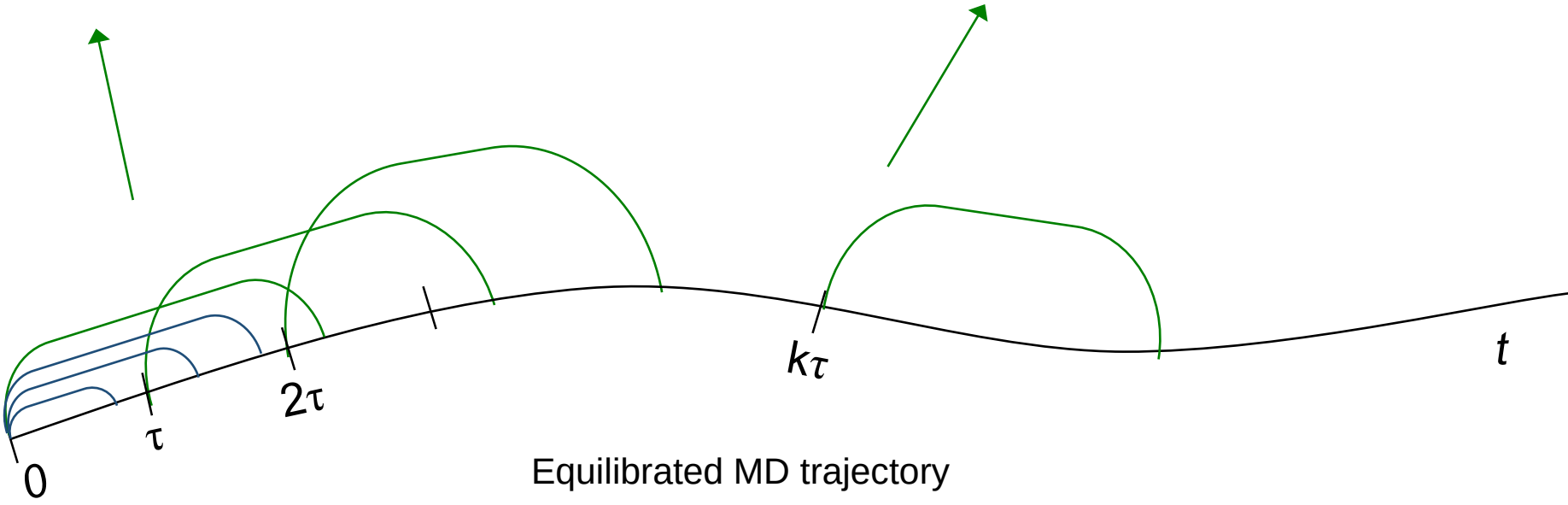
$$C_v(t) = \sum_N \vec{v}_i(0)\vec{v}_i(t) / N$$

N - Number of the molecules (8000)

The 2nd stage of the averaging:

$$C_v(t) = \sum_k^M C_v(t)_{k\tau} / M$$

M - Number of the zero shifts (~300)

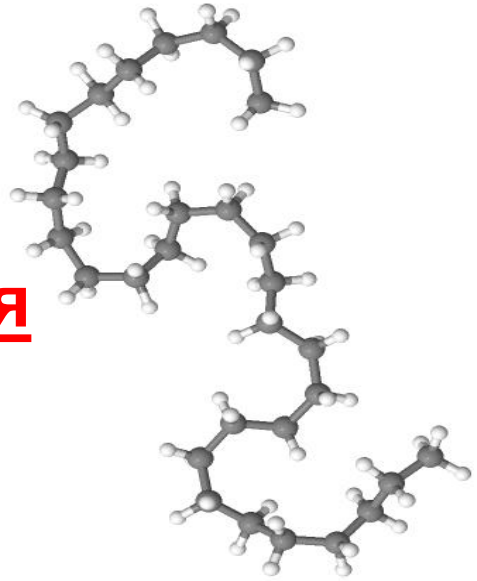


Equilibrated MD trajectory

План доклада

n-$C_{30}H_{62}$

1. Самодиффузия в жидком н-триаконтане



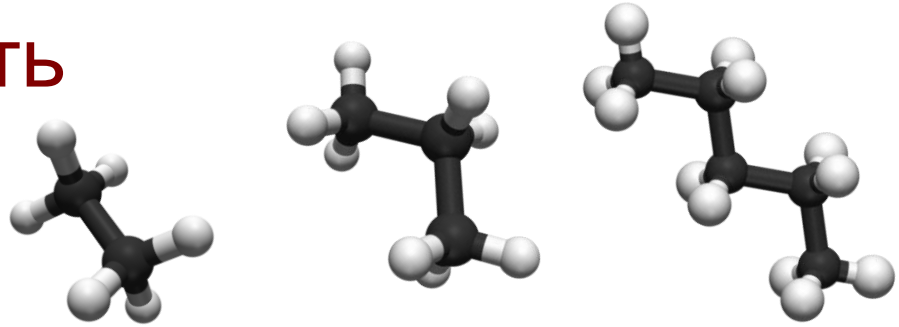
Молекула н-триаконтана

Потенциалы взаимодействия (+ COMPASS)

