# A semi-phenomenological approach to the structure and transport properties of macromolecules in solution

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**18/07/2006**

# A semi-phenomenological approach to the structure and transport properties of macromolecules in solution

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  - **Macromolecules in Solution**
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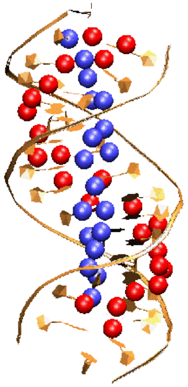
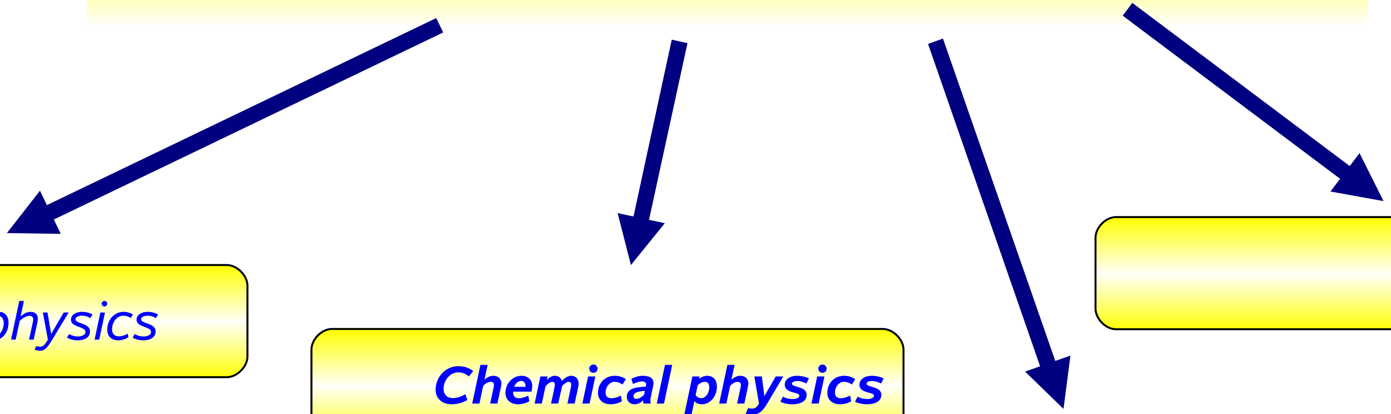
# Macromolecules in solution

*---- Introduction & Motivation*

**IUPAC definition:**

**A macromolecule is a larger complex molecule consisting of many smaller structural units (molecules, group of atoms, atoms) linked together.**





**Macromolecules**

**(polymers, proteins, lipids, PEO, ...)**

*Biophysics*

***Chemical physics***

*Material science*

...

# Macromolecules in solution

## *---- Introduction & Motivation*

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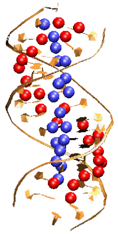
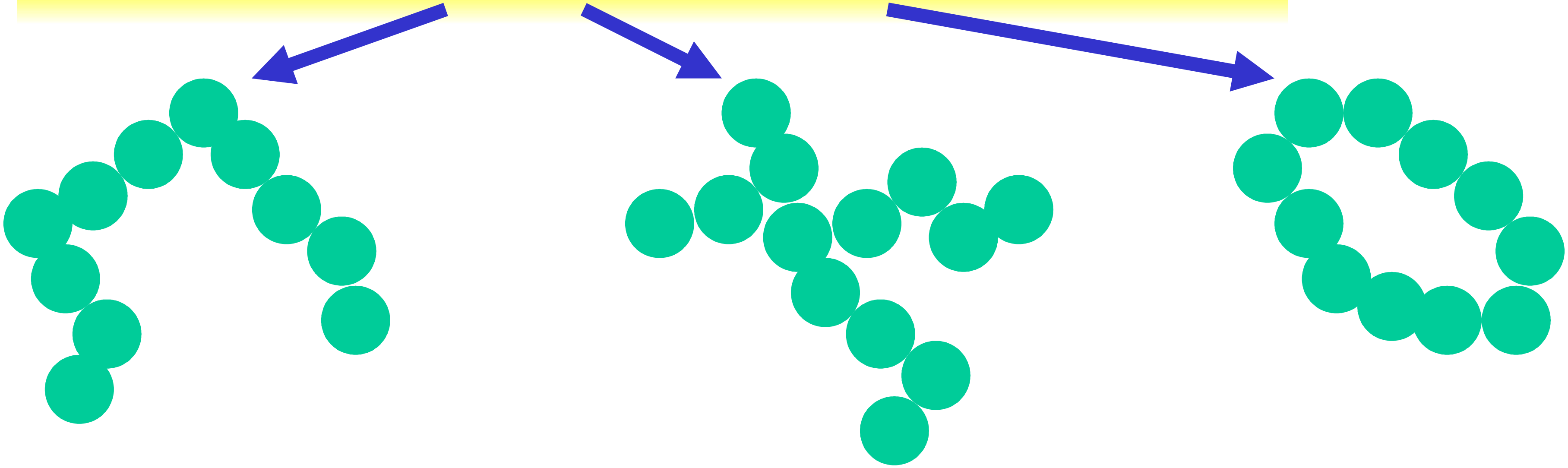


**Structural unit (so-called *bead* of the macromolecule)**



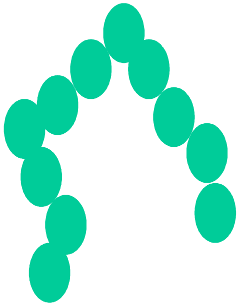
*Chain-shape*

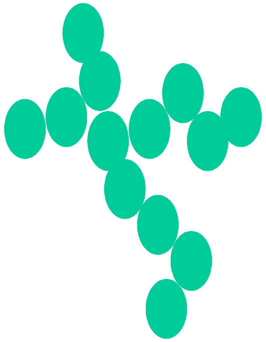
*Dendrimer-shape*

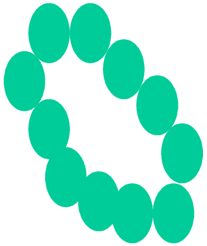
*Circle-shape*

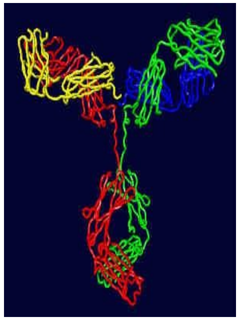
# Macromolecules in solution

## ---- *Structure & Transport properties*









Macromolecules:

- Very massive and complex ($10^3$-$10^5$ atoms)
- Slow ($v_{Macr} / v_{H2O} < 10^3$)
- Time scale of relaxation is much larger then the typical relaxation times of simple solvents

Translation diffusion coefficient:

$$D_T = \frac{\left\langle \left( R_a(0) - R_a(t) \right)^2 \right\rangle}{6t}$$

Center-of-mass (CM) diffusion coefficient:

$$D^{(CM)} = \frac{\left\langle \left( R_{cm}(0) - R_{cm}(t) \right)^2 \right\rangle}{6t}$$

Rotational diffusion coefficient:

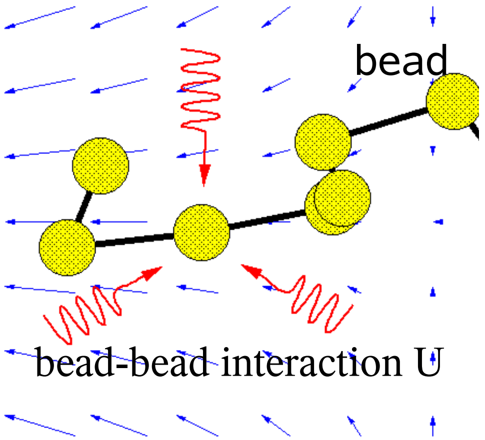
$$D_R = \frac{\left\langle \left( \Delta\theta(\Delta t) \right)^2 \right\rangle}{\Delta t}$$

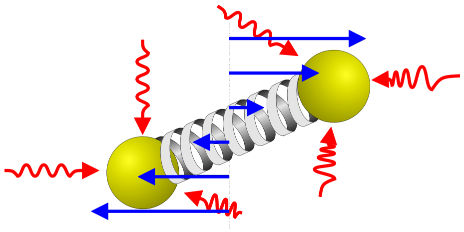
Time dependent correlation functions:

$$CF(t) = \left\langle A(0) A(t) \right\rangle$$

# Dynamics of the macromolecules in solution

## ---- *Macroscopic vs. Microscopic*





### Assumptions

- Molecule has internal structure (non-uniform).
- Molecule much more heavy and slower than solvent particles

### Macroscopic (phenomenological)

- **Solvent is a uniform non-compressible medium.**
- **Phenomenological boundary conditions**
- **Bead-solvent interaction: via random forces** **(Gaussian distributed)**

### Basic mathematical assumptions:

- The beads are assumed to be "embedded" to the solvent flow

  (Stoke's law: $F = -\xi v$)
- The transport and diffusion are described via the Diffusion Eq.

