Thermodynamics of a polymer chain in an attractive spherical cage

Handan Arkın[1,2], Wolfhard Janke[1]

1 Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany

2 Department of Physics Engineering, Faculty of Engineering, Ankara University Tandogan, 06100 Ankara, Turkey

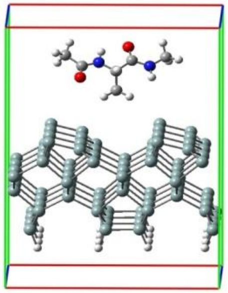
Outline

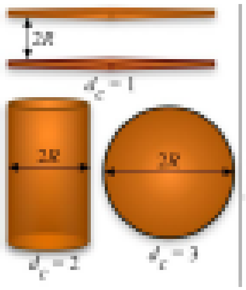
- Motivation
- Model: Off-lattice Polymer inside an Attractive Sphere
- Multicanonical Monte Carlo Method
- Some Simulation results

Motivation

❑ Investigating basis structure formation mechanisms of biomolecules at different interfaces is one of the major challenges of modern interdisciplinary research and possible application in nanotechnology

❑ Applications:
Polymer adhesion to metals, semiconductors biomedical implants and biosensors, smart drugs etc.





❑ Due to the complexity introduced by the huge amount of possible substrate structures and sequence variations this problem is not trivial.

❑ Therefore the theoretical treatment of the adsorption of macromolecules within the framework of minimalistic coarse-grained polymer models in statistical mechanics has been a longstanding problem.

The polymer Model

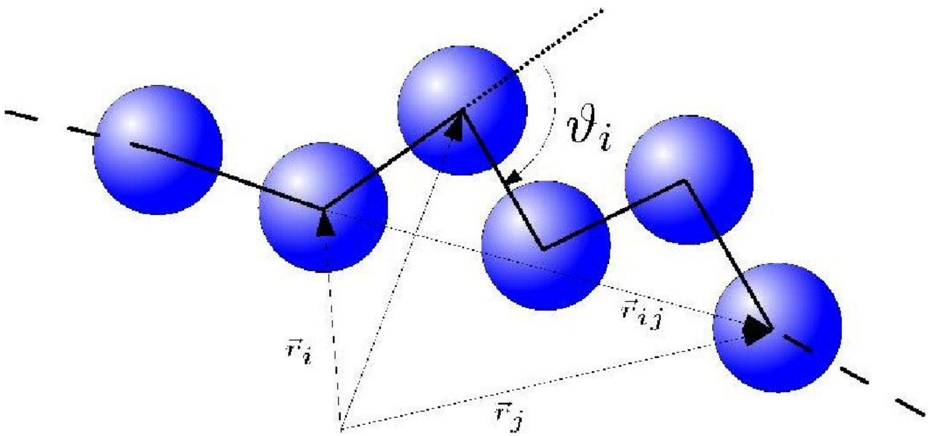
Interaction energy:

- Coarse-grained off-lattice
- Semi-flexible
- Three-dimensional

$$E_p = \frac{1}{4}\sum_{k=1}^{N-2} 1 - \cos\vartheta_i + 4\sum_{i=1}^{N-2}\sum_{j=i+2}^{N}\left(\frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^{6}}\right)$$

Bending energy

Lennard-Jones potential



Adjacent monomers are connected by rigid covalent bonds and the distance between them is fixed and set to unity
The position vector of the ith monomer is r_i

Polymer Chain inside an Attractice Sphere Potential

- The interaction of polymer monomers and the attractive sphere is of van der Walls type, modeled by LJ 12-6

$$V_{LJ}(r) = 4\epsilon_c \left[\left(\frac{\sigma}{r}\right)^{12} - \epsilon \left(\frac{\sigma}{r}\right)^{6} \right]$$