Сходимость Г-К

Предсказательная способность

2. Сдвиговая вязкость



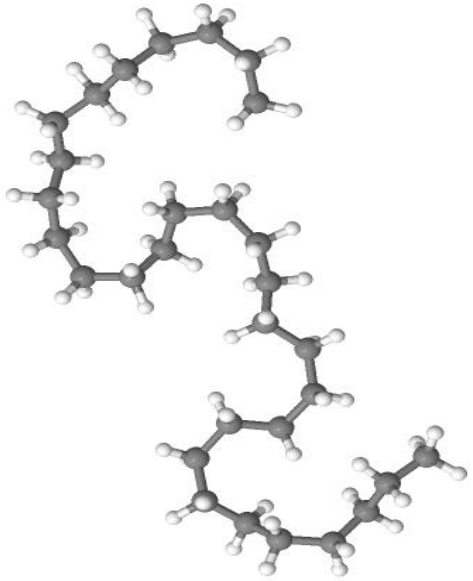
Сходимость Г-К

Неравновесная МД + эксперимент

План доклада

n-$C_{30}H_{62}$

1. Самодиффузия в жидком н-триаконтане



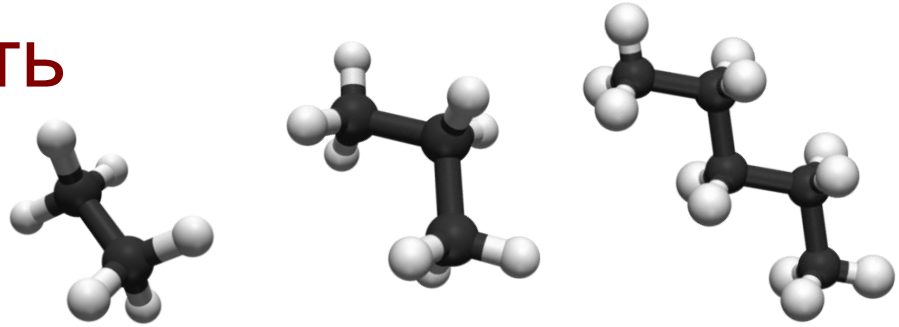
Молекула н-триаконтана

Потенциалы взаимодействия (+ COMPASS)