  (Fick's laws)

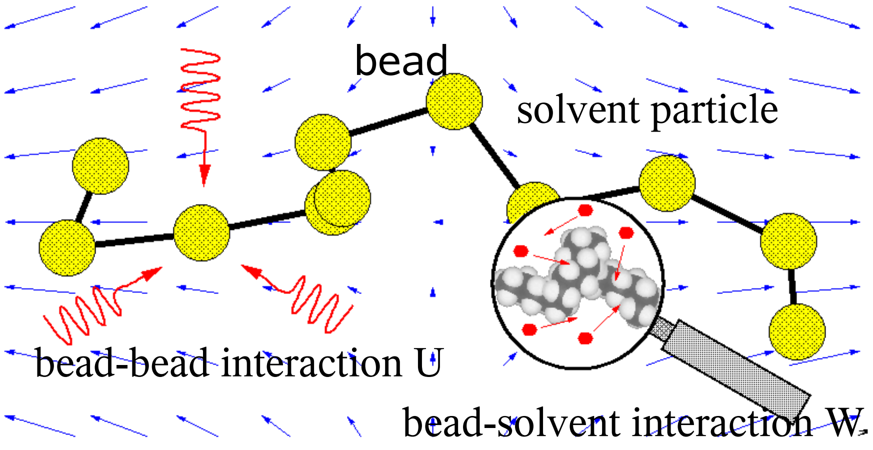
**The dynamical behaviour of the macromolecules more complex!**

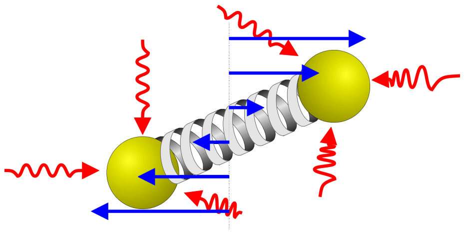
*„... these mathematical assumptions must be questioned since macromolecule can not be considered as „embedded" into the surroundings but dramastically start to „emancipate" from the solvent".*

**B. Dünweg and K. Kremer, *J. Chem. Phys.* 99 (1993) 6984.**

# Dynamics of the macromolecules in solution

## *---- Macroscopic vs. Microscopic*





### Assumptions

- Molecule has internal structure (non-uniform).
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### Macroscopic (phenomenological)

- Solvent is a uniform non-compressible medium.
- Phenomenological boundary conditions
- Bead-solvent interaction: via random forces (Gaussian distributed)

### **Microscopic**

- **Solvent as set of particles with given mass m**
- **Discrete structure of the solvent ('solvent-solvent' interaction V)**
- **Bead-solvent interaction: via potentials W**

**Semi-phenomenological approach to the study of the macromolecular dynamics**

***Total energy of the system (Hamiltonian)***

$$\mathbf{H} = \mathbf{H}_{M} + \mathbf{H}_{S} + \mathbf{H}_{MS}$$

Macromolecular Dynamical Simulations (Newton's equations)

Phase-space formalism (Liouville equation)

# Microscopic theory of molecules in solution

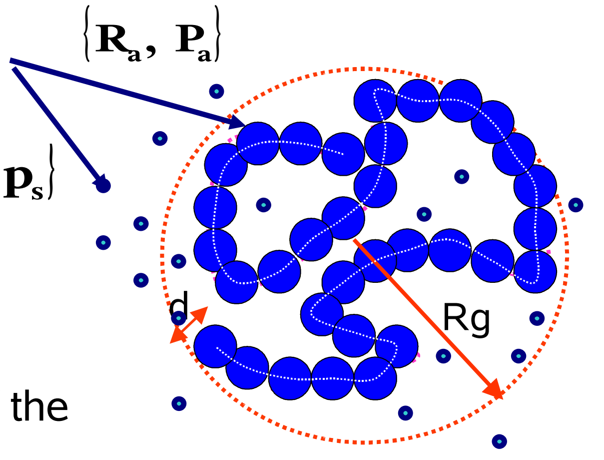
## ---- *Molecular Dynamics Simulation (MDS)*

Hamiltonian of the system

$$H = H_M + H_S + H_{MS}$$

$$= \underbrace{\sum_{a=1}^{N} \frac{P_a^2}{2M} + \sum_{a<b}^{N} U(|R_a - R_b|)}_{M} + \underbrace{\sum_{s=1}^{n} \frac{p_s^2}{2m} + \sum_{s<t}^{n} V(|r_s - r_t|)}_{S} + \underbrace{\sum_{a=1}^{N}\sum_{s=1}^{n} W(|R_a - r_s|)}_{MS} \qquad \{r_s, p_s\}$$

$\{R_a, P_a\}$



Numerical solution of the equations of the motion for given interactions U, V, W

**Equations of the motion**

Macrom.:

$$\frac{dR_a}{dt} = \frac{\partial [H_M + H_{MS}]}{\partial P_a}, \quad \frac{dP_a}{dt} = -\frac{\partial [H_M + H_{MS}]}{\partial R_a}$$

Solvent:

$$\frac{dr_s}{dt} = \frac{\partial [H_S + H_{MS}]}{\partial p_s}, \quad \frac{dp_s}{dt} = -\frac{\partial [H_S + H_{MS}]}{\partial r_s}$$

**MDS covers only time relaxation processes with duration approx. 100nsec, while relaxation time of the typical macromolecules $10^{-5}$ - $10^{-3}$sec, and longer.**

(A resent "larger" MD Simulation:
P[illegible] et al. JACS 127, 4576 (2005)
(7400 water molecules + macromolecules)-
118 ns duration

**Simulation of the relaxation processes of 1 ms is ~ $10^{9}$ more expensive than our abilities in 2006**

**Moore's law: this might be possible not before 2050**

# Microscopic theory of molecules in solution

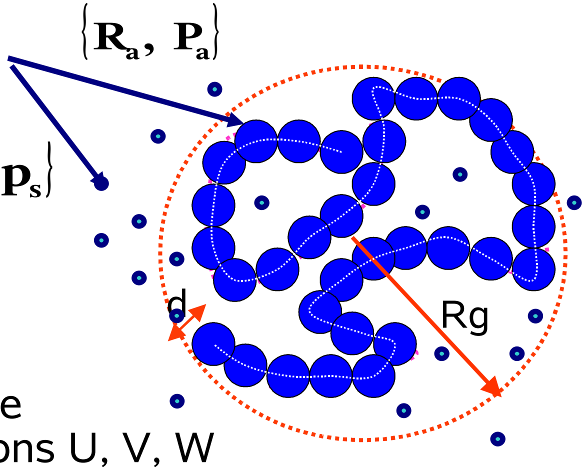
## ---- *phase-space dynamics*

Hamiltonian of the system

$$H = H_M + H_S + H_{MS}$$

$$= \underbrace{\sum_{a=1}^{N} \frac{P_a^2}{2M} + \sum_{a<b}^{N} U(|R_a - R_b|)}_{M} + \underbrace{\sum_{s=1}^{n} \frac{p_s^2}{2m} + \sum_{s<t}^{n} V(|r_s - r_t|)}_{S} + \underbrace{\sum_{a=1}^{N}\sum_{s=1}^{n} W(|R_a - r_s|)}_{MS}$$

$\{r_s,\ p_s\}$



**Liouville equation (LE)**

Liouville equations for the phase-space distribution function for given interactions U, V, W

$$\boxed{\frac{\partial \rho}{\partial t} = \left[\hat{L}_M + \hat{L}_S + \hat{L}_{MS}\right] \rho \ (\{R,P\},\{r,p\};t)}$$

Liouville operators: $\hat{L}_i = \sum_i \left[ \frac{\partial H_i}{\partial \vec{r}_i} \frac{\partial}{\partial \vec{p}_i} + \frac{\partial H_i}{\partial \vec{p}_i} \frac{\partial}{\partial \vec{r}_i} \right], \quad i = M, S, MS$

$$\langle B(\{R(t),P(t)\},\{r(t),p(t)\})\rangle = \int B(\{R,P\},\{r,p\})\rho\ (\{R,P\},\{r,p\};t)d\{R,P\}d\{r,p\}$$

**Liouville Eq. describes fully the time evolution of the phase-space df of the overall system 'macromolecule + solvent' and contains all information about dynamics of the system.**

**Integration of the Liouville Eq. has the same difficulties like in the case of MDS**

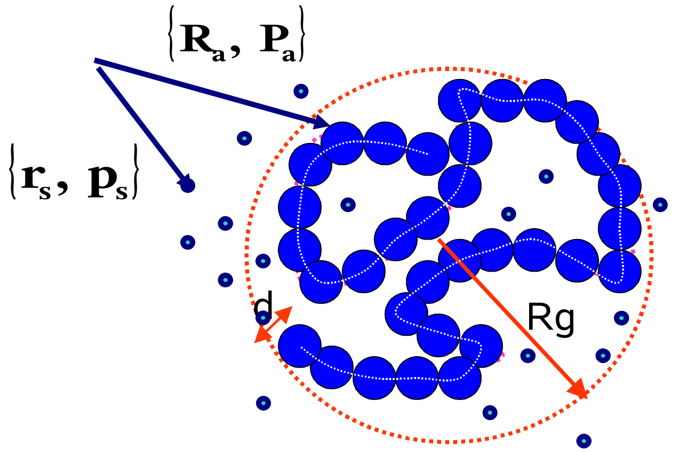
**Fortunately, this ansatz can be the starting point for further simplifications.**

# Microscopic theory of molecules in solution

## *---- phase-space dynamics*

## Liouville equation

$$\frac{\partial \rho}{\partial t} = \left[\hat{L}_M + \hat{L}_S + \hat{L}_{MS}\right] \rho \; (\{R,P\},\{r,p\};t)$$



Liouville operators

$$\hat{L}_i = \sum_i \left[ \frac{\partial H_i}{\partial \vec{r}_i}\frac{\partial}{\partial \vec{p}_i} + \frac{\partial H_i}{\partial \vec{p}_i}\frac{\partial}{\partial \vec{r}_i} \right], \quad i = M, S, MS$$

Integration over all coordinates of the solvent

$$\rho_N(\{R_a,P_a\};t) = \int d\{r_s,p_s\}\,\rho(\{R_a,P_a\},\{r_s,p_s\};t)$$

## Initial conditions:

- Solvent is in equilibrium state $\Phi_{eq}$
- Macromolecule and solvent do not interact before initial time
- At the initial time, the full distribution can be factorized as $\rho(0)=\rho_N(0)\ \Phi_{eq}$

$$\boxed{\frac{\partial \rho_N}{\partial t} = Z(\ldots;U,W)}$$

Bead-bead

Bead-solvent

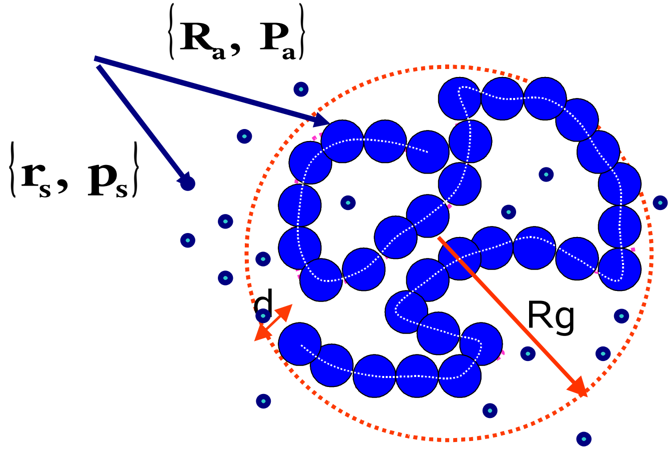
## Projection operator formalism:

$$\boxed{\hat{P}\,(\ldots) = \int d\{r_s,p_s\}\,(\ldots) \qquad \hat{Y} = 1 - \hat{P}}$$