We integrate this potential over the entire sphere inner surface

$$V_s = \int_S \rho V_{LJ}(r) dS$$

Where the surface element in spherical coordinates is

$$dS = R_c^2 \sin\phi d\phi d\theta$$

Polymer Chain inside an Attractice Sphere Potential

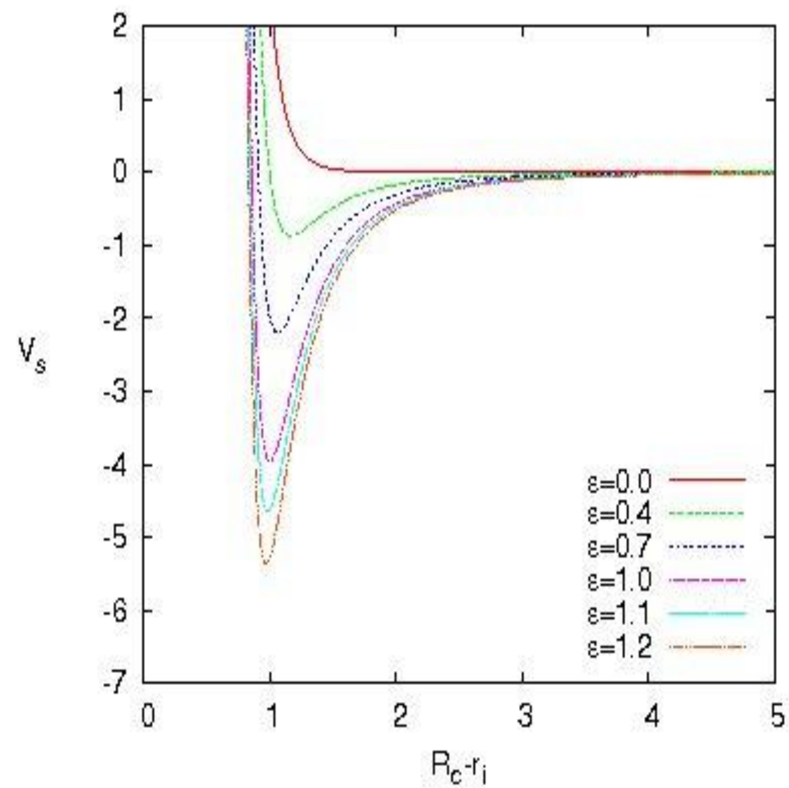
$$V_s(r) = 4\,\varepsilon_c \frac{\pi R_c}{r_i}\left(\frac{1}{5}\left[\left(\frac{\sigma}{R_c - r_i}\right)^{10} - \left(\frac{\sigma}{R_c + r_i}\right)^{10}\right] - \frac{\varepsilon}{2}\left[\left(\frac{\sigma}{R_c - r_i}\right)^{4} - \left(\frac{\sigma}{R_c + r_i}\right)^{4}\right]\right)$$

$R_c \longrightarrow$ The radius of the sphere

$r_i \longrightarrow$ The distance of a monomer to the origin

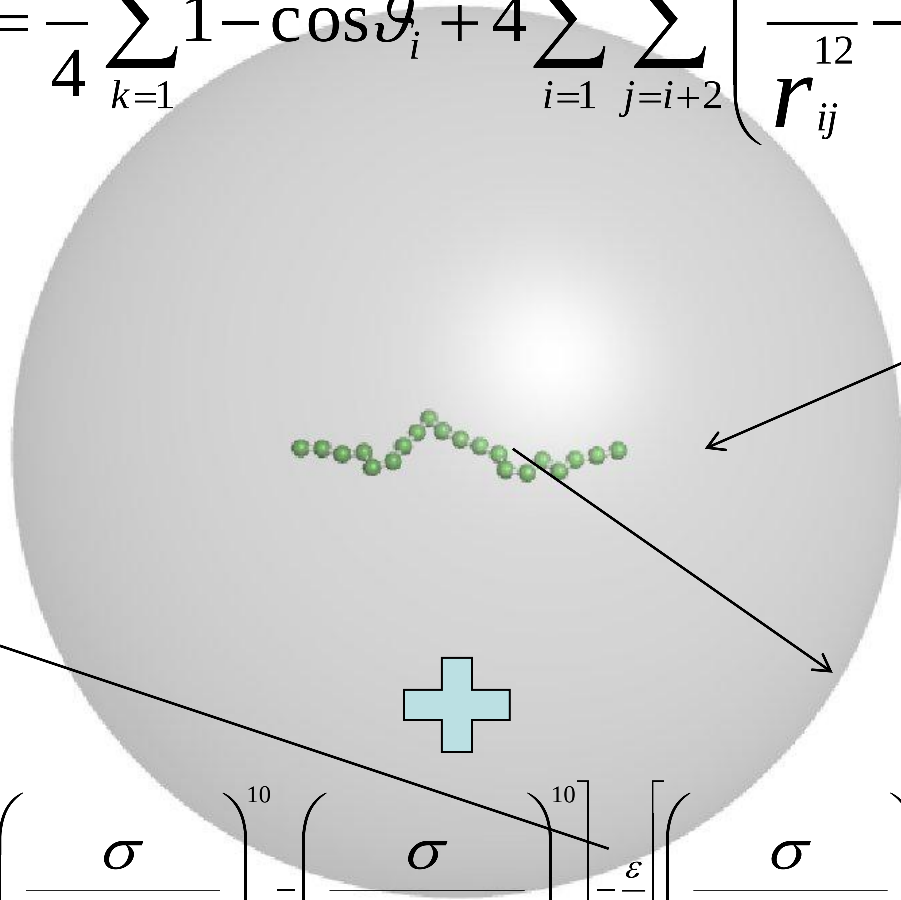
$\varepsilon_c \longrightarrow$ Set to unity