Сходимость Г-К

Предсказательная способность

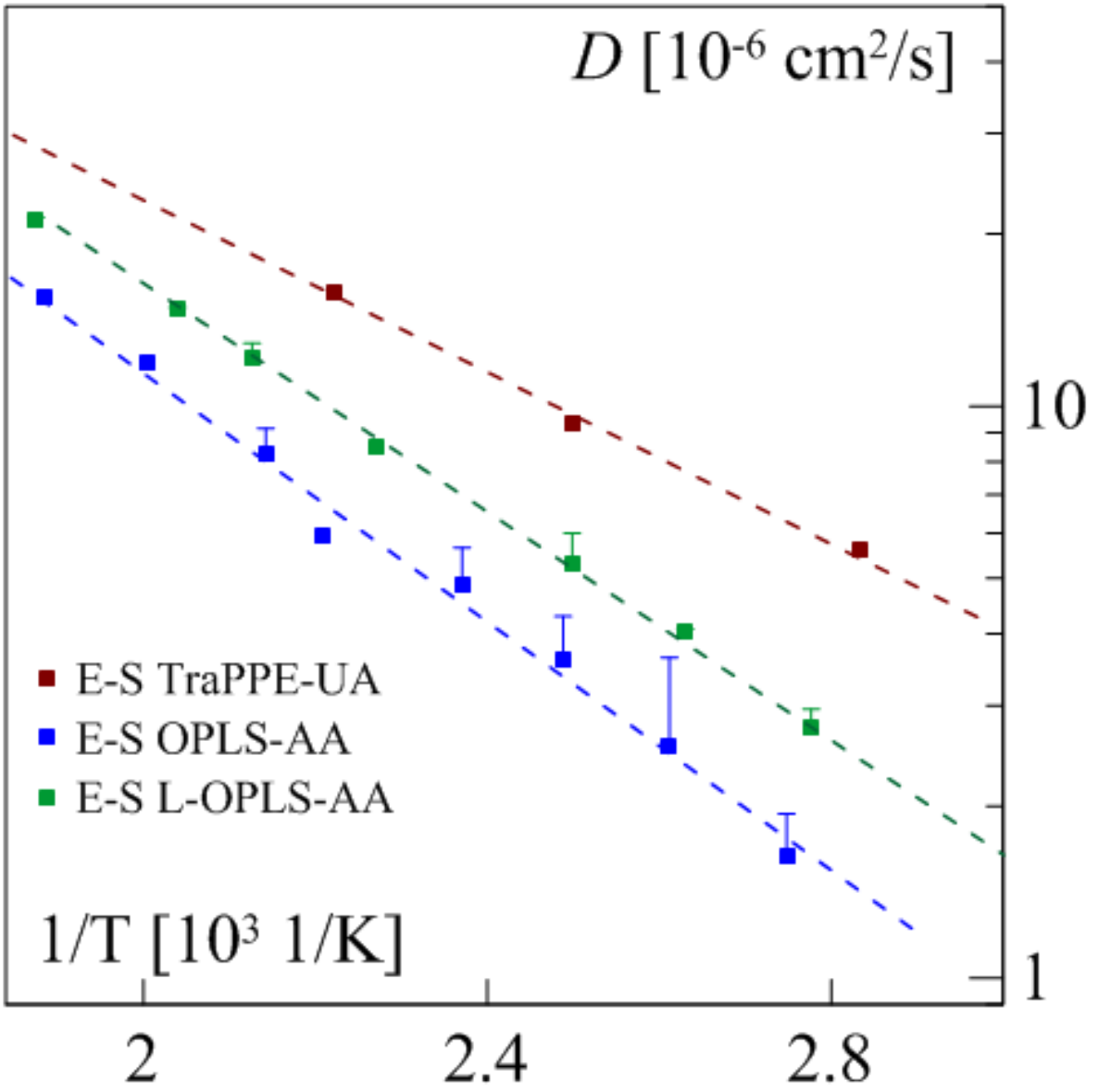
2. Сдвиговая вязкость



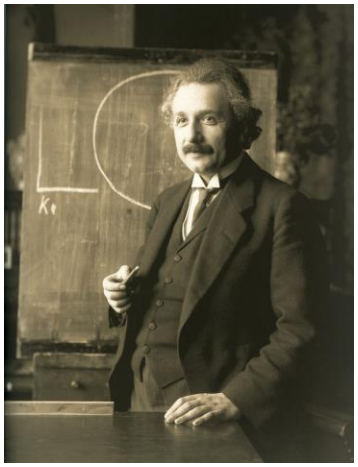
Сходимость Г-К

Неравновесная МД + эксперимент

Результаты расчета методом Э-С



Уравнения для D



Albert Einstein (1905)

They are theoretically equivalent:

$$D = \lim_{t\to\infty} \frac{1}{2dt} < |x(t) - x(0)|^2 >$$

$$= \frac{1}{2d} \lim_{t\to\infty} \frac{d}{dt} < |r(r) - r(0)|^2) >$$

$$= \lim_{t\to\infty} \frac{1}{d} < (r(t) - r(0)) \cdot v(t) >$$

$$= \lim_{t\to\infty} \frac{1}{d} \int_0^t d\tau < v(\tau) \cdot v(t) >$$

$$= \lim_{t\to\infty} \frac{1}{d} \int_0^t d\tau < v(0) \cdot v(t-\tau) >$$

$$= \frac{1}{d} \int_0^\infty dt < v(0) \cdot v(t) >$$

ан Smoluchowski (1906)

Melville S. Green (1954)

Ryogo Kubo (1957)

Сходимость в “простых” системах

$$D_{E\text{-}S} = D_{G\text{-}K}$$

S. H. Lee, D. K. Park, D. B Kang