A. Uvarov and S. Fritzsche, *Macromol. Theo. Sim.* **13** (2004) 241

# Microscopic theory of molecules in solution

## ---- *Fokker-Planck equation & Friction tensor*



## Liouville equation

$$\frac{\partial \rho}{\partial\, t} = \left[\hat{L}_M + \hat{L}_S + \hat{L}_{MS}\right] \rho\ \ (\{R,P\},\{r,p\};t)$$

Liouville operators

$$\hat{L}_i = \sum_i \left[ \frac{\partial\, H_i}{\partial\, \vec{r}_i} \frac{\partial}{\partial\, \vec{p}_i} + \frac{\partial\, H_i}{\partial\, \vec{p}_i} \frac{\partial}{\partial\, \vec{r}_i} \right], \quad i = M, S, MS$$

Integration over all
coordinates of the solvent

$$\rho_N(\{R_a, P_a\}; t) = \int d\{r_s, p_s\}\, \rho(\{R_a, P_a\}, \{r_s, p_s\}; t)$$

## Fokker-Planck equation

$$\frac{\partial \rho_N}{\partial t} + \frac{P_a}{M} \frac{\partial \rho_N}{\partial R_a} - \frac{\partial U(|R_a - R_b|)}{\partial P_a} \frac{\partial \rho_N}{\partial P_a} = \frac{\partial}{\partial P_a} \xi^{ab} \left[ \frac{\partial}{\partial P_b} + \frac{P_b}{k_B T M} \right] \rho_N$$

Bead-bead

Friction tensors

**dynamical coupling between solvent and molecule**

**Structure factor of the solution**

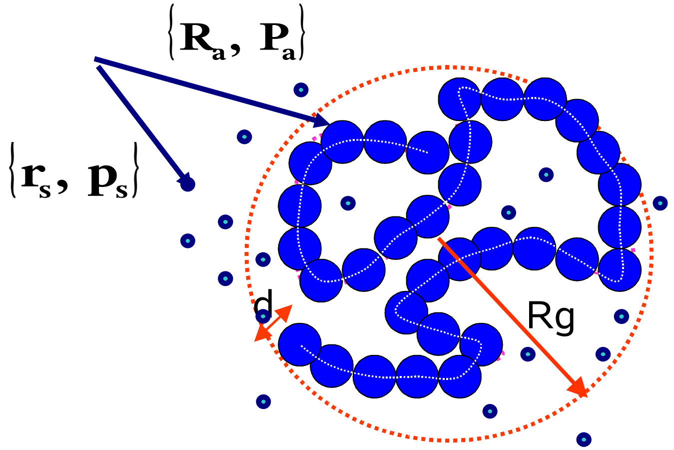
**bead-solvent interaction**

A. Uvarov and S. Fritzsche, *Macromol. Theo. Sim.* **13** (2004) 241; *Phys. Rev. Letter* (2006) *submitted*

# Fokker-Planck equation & Friction tensors

## ---- *phase-space dynamics*

$$\frac{\partial \rho_N}{\partial t}+\frac{P_a}{M}\frac{\partial \rho_N}{\partial R_a}-\frac{\partial U(|R_a-R_b|)}{\partial P_a}\frac{\partial \rho_N}{\partial P_a}=\frac{\partial}{\partial P_a}\xi^{ab}\left[\frac{\partial}{\partial P_b}+\frac{P_b}{k_B T M}\right]\rho_N$$



Thermodynamic limit: $\mathbf{n}\to\infty;\ \mathbf{V}\to\infty;\ \mathbf{n}/\mathbf{V}\to\mathbf{n}_0$

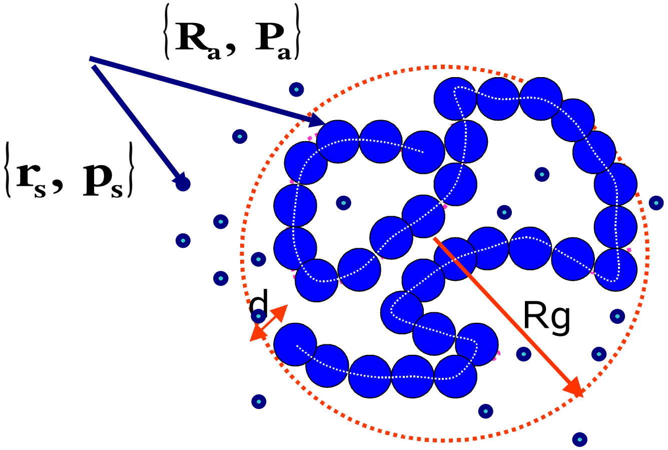
Series expansion of the time evolution operator: $\exp\left[-t\hat{Y}\hat{L}_{MS}\right]=\sum_{j=0}^{\infty}\frac{t^j}{j!}\left[\hat{Y}\hat{L}_{MS}\right]^j$

$$\boxed{\xi_{\alpha\beta}^{(ab)}=\sum_j \xi_{\alpha\beta}^{(ab)}{}_{[j]}=\xi_{\alpha\beta}^{(ab)}{}_{0}+\xi_{\alpha\beta}^{(ab)}{}_{[1]}+\xi_{\alpha\beta}^{(ab)}{}_{[2]}+\ldots}$$

# Fokker-Planck equation & Friction tensors

***---- phase-space dynamics***

$$\frac{\partial \rho_N}{\partial t}+\frac{P_a}{M}\frac{\partial \rho_N}{\partial R_a}-\frac{\partial U(|R_a-R_b|)}{\partial P_a}\frac{\partial \rho_N}{\partial P_a}=\frac{\partial}{\partial P_a}\xi^{ab}\left[\frac{\partial}{\partial P_b}+\frac{P_b}{k_B T M}\right]\rho_N$$



## Translational motion

✓ friction tensors parameters

✓ single-bead molecules

✓ dumbbell molecules

✓ N-bead macromolecules

o *various masses, shapes and bead-bead interactions*

o *different topologies*

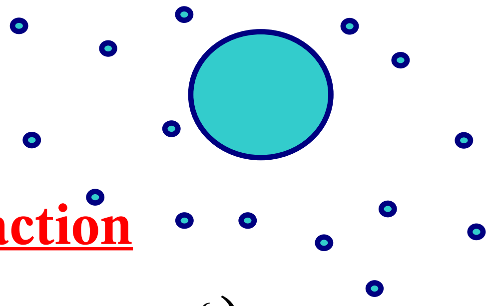
o …

## Rotational motion

A. Uvarov, S. Fritzsche, *Chem. Phys. Lett.*, 401 (2005) 296

# Translational motion of the macromolecule

## ---- *a few, short examples*



### 1. Friction tensor for the various bead-solvent interaction

Charge particles: (*Coulomb-like interaction*)
Neutral particles: (*Born-Mayer and van der Waals interaction*)

### 2. Diffusion coefficient for the „*weak*“ van der Waals interaction

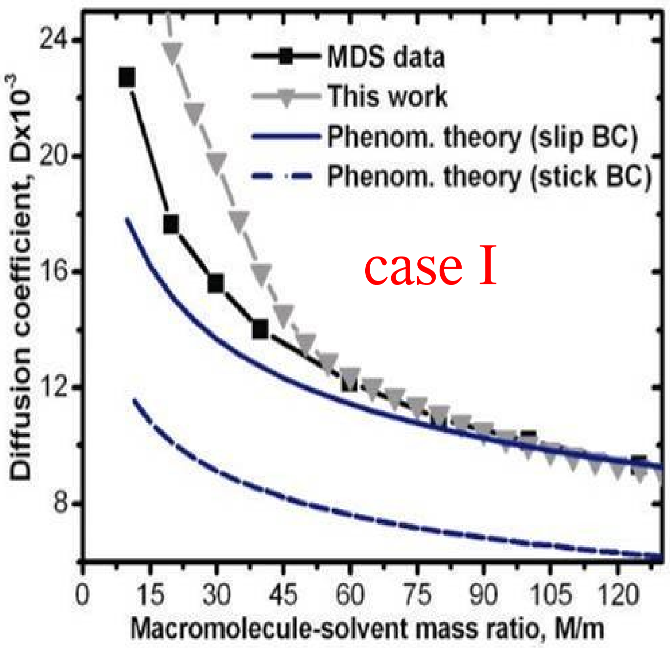
$$\boxed{D^{(cm)} = k_B T \xi^{(cm)-1}}$$

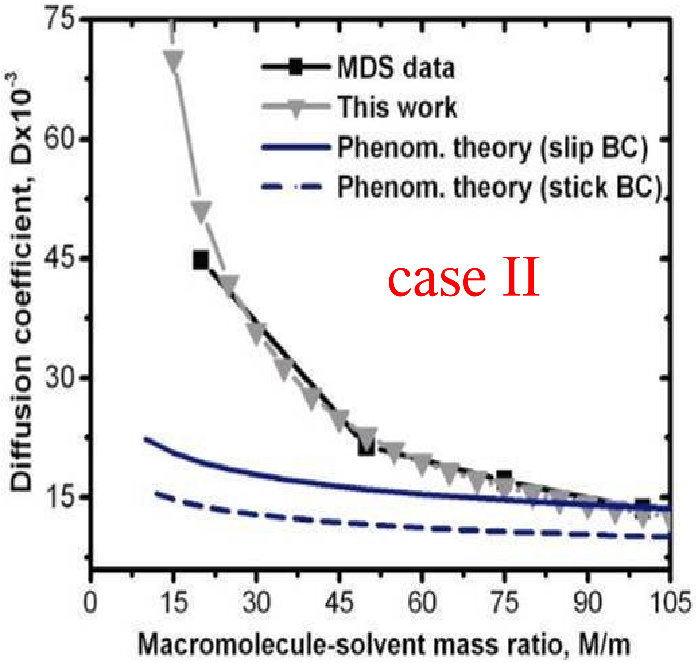
$$W = \begin{cases} 4\varepsilon_{MS}\left(\left[\frac{\sigma}{(r-1_M)}\right]^{12} - \left[\frac{\sigma}{(r-1_M)}\right]^{6}\right) & \text{if} \quad r \le 2.5\sigma \\ 0, & \text{otherwise} \end{cases}$$

### A: *Single-bead macromolecule:*

Diffusion coefficient as function of the mass ratio M/m.