$\varepsilon \longrightarrow$ Varied during simulation



Polymer Chain inside an Attractice Sphere Potential

$$E_p = \frac{1}{4}\sum_{k=1}^{N-2} 1-\cos\vartheta_i + 4\sum_{i=1}^{N-2}\sum_{j=i+2}^{N}\left(\frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^{6}}\right)$$



$$N = 20$$

$$\varepsilon = 0.1 - 1.4$$

$$R_c = 20$$

$$V_s(r) = 4\varepsilon_c \pi R_c \sum_{i=1}^{N} \frac{1}{r_i}\left(\frac{1}{5}\left[\left(\frac{\sigma}{R_c - r_i}\right)^{10} - \left(\frac{\sigma}{R_c + r_i}\right)^{10}\right] - \frac{\varepsilon}{2}\left[\left(\frac{\sigma}{R_c - r_i}\right)^{4} - \left(\frac{\sigma}{R_c + r_i}\right)^{4}\right]\right)$$

Simulations in Generalized Ensembles

- **Idea:** choose ensemble that allows **better sampling**
- **Example: Multicanonical Ensemble**
- **General Procedure:**
  Determine the **weight factors**
  Large scale **simulation**
  Calculate **expectation values** for desired temperatures
- **Problem:** Find good **estimators** for the weights
- **Advantages:**
  Any **energy barrier** can be crossed.
  The probability of finding the **global minimum** is enhanced.
  Thermodynamic quantities for a range of temperatures

Multicanonical Monte Carlo Method

- The canonical ensemble samples with the Boltzmann probability density

$$P^{B}(x) = \exp[-E_x / k_B T] / Z$$

where x labels the configuration. The probability of the energy E is

$$P_T^{B}(E) = n(E)\exp[-E / k_B T] / Z$$

where n(E) is the density of states.

- The Muca ensemble is based on a probability function in which the different energies are equally probable:

$$P^{MU}(E) \approx n(E)w(E) = const.$$

where w(E) are multicanonical weight factors.

Observables

Specific Heat:

$$C_V(T) = \frac{\langle E^2 \rangle - \langle E \rangle^2}{NT^2}$$

Radius of gyration:

$$R_g^2 = \sum_{i=1}^{N} (\vec{r}_i - \vec{r}_{cm})^2 / N = \sum_{i=1}^{N} \sum_{j=1}^{N} (\vec{r}_i - \vec{r}_j)^2 / 2N^2$$

Mean number of adsorbed monomers to the inner wall of the sphere:

We define a monomer i is being adsorbed if $R_c - r_i < r_c \equiv 1.2$

and this can be expressed as .

$$N_s = \sum_{i=1}^{N} \Theta(r_c - r_i)$$

Observables

- **Gyration Tensor**

$$S = \frac{1}{N}\begin{pmatrix} \sum(x_i - x_{\mathrm{cm}})^2 & \sum(x_i - x_{\mathrm{cm}})(y_i - y_{\mathrm{cm}}) & \sum(x_i - x_{\mathrm{cm}})(z_i - z_{\mathrm{cm}}) \\ \sum(x_i - x_{\mathrm{cm}})(y_i - y_{\mathrm{cm}}) & \sum(y_i - y_{\mathrm{cm}})^2 & \sum(y_i - y_{\mathrm{cm}})(z_i - z_{\mathrm{cm}}) \\ \sum(x_i - x_{\mathrm{cm}})(z_i - z_{\mathrm{cm}}) & \sum(y_i - y_{\mathrm{cm}})(z_i - z_{\mathrm{cm}}) & \sum(z_i - z_{\mathrm{cm}})^2 \end{pmatrix}$$