Molecular Dynamics Simulations for Transport Coefficients of Liquid Argon : New Approaches,
Bull. Korean Chem. Soc. **2003**. V. 24(2). P. 178.

I. Gholami, A. Fiege, A. Zippelius
Slow dynamics and precursors of the glass transition in granular fluids.
Phys. Rev. E. **2011.** V. 84. P. 1.

M. Śmiechowski
Molecular hydrogen solvated in water – A computational study.
J. Chem. Phys. **2015**. V. 143(24). P. 244505.

Сходимость в “сложных” системах

J.P. Ryckaert, A. Bellemans
Molecular dynamics of liquid n-butane near its boiling point.
Chem. Phys. Lett. **1975**. V. 30(1). P. 123.

$D_{E-S} < D_{G-K}$

P. Padilla, S. Toxvaerd
Self-diffusion in n-alkane fluid models.
J. Chem. Phys. **1991**. 94(8). P. 5650.

D_{E-S} only

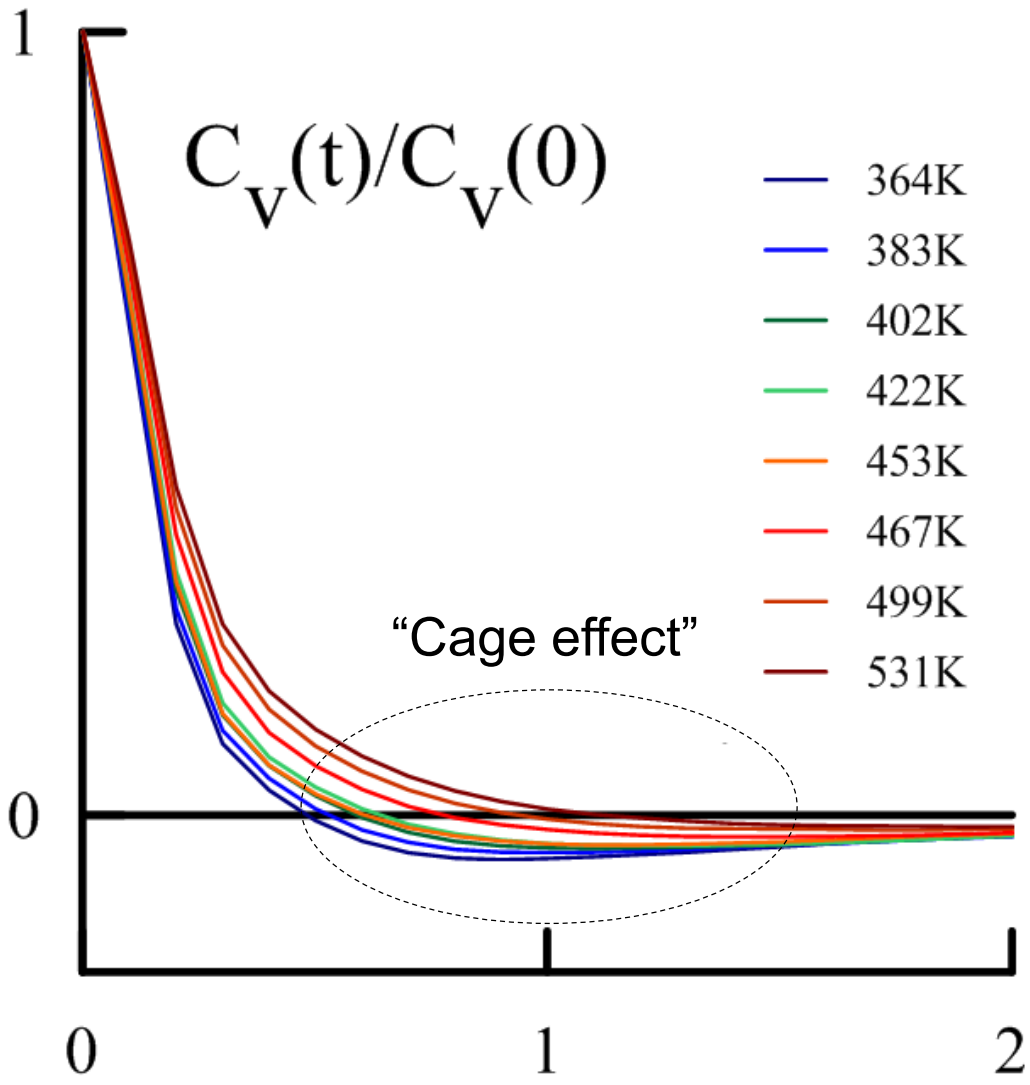
P. Padilla, S. Toxvaerd.
Structure and dynamical behavior of fluid n-alkanes.
J. Chem. Phys. **1991**. V. 95(1). P. 509.