Equal mass density of the bead and solvent particles





case I

$$k_B T = \varepsilon_{SS}; \quad n_0 = 0.85/\sigma^3$$

MD: J. Schmidt and S. Skiner,
J. Chem. Phys. 119, 8062 (2003).

case II

$$k_B T = 2.95\varepsilon_{SS}; \quad n_0 = 0.60/\sigma^3$$

MD: Ould-Kaddour et al.,
Phys. Rev. E63, 011205 (2001).

A. Uvarov, S. Fritzsche, *Phys. Rev.* E73 (2006) 011111

# Translational motion of the macromolecule

## ---- *a few, short examples*

1. Friction tensor for the various bead-solvent interaction

Charge particles: (*Coulomb-like interaction*)
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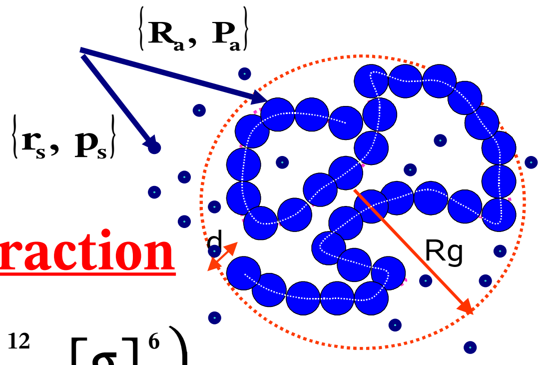


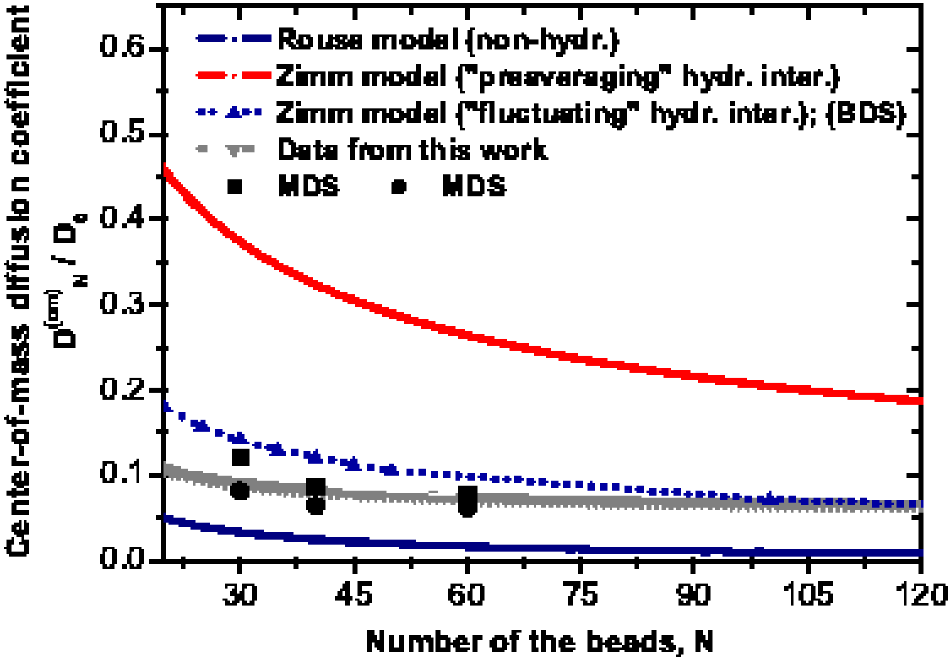
## 2. Diffusion coefficient for the „*weak*“ van der Waals interaction

$$\boxed{D^{(cm)} = k_B T \xi^{(cm)-1}}$$

$$W = \begin{cases} 4\varepsilon_{MS}\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right) & \text{if} \quad r \le 2.5\sigma \\ 0, & \text{otherwise} \end{cases}$$

## B: *N-bead chain molecule:*

CM Diffusion coefficient as function of the degree of polymerization N



$$k_B T = 1.12\varepsilon_{SS}; \quad n_0 = 0.90/\sigma^3$$

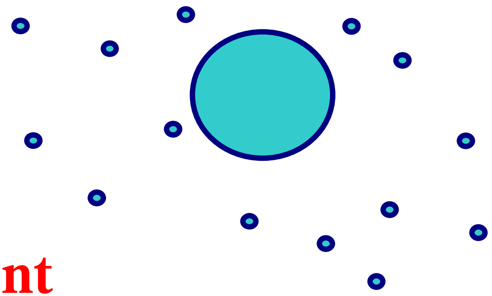
MD (square): B. Dünweg et al.,
J. Chem. Phys. 117, 930 (2002).

MD (hexagonal): K. Kremer et al.,
J. Chem. Phys. 119, 6983 (1993).

A. Uvarov, S. Fritzsche, *Phys. Rev. Lett.* (2006), *submitted*

# Translational motion of the macromolecule

## *---- a few, short examples*



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   Charge particles: (*Coulomb-like interaction*)
   Neutral particles: (*Born-Mayer and van der Waals interaction*)

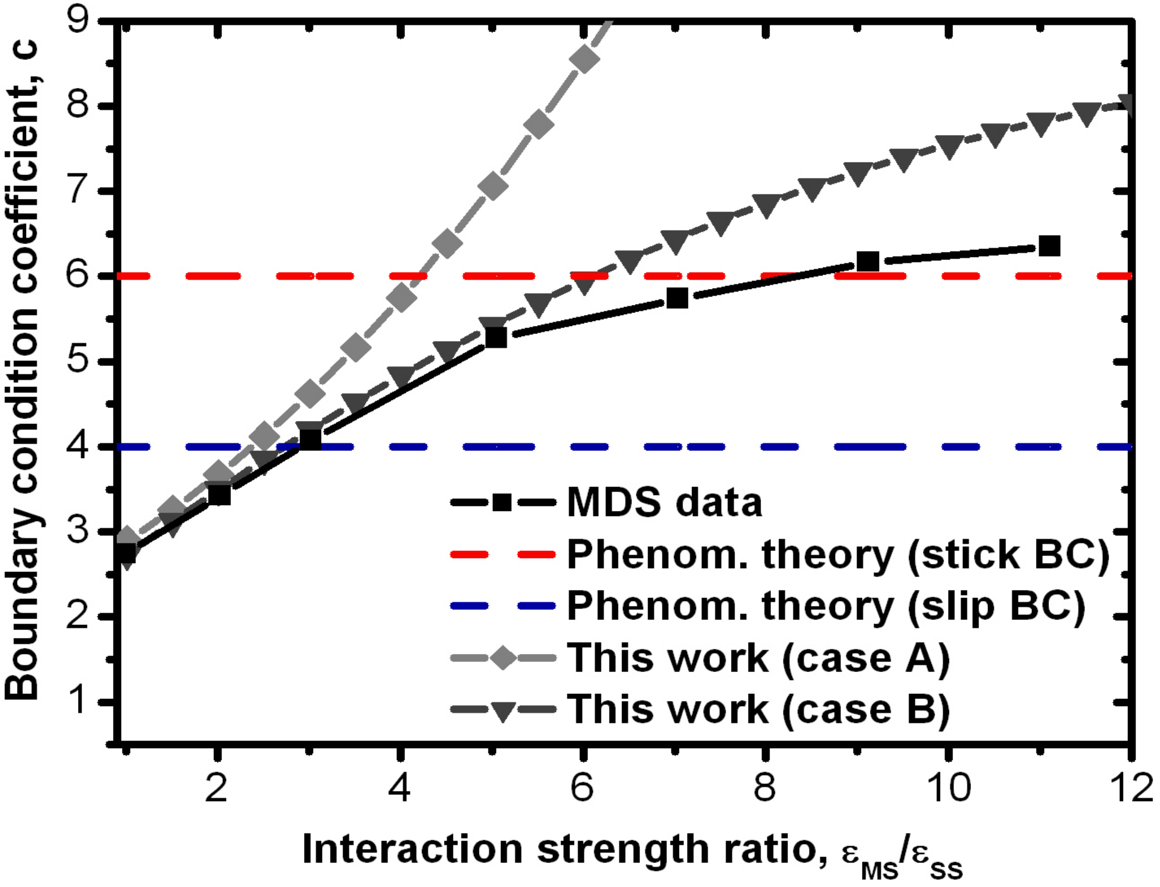
2. Diffusion coefficient for the „*weak*“ van der Waals interaction

3. **Transition from slip to stick boundary condition coefficient**

$$c = \frac{k_B T}{D^{(cm)} \pi \eta R_{hydr}}$$

Boundary condition coefficient as function of the strength ratio $\varepsilon_{MS} / \varepsilon_{SS}$