Transformation to principal axis system diagonalizes S

$$S = \mathrm{diag}(\lambda_1, \lambda_2, \lambda_3)$$

Where the eigenvalues are sorted in descending order

$$\lambda_1 \geq \lambda_2 \geq \lambda_3$$

Observables

- **The first invariant of Gyration Tensor**

$$\mathrm{Tr}\, S = \lambda_1 + \lambda_2 + \lambda_2 = R_g^2$$

The second invariant shape descriptor is Shape Anisotropy (reflects both symmetry and dimensionality)

$$\kappa^2 \equiv A_3 = \frac{3}{2}\frac{\mathrm{Tr}\,\hat{S}^2}{(\mathrm{Tr}\,S)^2} = 1 - 3\frac{\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1}{(\lambda_1 + \lambda_2 + \lambda_3)^2}$$

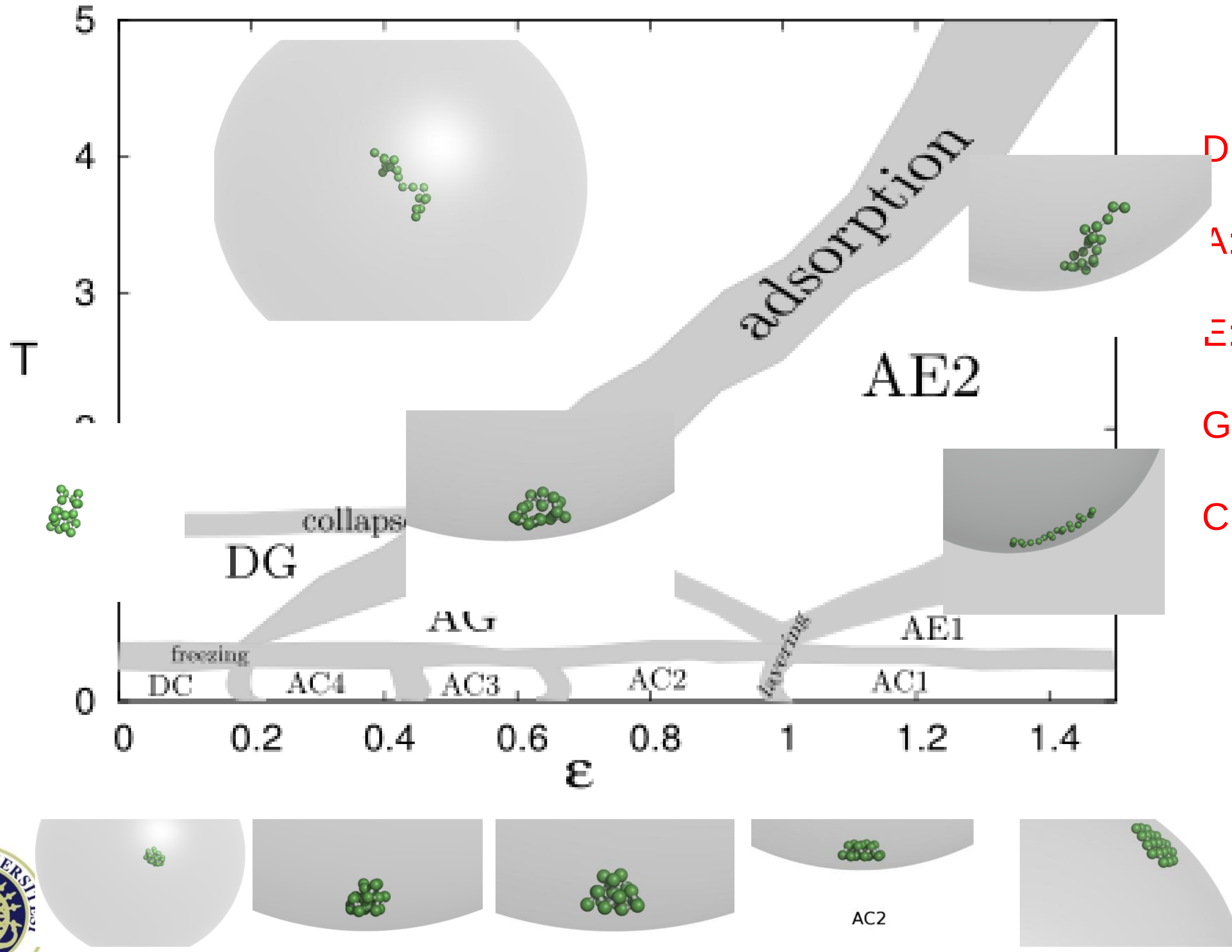
Where $\hat{S} = S - \frac{1}{3}(\mathrm{Tr}S)E$