H. Lee, H. Pak Molecular dynamics simulation of liquid alkanes. II. Dynamic properties of normal alkanes: n-butane to n-heptadecane.
Bull. Kor. Chem. Soc. **1997**. V. 18(5). P. 478.

M. H. Kowsari, S. Alavi, M. Ashrafizaadeh, B. Najafi
Molecular dynamics simulation of imidazolium-based ionic liquids. I. Dynamics and diffusion coefficient. J. Chem. Phys. **2008**. V. 129(22). P. 224508.

H. Liu, E. Maginn, A. E. Visser, N. J. Bridges, E. B. Fox
Thermal and Transport Properties of Six Ionic Liquids: An Experimental and Molecular Dynamics Study. Ind. Eng. Chem. Res. **2012**. V. 51(21). P. 7242.

Автокорреляторы скорости



“Cage effect”

$$N_{rebounding} > N_{scattering}$$

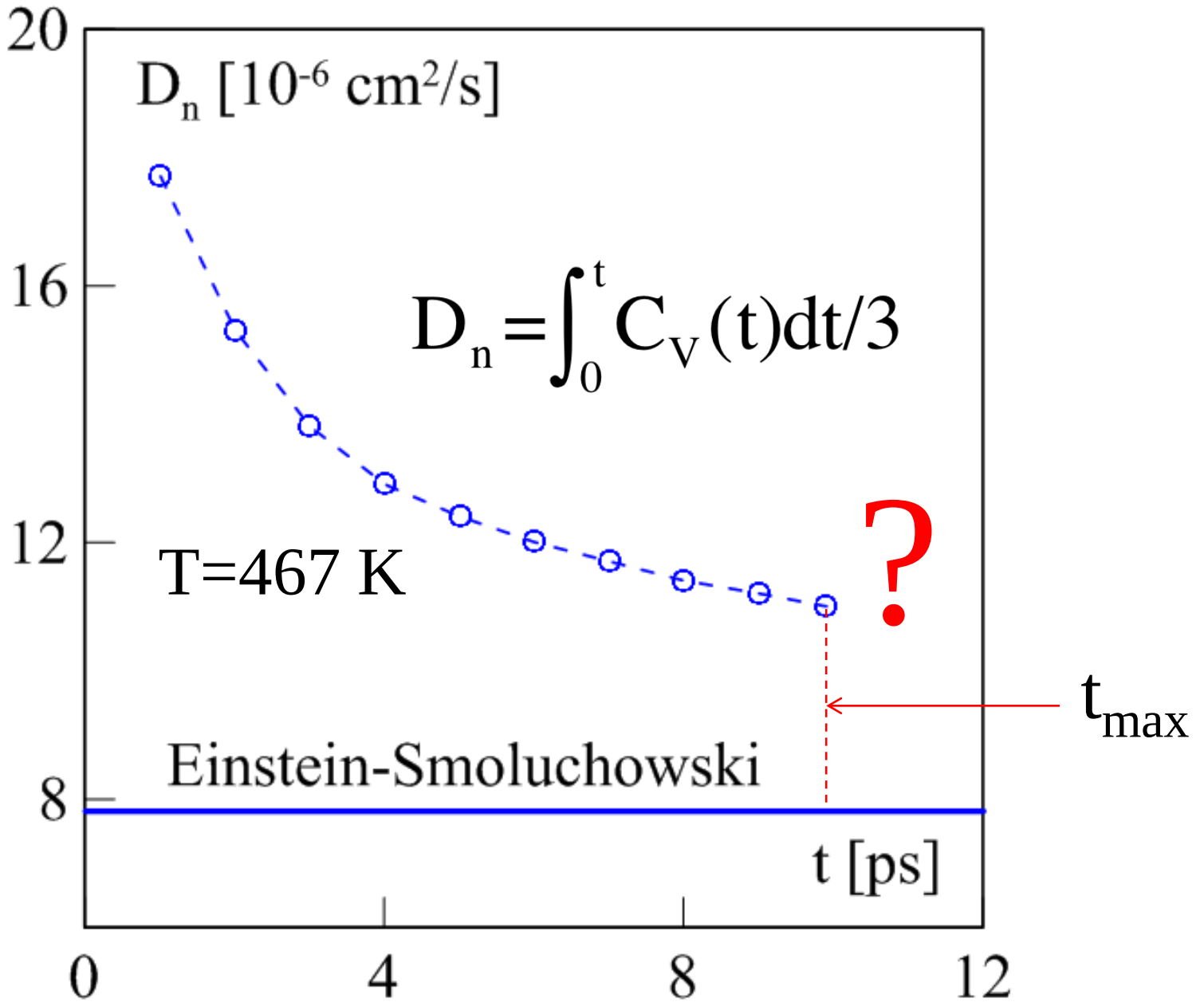
$$C_v(t) < 0$$

With the increase of T

$\rho \searrow$

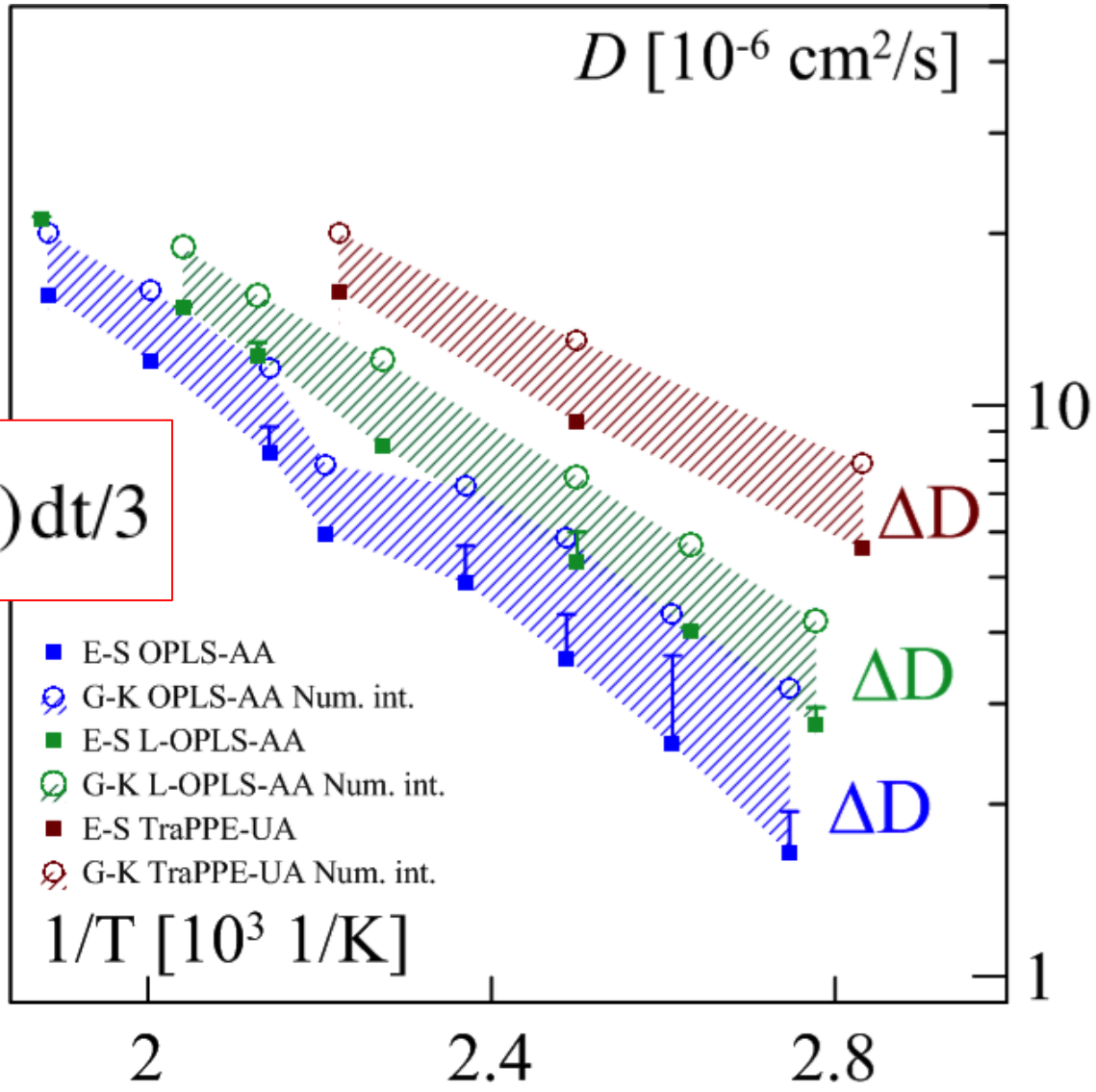
“Cage effect” disappears

Результаты численного интегрирования



Различие между Г-К и Э-С

$$D = \int_{t=0}^{7\,ps} C_V(t)\,dt/3$$

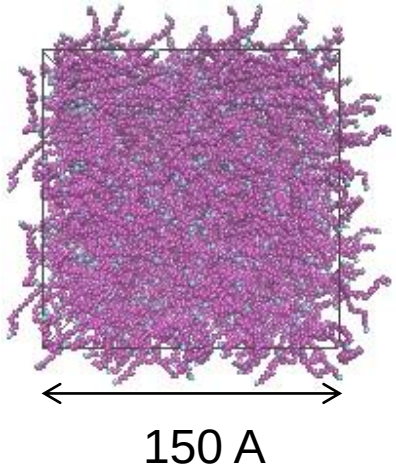


Значения Г-К **завышены**

Правила интегрирования

1) Влияние периодических условий*

$$t_{max} \sim L / v_s \sim 150\ \text{A}/1500\ \text{m/s} \sim 10\ \text{ps}$$