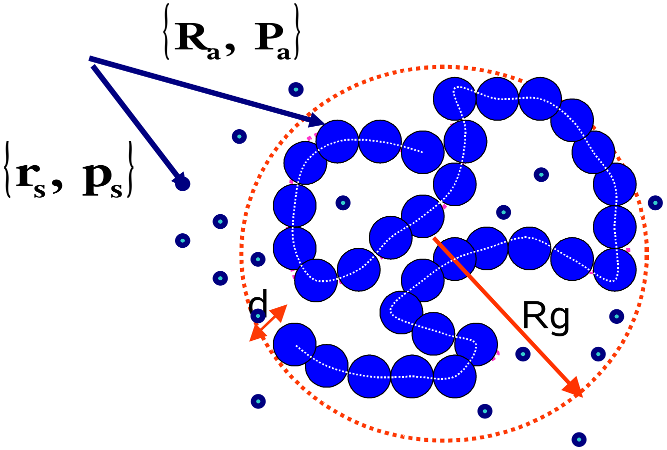
M/m=200



# Fokker-Planck equation & Friction tensors

*---- phase-space dynamics*

$$\frac{\partial \rho_N}{\partial t}+\frac{P_a}{M}\frac{\partial \rho_N}{\partial R_a}-\frac{\partial U(|R_a-R_b|)}{\partial P_a}\frac{\partial \rho_N}{\partial P_a}=\frac{\partial}{\partial P_a}\xi^{ab}\left[\frac{\partial}{\partial P_b}+\frac{P_b}{k_B T M}\right]\rho_N$$



## Translational motion

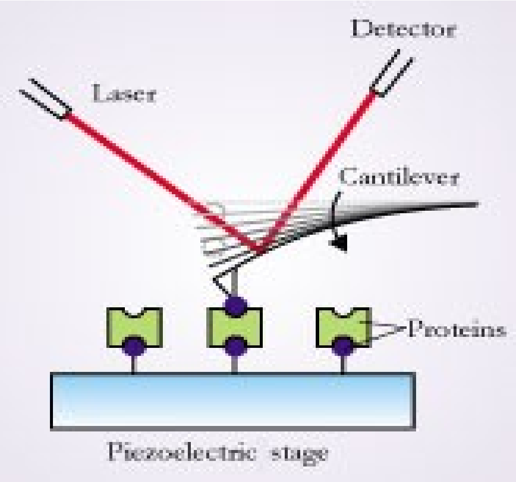
- ✓ friction tensors parameters
- ✓ single-bead molecules
- ✓ dumbbell molecules
- ✓ N-bead macromolecules
- ○ *various masses, shapes and bead-bead interactions*
- ○ *different topologies*
- ○ …

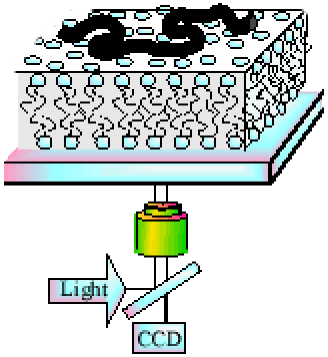
## Rotational motion

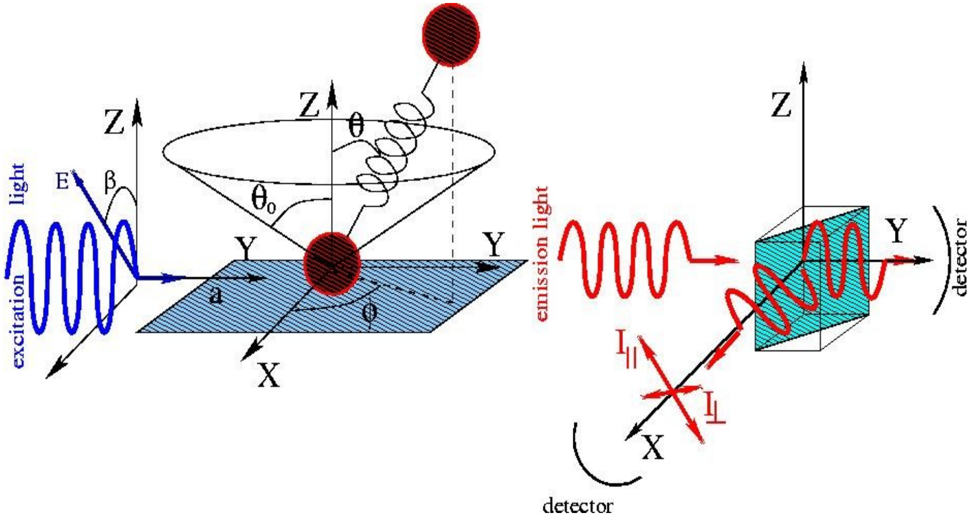
- ✓ Restricted rotation of dumbbell molecules
- ✓ Bead-bead and bead-surface interactions
- ○ *3- and 4-bead chains*
- ○ *different topologies*
- ○ …

# Rotational motion of macromolecules

## *---- immobilized on the surface*







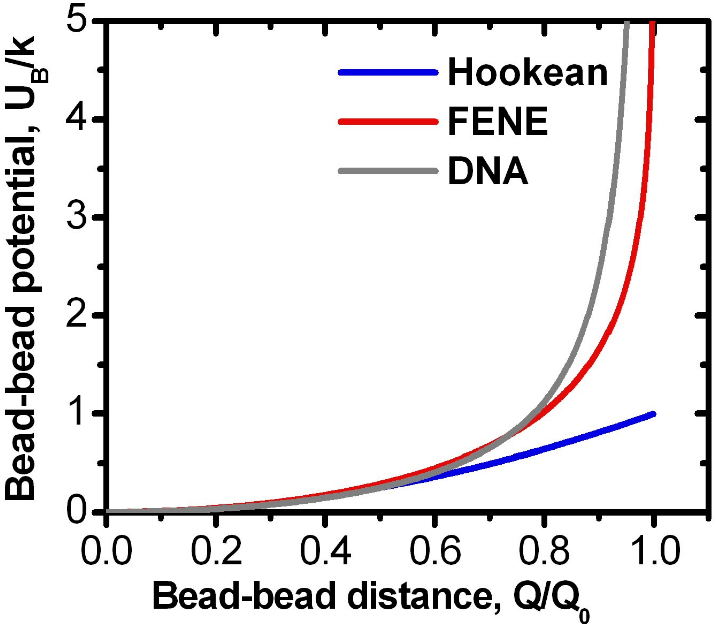
Rotational diffusion coefficient: $$D_R = \frac{\left\langle \left( \Delta\theta(\Delta t) \right)^2 \right\rangle}{\Delta t}$$

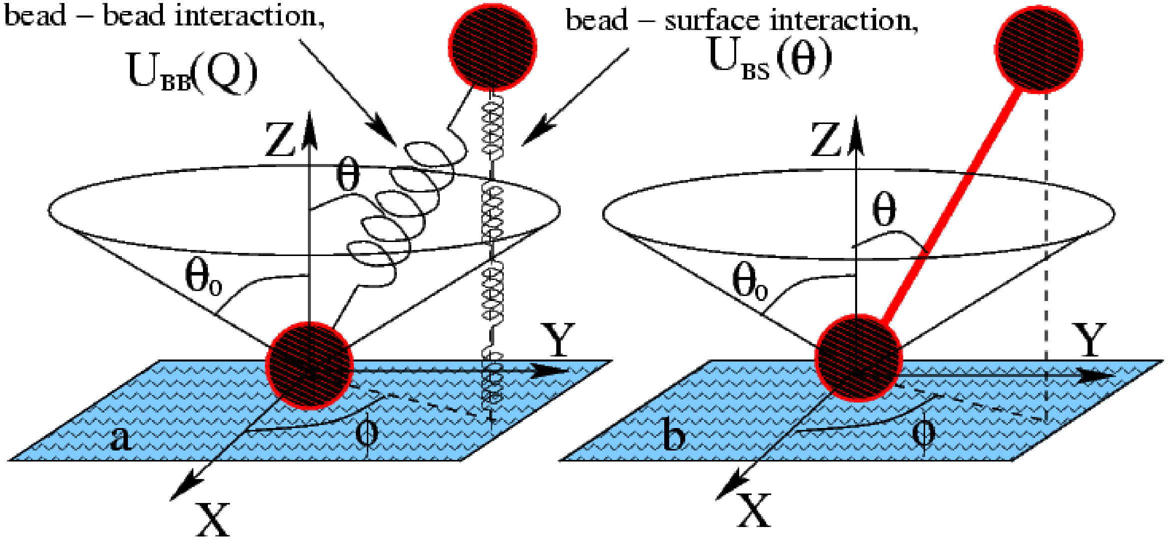
Orientation correlation function: $$C(t) = \frac{1}{2}\left\langle 3\cos^2\theta(t) - 1 \right\rangle$$

Phenomenological view point of the solvent

# Rotational motion of macromolecule

## *---- immobilized on the surface*





Bead-bead interaction:

- Hookean
- FENE
- Fraenkel
- DNA-type

Bead-surface interaction:

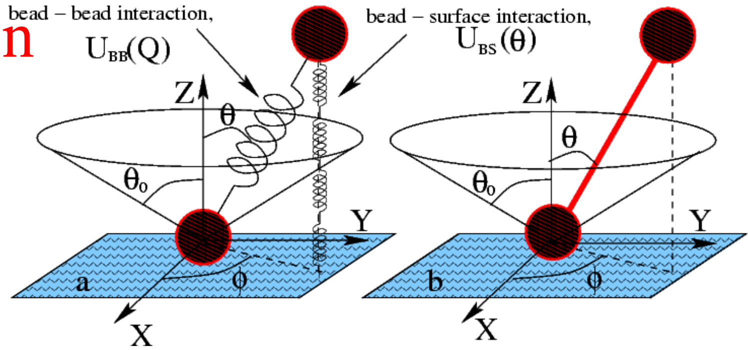
- Cone
- Effective double well (Sin)

$$U_B^{DNA} = k_{DNA}\left( \frac{1}{4\left(1 - \frac{Q}{Q_0}\right)} - \frac{1}{4}Q + \frac{Q^2}{2Q_0^2} - \frac{1}{4} \right)$$