Derivative of all these quantities

The last shape desciptor is the asphericity parameter

$$b = \lambda_1 - \frac{1}{2}(\lambda_2 + \lambda_3) \qquad \lambda_1 \text{ is the largest eigenvalue}$$

Results: Pseudo Phase Diagram



D : Desorbed

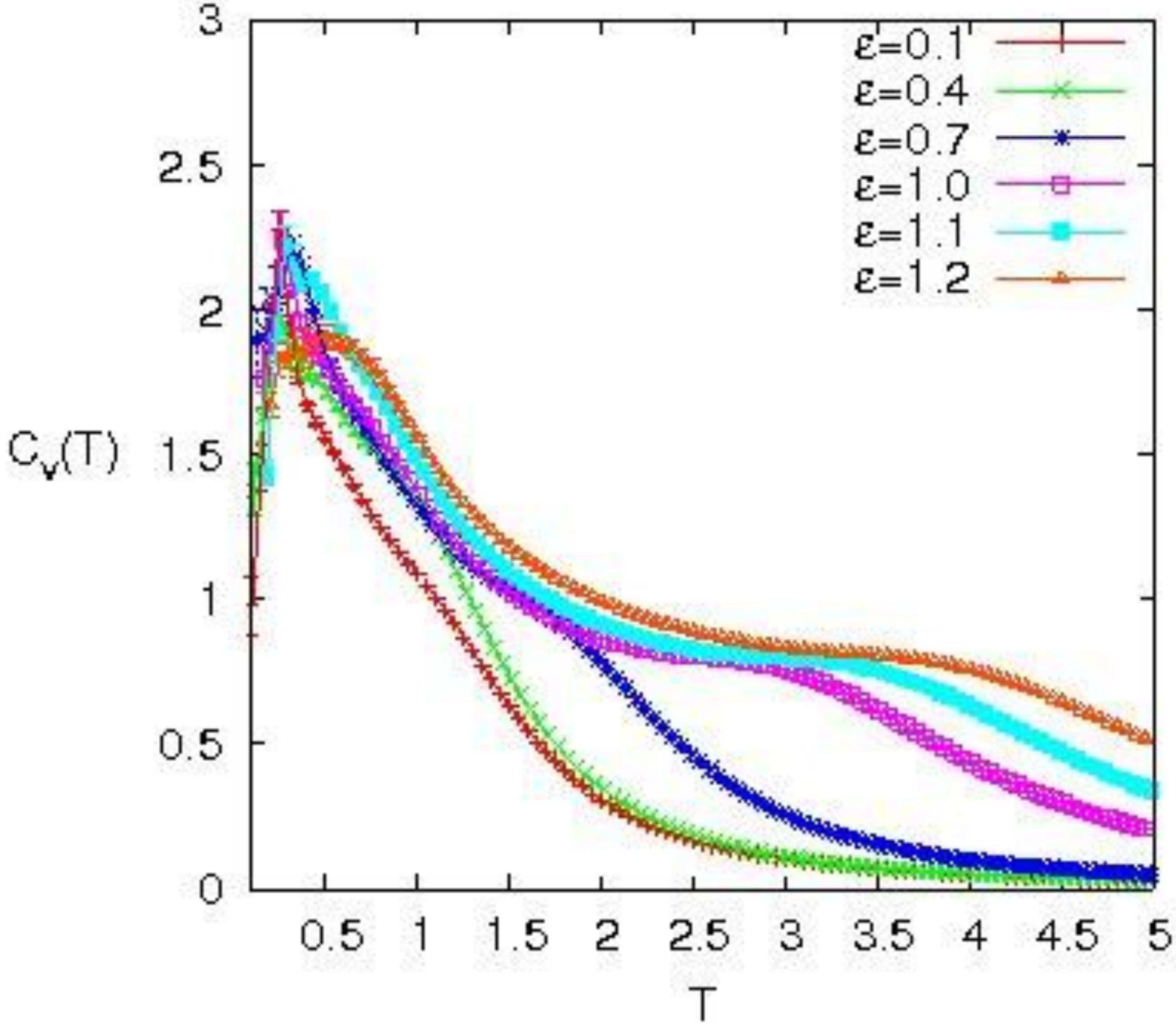
A: Adsorbed

E: Extended

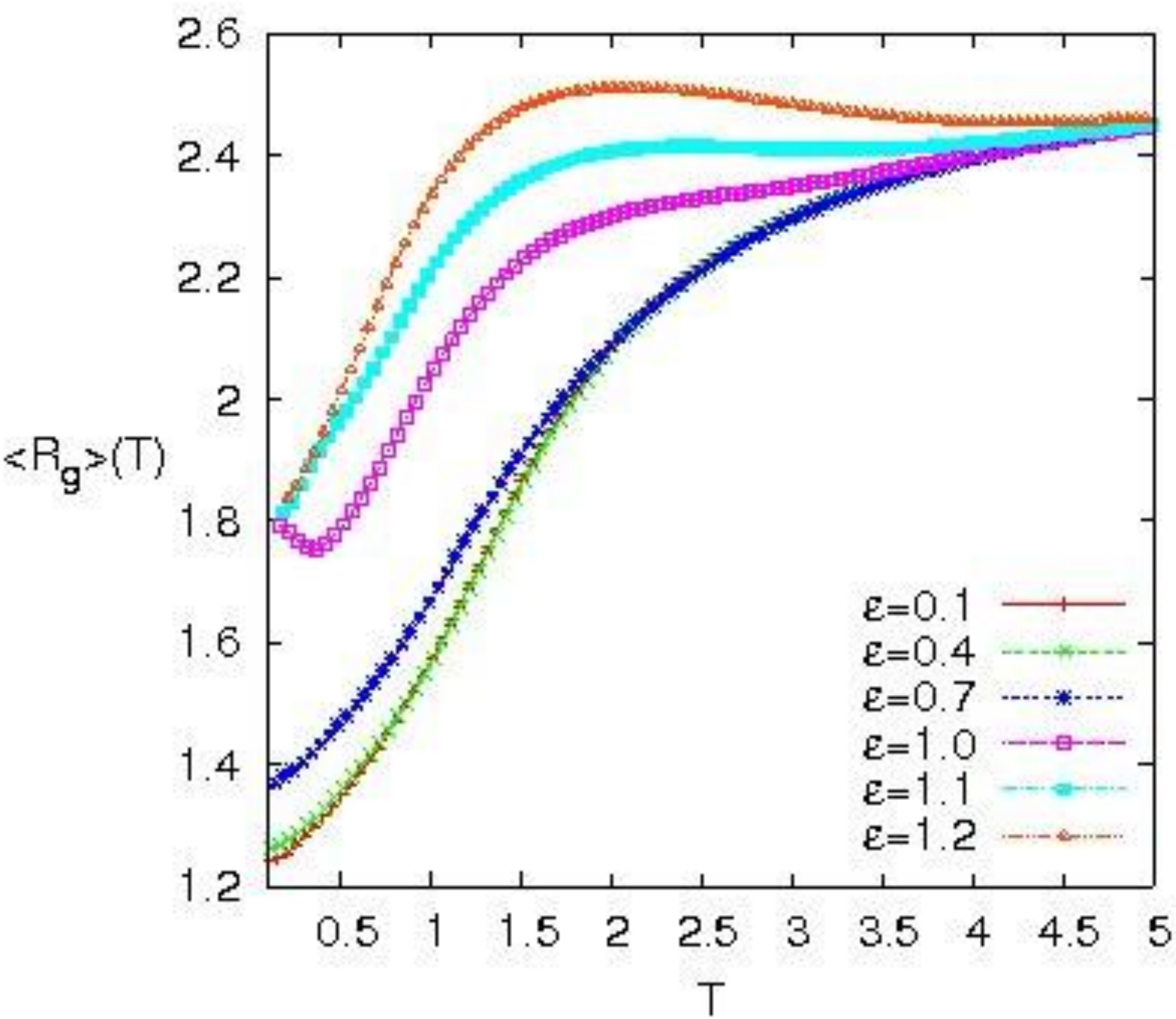
G: Globular

C:Compact