*V. Ya. Rudyak, G. V. Kharlamov, and A. A. Belkin
Diffusion of nanoparticles and macromolecules in dense gases and liquids // High Temp. **2001**. V. 39. No. 2. P. 264.

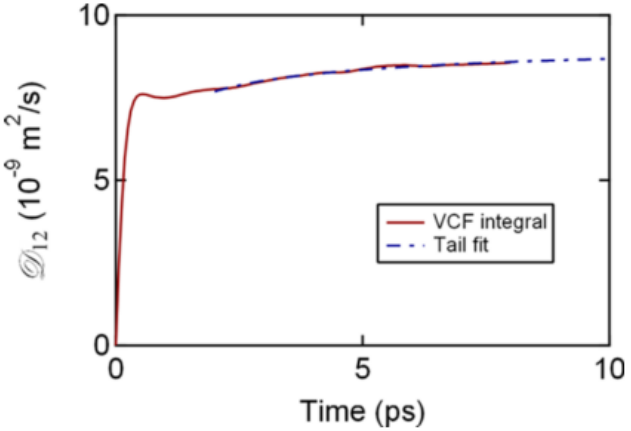
2) Момент, когда величина интеграла постоянна

I. Gholami, A. Fiege, A. Zippelius
Slow dynamics and precursors of the glass transition in granular fluids.
Phys. Rev. E. **2011.** V. 84. P. 1.

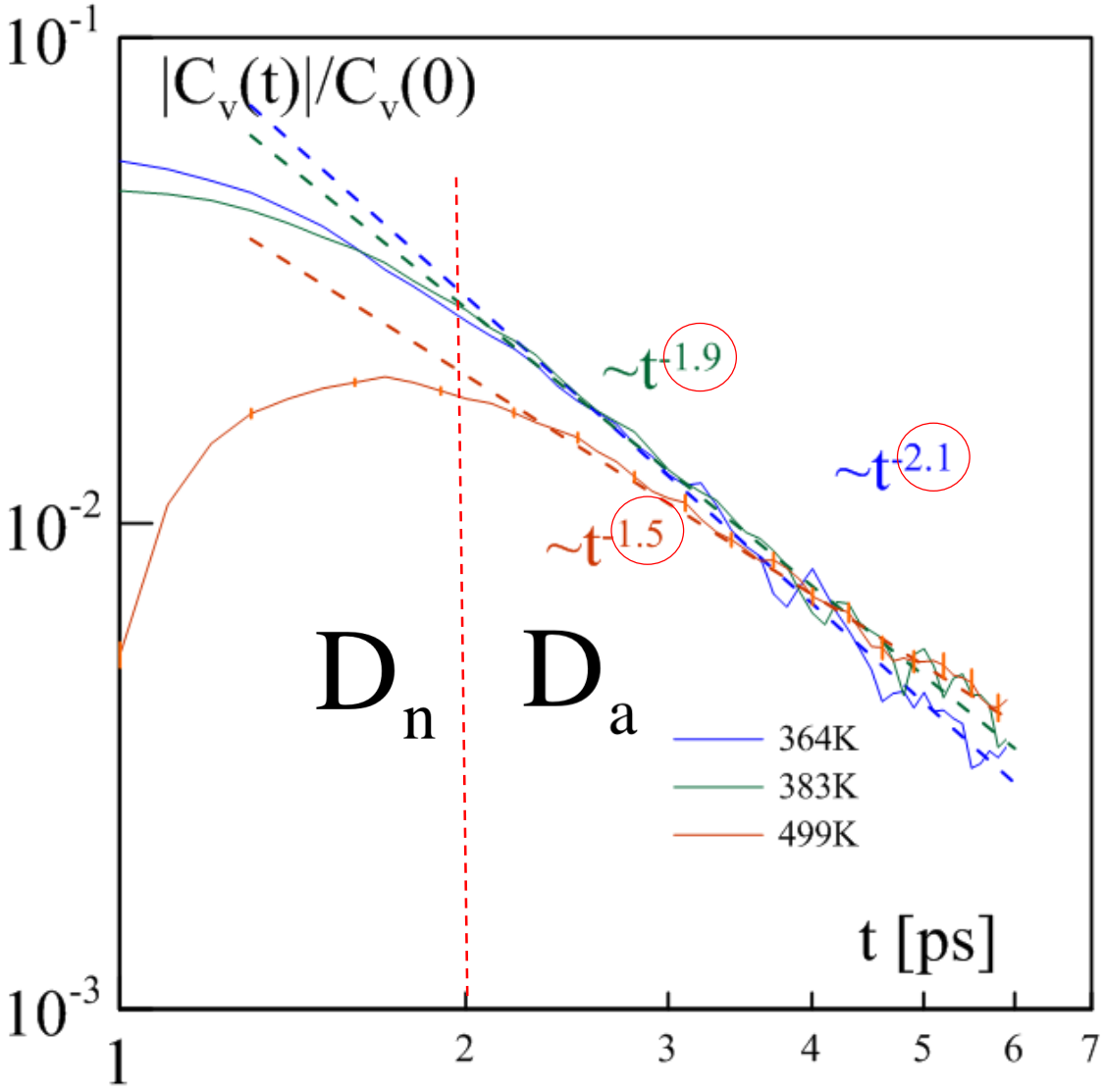
M. Śmiechowski
Molecular hydrogen solvated in water – A computational study.
J. Chem. Phys. **2015**. V. 143(24). P. 244505.