A. Uvarov and S. Fritzsche, *J. Chem. Phys.* **121** (2004) 6566

# Rotational motion of macromolecule

## ---- *Configuration-space distribution*



Fokker-Planck equation

$$\frac{\partial \rho_N}{\partial t}+\frac{P_a}{M}\frac{\partial \rho_N}{\partial R_a}-\frac{\partial U(|R_a-R_b|)}{\partial P_a}\frac{\partial \rho_N}{\partial P_a}=\frac{\partial}{\partial P_a}\xi^{ab}\left[\frac{\partial}{\partial P_b}+\frac{P_b}{k_B T M}\right]\rho_N$$

Restricted boundary conditions

$$0 \le \theta \le \theta_0 (\le \pi/2)$$
$$0 \le \varphi \le 2\pi$$
$$0 \le Q \le Q_0$$

Integration over all moments of the beads

$$\psi(Q=\Delta_{12},\theta,\varphi;t)=\int dP_1 dP_2\ \rho_2(R_1,R_2,P_1,P_2;t)$$

Configuration-space distribution

Bead-bead

Bead-surface

$$\psi(Q,\theta,\varphi;t)=\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}e^{-\nu_n^m\left(\nu_n^m+1\right)D_R t}Y_{\nu_n^m}^m(\Omega(0))Y_{\nu_n^m}^m(\Omega(t))\Psi_{\nu_n^m}\left(Q;U_{BB},U_{BS}\right)$$

***Radial distribution function***

A. Uvarov and S. Fritzsche, *Progr. Coloid. Scien.* **133** (2006) 95

# Rotational motion of the macromolecule

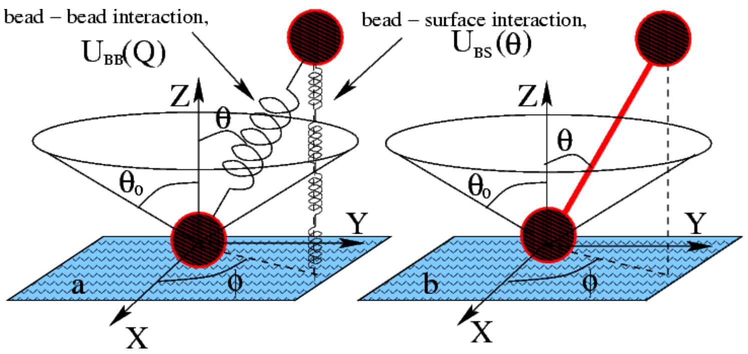
*---- a few, short examples*

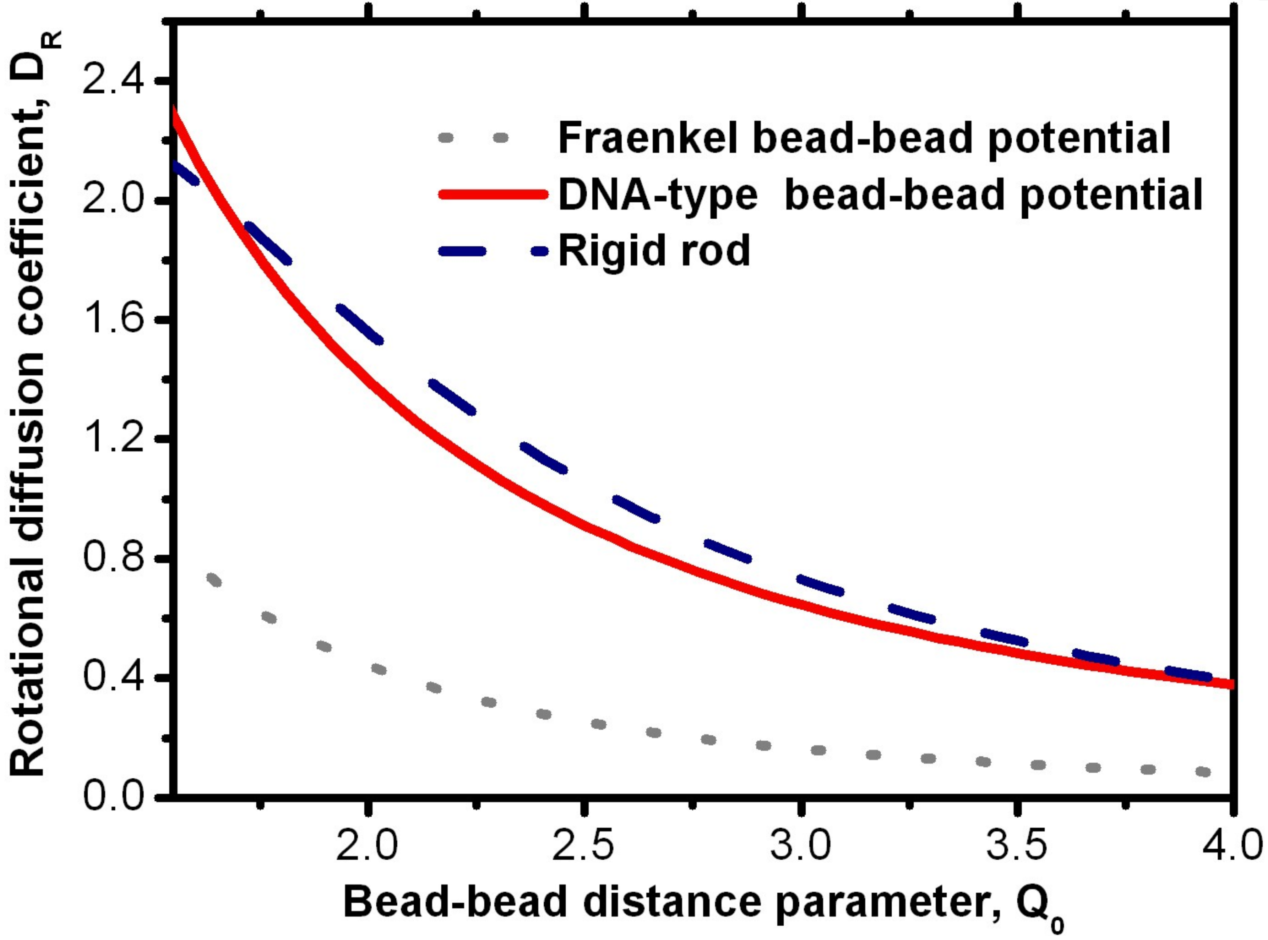
## 1. Rotational diffusion coefficient

$$D_R = D_0 \left\langle 1/Q^2 \right\rangle$$

***Dumbbell-type immobilized macromolecule:***

Rotational diffusion coefficient $D_R$





bead-bead interaction:

- Freankel potential

$$U_{BB}^{Fr} = k_{Fr}\left(Q - Q_0\right)^2$$

- DNA-type potentila

$$U_B^{DNA} = k_{DNA}\left(\frac{1}{4\left(1-\frac{Q}{Q_0}\right)} - \frac{1}{4}Q + \frac{Q^2}{2Q_0^2} - \frac{1}{4}\right)$$

A. Uvarov and S. Fritzsche, *Chem. Phys. Letter* (2006) *in print*

# Rotational motion of the macromolecule

***---- a few, short examples***

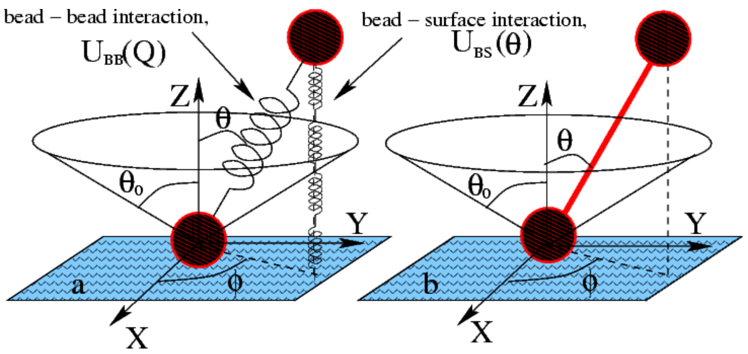
1. Rotational diffusion coefficient

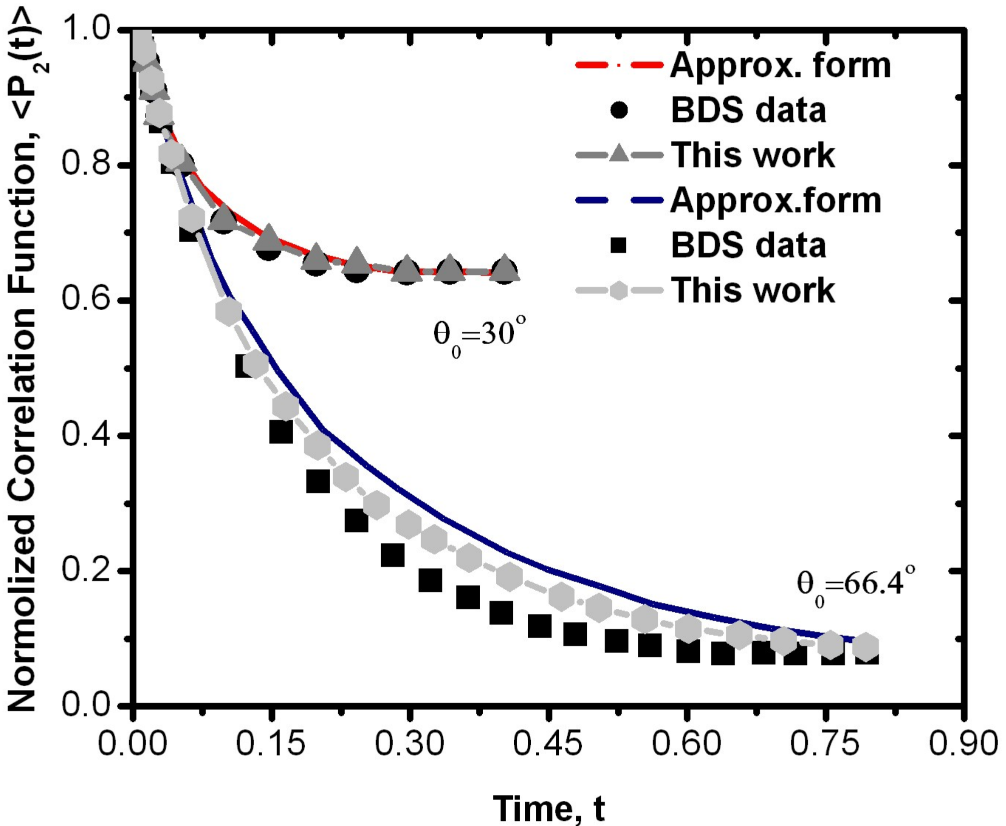
## 2. Orientational correlation function

$$\mathbf{P_2(t) = \frac{1}{2}\left(3\left\langle \cos^2 \theta(t)\right\rangle - 1\right)}$$

***Dumbbell-type immobilized macromolecule:***

Time dependent orietational CF, $P_2(t)$





bead-bead interaction:

- Frenkel potential

$$\mathbf{U_{BB}^{Fr} = k_{Fr}\left(Q - Q_0\right)^2}$$

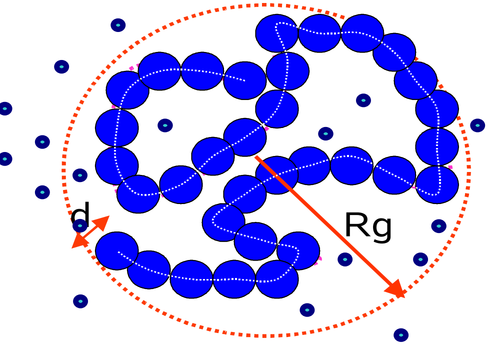
bead-surface interaction:

- Sin+cone potential

$$\mathbf{U_{BS} = \begin{cases} k_{Sin}\mathrm{Sin}^2\theta, & \text{if} \quad \theta \le \theta_0 \\ 0, & \text{otherwise} \end{cases}}$$

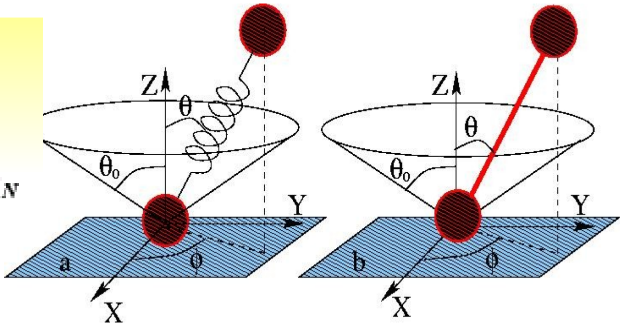
# A semi-phenomenological approach to the structure and transport properties of macromolecules in solution

## ---- *Summary*



A semi-phenomenological approach

$$\frac{\partial \rho_N}{\partial t}+\frac{P_a}{M}\frac{\partial \rho_N}{\partial R_a}-\frac{\partial U(|R_a-R_b|)}{\partial P_a}\frac{\partial \rho_N}{\partial P_a}=\frac{\partial}{\partial P_a}\xi^{ab}\left[\frac{\partial}{\partial P_b}+\frac{P_b}{k_B T M}\right]\rho_N$$



## Translational motion

- ✓ friction tensor parameters
- ✓ single-bead molecules
- ✓ dumbbell molecules
- ✓ N-bead macromolecules
- ✓ various thermo dynamical regimes

## Rotational motion

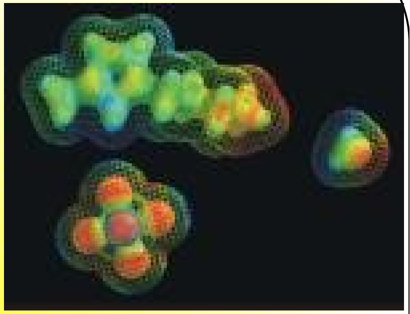
- ✓ Restricted rotation of dumbbell molecules
- ✓ Bead-bead and bead-surface interactions

A. Uvarov, S. Fritzsche, *Macr. Theor. Sim.* **13** (2004), 241;
A. Uvarov, S. Fritzsche, *Chem. Phys. Letter* **401** (2005) 296;
A. Uvarov, S. Fritzsche, *Phys. Rev.* **E73**. (2006) 011111;
A. Uvarov, S. Fritzsche, *Phys. Rev. Letter* (2006), *submitted.*
A. Uvarov, S. Fritzsche, *J. Chem. Phys.* **121**, (2004), 6566;
A. Uvarov, S. Fritzsche, *Progr. Coloid Polym Scien* **133**. (2006), **95;**
A. Uvarov, S. Fritzsche, *Chem. Phys. Letter* (2006), *in print.*

# Structure and transport of macromolecules in solution

## ---- *Goals for future studies*

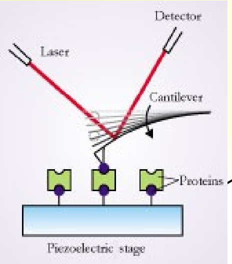
- **Salvation dynamics & transport properties of the dense MS**
  - ***friction, diffusion and conductivity of the solution***
  - ***different thermodynamics states of the MSs.***
  - ***behaviour of time-dependent correlation functions.***



- **Semi-phenomenological approach for the ILs**
  - ***interaction among the molecular components of IL (cations and anions)***
  - ***interplay with various dissolved nanoparticles and clusters***

- **Choice and parameterization of the interactions**
  - ***Coulomb***
  - ***Van der Waals***
  - ***Hydrogen-bonds***

- **Orientational properties of free and immobilized macromolecules**
  - ***Extension of the semi-phenomenological approach on the rotational motion***
  - ***3- and 4- … N- bead chains***
  - ***Complex molecular structures (different topologies)***



# Acknowledgements

***Universität Kassel***

- **Prof. Dr. Stephan Fritzsche**
- **Prof. Dr. Burkhard Fricke**
  - Drs: W.-D. Sepp, J. Anton, A. Surzikov, E. Rykhlinskaia, P. Kovals, T. Inghoff, C. Sarpe-Tudoran
  - T. Radke, L. Borowska, L. Tatarinova,...

***Institute Molecular and Atomic Physics***

- **Dr. Alexander Blokhin**
- **Dr. Maxim Gelin**
- **Acad. Prof. Vitaliy Tolkachev**

## Thank you for your attention!

# Appendix

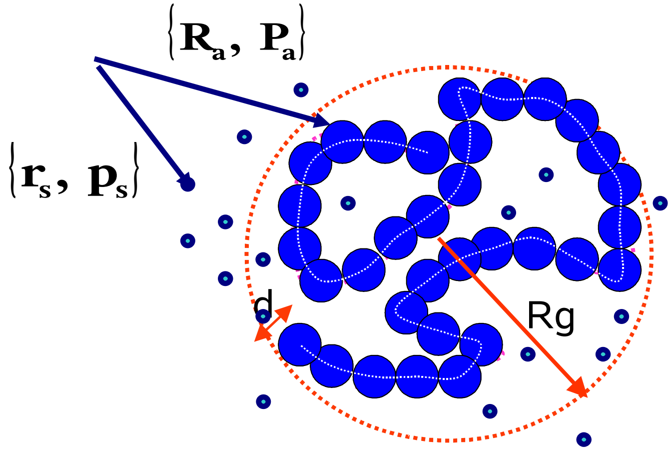
## *---- a few additional results*

A. Uvarov and S. Fritzsche, *Macromol. Theo. Sim.* **13** (2004) 241; *Phys. Rev. Letter* (2006) *submitted*

# Fokker-Planck equation & Friction tensors

## *---- phase-space dynamics*

$$\frac{\partial\rho_N}{\partial t}+\frac{P_a}{M}\frac{\partial\rho_N}{\partial R_a}-\frac{\partial U(|R_a-R_b|)}{\partial P_a}\frac{\partial\rho_N}{\partial P_a}=\frac{\partial}{\partial P_a}\xi^{ab}\left[\frac{\partial}{\partial P_b}+\frac{P_b}{k_B TM}\right]\rho_N$$



Thermodynamic limit: $n\to\infty;\ V\to\infty;\ {}^{n}\!/_{V}\to n_0$

Series expansion of time evolution operator: $\exp\left[-t\hat{Y}\hat{L}_{MS}\right]=\sum_{j=0}^{\infty}\frac{t^j}{j!}\left[\hat{Y}\hat{L}_{MS}\right]^j$

$$\boxed{\xi^{(ab)}_{\alpha\beta}=\sum_j\xi^{(ab)}_{\alpha\beta_{[j]}}=\xi^{(ab)}_{\alpha\beta_0}+\xi^{(ab)}_{\alpha\beta_{[1]}}+\xi^{(ab)}_{\alpha\beta_{[2]}}+\dots}$$

$$q^{(ab)}=\frac{R_a-R_b}{|R_a-R_b|};$$

$$\xi^{(ab)}_{\alpha\beta_{[j]}}=f_{[j]}\left(R_a,R_b;W;;CF^{(solvent)}_{[j+2]}\right)=A^{(ab)}_{[j]}\left(R_a,R_b;W;CF^{(solvent)}_{[j+2]}\right)\delta_{\alpha\beta}+B^{(ab)}_{[j]}(R_a,R_b;W;CF^{(solvent)}_{[j+2]})\ q^{(ab)}_\alpha q^{(ab)}_\beta$$