3) Найти асимптотику и продолжить интеграл

J. W. Nichols, D. R. Wheeler
Fourier Correlation Method for Simulating Mutual Diffusion Coefficients in Condensed Systems at Equilibrium.
Ind. Eng. Chem. Res. **2015**. V. 54(48). P. 12156.



Вклад асимптотики



$$\int_{t=0}^{2\,ps} C_V(t)\,dt/3$$

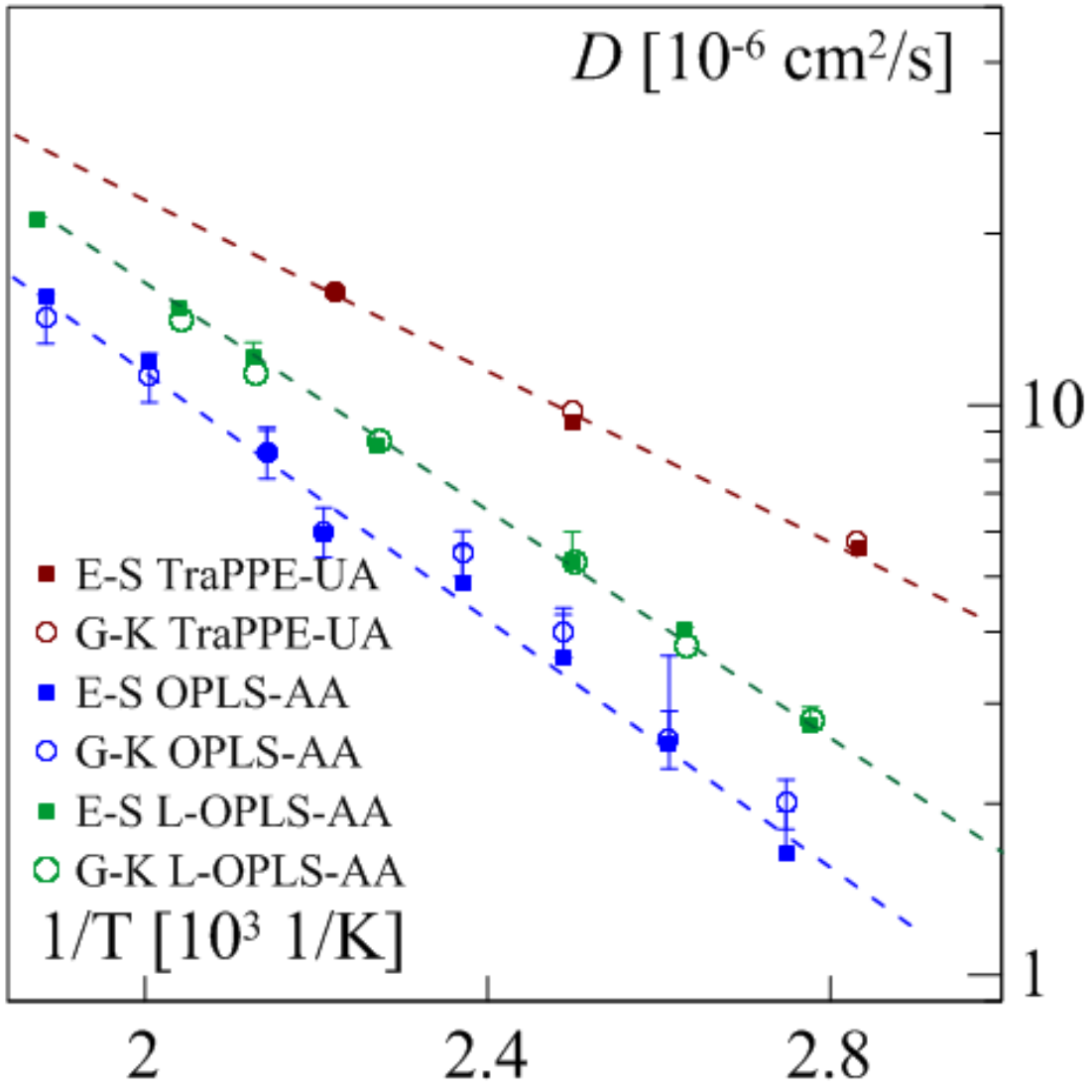
$$\shortparallel$$

$$D = D_n + D_a$$

$$\shortparallel$$

$$\int_{t=2ps}^{\infty} At^{-\beta}\,dt$$

Сходимость методов Г-К и Э-С



$$\sigma_\beta = 0.1$$

$$D_a^{max} = \int_{t=2\ ps}^{\infty} A t^{-\beta_{max}}\, dt/3$$

$$D_a^{min} = \int_{t=2\ ps}^{\infty} A t^{-\beta_{min}}\, dt/3$$

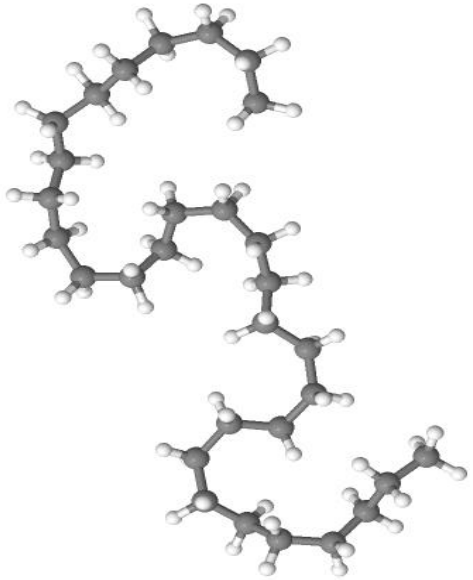
$$D_a^{ave} = \frac{[D_a^{max}(\beta_{max}) + D_a^{min}(\beta_{min})]}{2}$$

$$\sigma_D = D_a^{max} - D_a^{ave}$$

План доклада

n-$C_{30}H_{62}$

1. Самодиффузия в жидком н-триаконтане



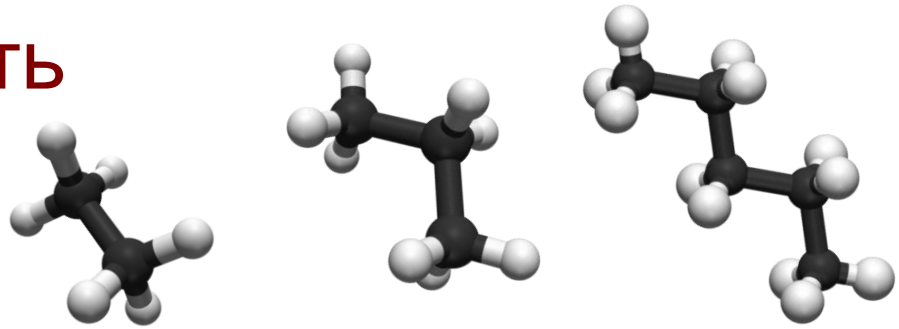
Молекула н-триаконтана

Потенциалы взаимодействия (+ COMPASS)

Сходимость Г-К

Предсказательная способность

2. Сдвиговая вязкость



Сходимость Г-К

Неравновесная МД + эксперимент

Выводы по части I

$$\int_{t=0}^{2\,ps} C_V(t)\,dt/3$$

$$\shortparallel$$

$$D = D_n + D_a$$

$$\shortparallel_{-\beta}$$

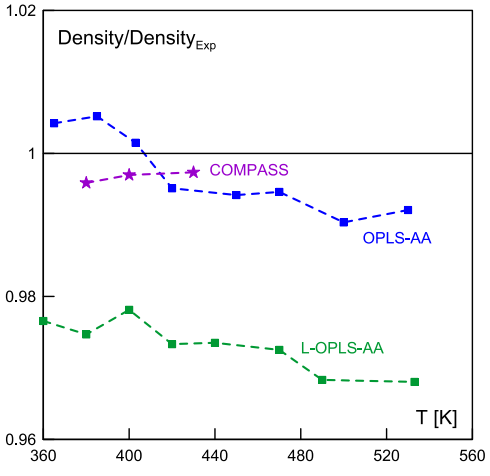
$$\int_{t=2ps}^{\infty} At^{\beta}\,dt$$

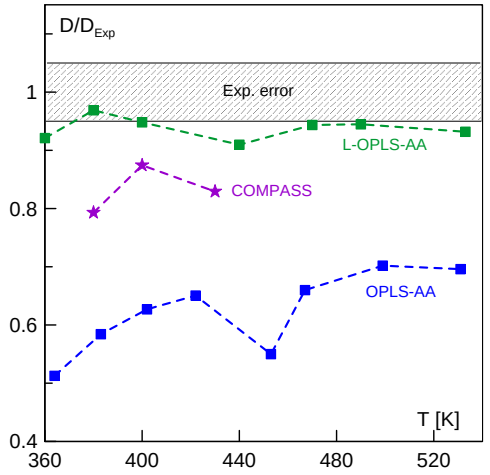
В системах с большими временами корреляции нельзя **численно** взять интеграл Грина-Кубо

Сходимость методов Грина-Кубо и Эйнштейна-Смолуховского с помощью **аналитического продолжения**

Модели класса I не воспроизводят **одновременно** УРС и D

У COMPASS **почти** получилось





N.D. Kondratyuk, G.E. Norman and V.V. Stegailov // J. Chem. Phys. 2016. **145**. 204504

Работа поддержана грантом РНФ 14-50-00124