A. Uvarov and S. Fritzsche, *Macromol. Theo. Sim.* **13** (2004) 241; *Phys. Rev. E*73 (2006) 011111

# Translational motion of the macromolecule

***---- a few, short examples***

## 1. Friction tensor for the various „weak“ bead-solvent interaction

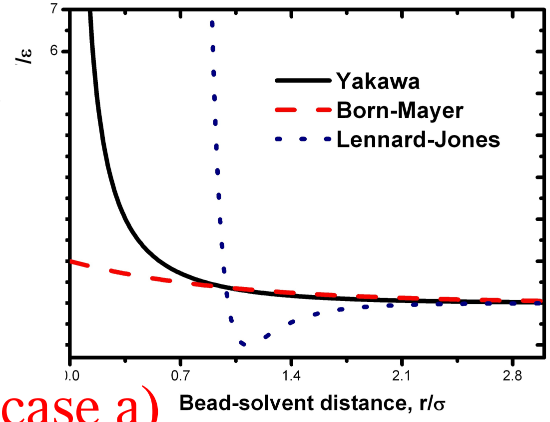
$$\xi_{\alpha\beta}^{(ab)} = \sum_j \xi_{\alpha\beta[j]}^{(ab)} \approx \xi_{\alpha\beta[0]}^{(ab)}$$

$$W^{(Y)} = \varepsilon_{MS}^{(Y)} \frac{\exp[-r/\sigma]}{r/\sigma}$$

$$W^{(BM)} = \varepsilon_{MS}^{(BM)} \exp[-r/\sigma]$$

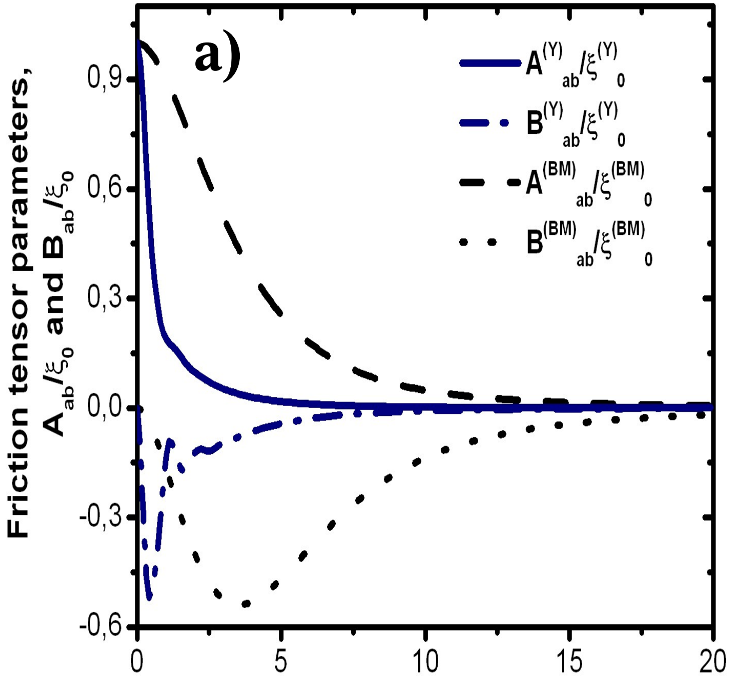
$$W^{(LJ)} = 4\varepsilon_{MS}^{(LJ)} \left( \left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6} \right)$$

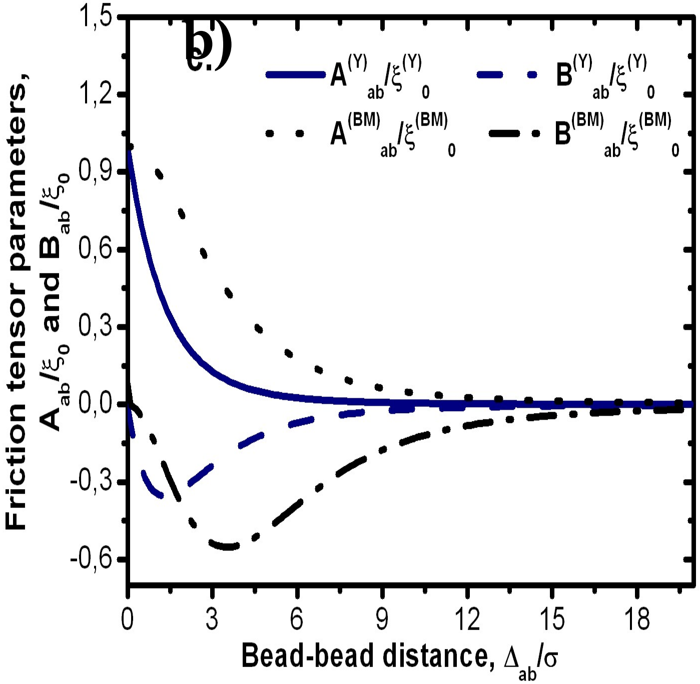
Charge particles: (*Coulomb-like interaction*)
Neutral particles: (*Born-Mayer and van der Waals interaction*)



### *N-bead macromolecule:*

Friction tensor parameters as function of the bead-bead distance $\Delta_{ab}=R_a-R_b$





case a)

$$k_B T = 1.2\varepsilon_{SS}; \quad n_0 = 0.86/\sigma^3$$

case b)

$$k_B T = 1.2\varepsilon_{SS}; \quad n_0 = 0.30/\sigma^3$$

A. Uvarov and S. Fritzsche, *Progr. Coloid. Scien.* **133** (2006) 95

# Rotational motion of macromolecule

## *---- Configuration-space distribution*

$$\Psi_{\nu_n^m}\left(Q; U_{BB}, U_{BS}\right)$$

Restricted boundary conditions

$$0 \le \theta \le \theta_0 (\le \pi/2)$$
$$0 \le \varphi \le 2\pi$$
$$0 \le Q \le Q_0$$

Bead-bead interaction:

- Hookean
- FENE
- Frankel
- DNA-type

$$U_{BB}^{Fr} = k_{Fr}\left(Q - Q_0\right)^2$$

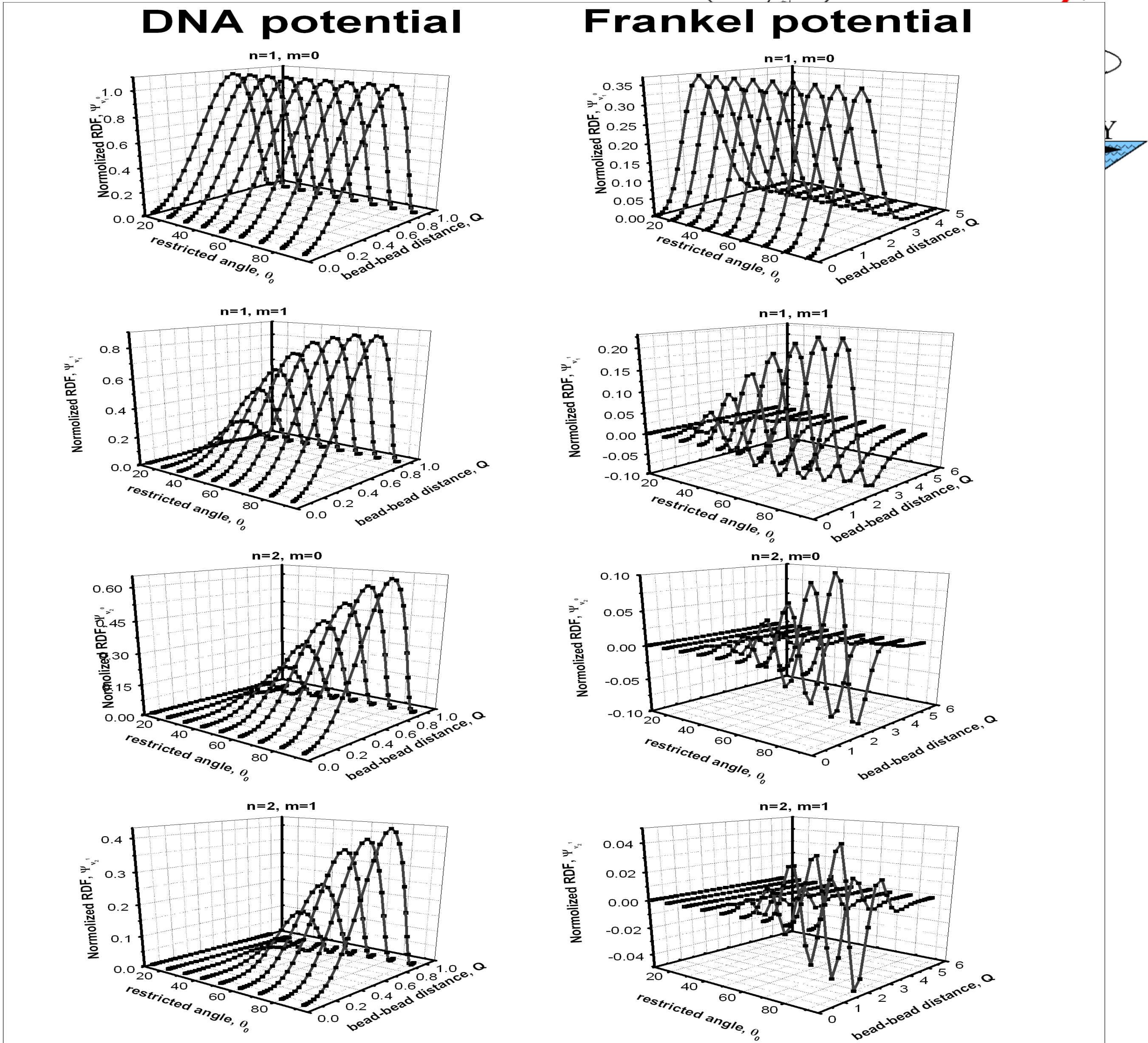
$$U_{BB}^{DNA} = k_{DNA}\left(\frac{1}{4\left(1-\frac{Q}{Q_0}\right)} - \frac{1}{4}Q + \frac{Q^2}{2Q_0^2} - \frac{1}{4}\right)$$

Bead-surface interaction:

- Cone
- Effective double well (Sin)

$$U_{BS}^{(Sin)} = k_{BS}\sin^2\theta$$

## Radial distribution



A. Uvarov and S. Fritzsche, *Progr. Coloid. Scien.* **133** (2006) 95

# Rotational motion of the macromolecule

***---- a few, short examples***

## 1. Rotational diffusion coefficient

$$D_R = D_0 \left\langle \frac{1}{Q^2} \right\rangle$$

***Dumbbell-type immobilized macromolecule:***

Rotational diffusion coefficient $D_R$