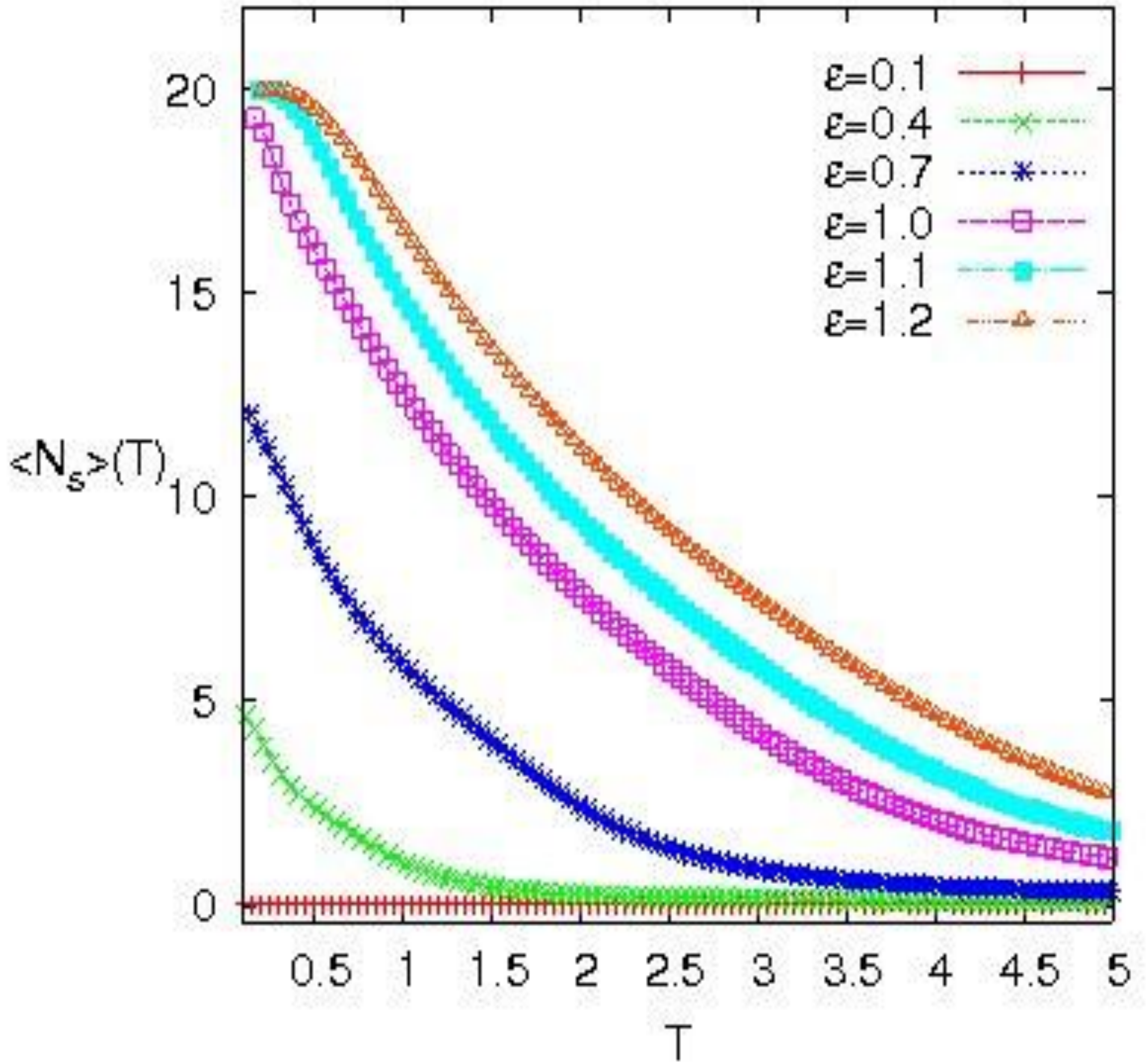
Results: Specific -Heat



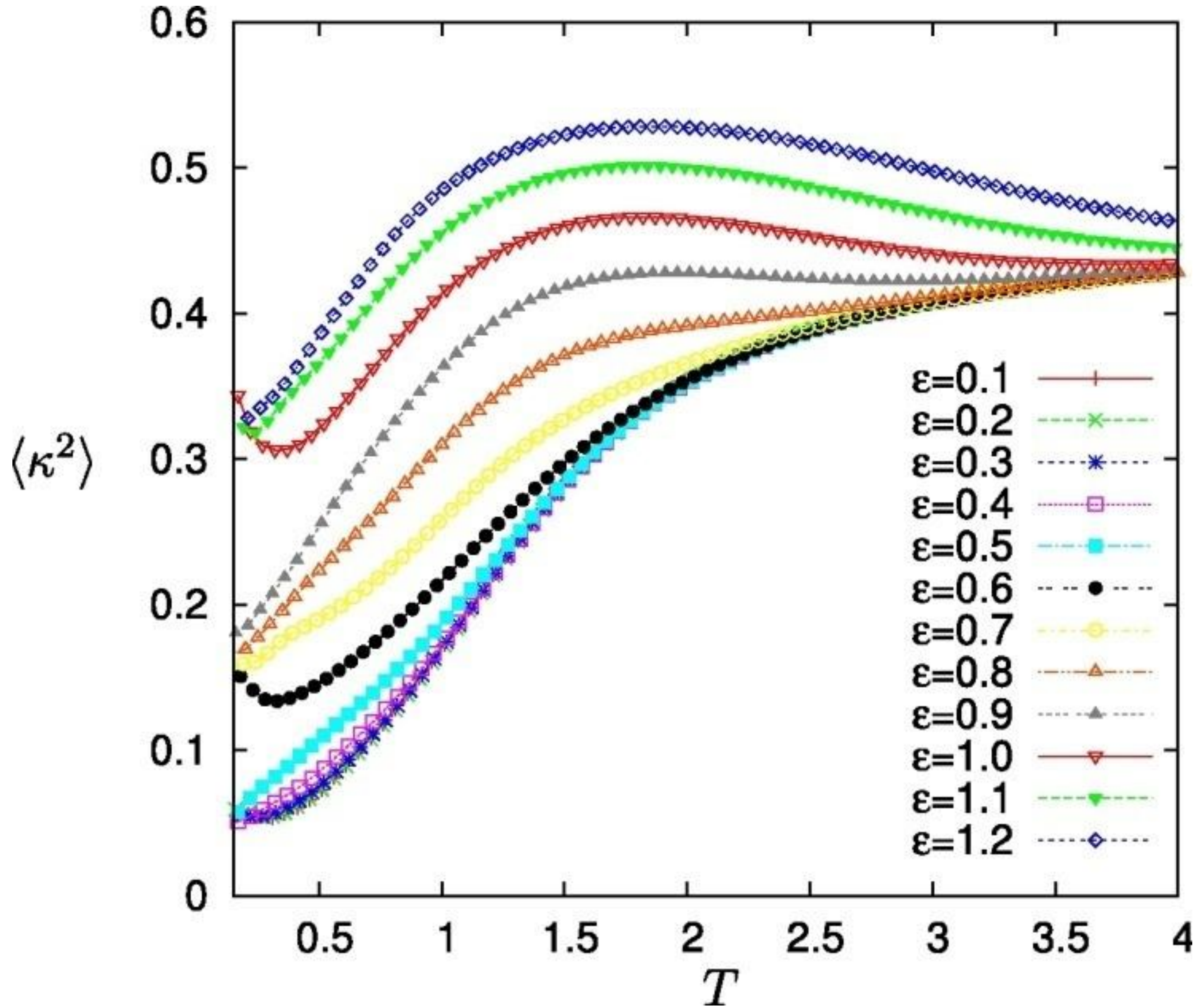
Results: Radius of Gyration



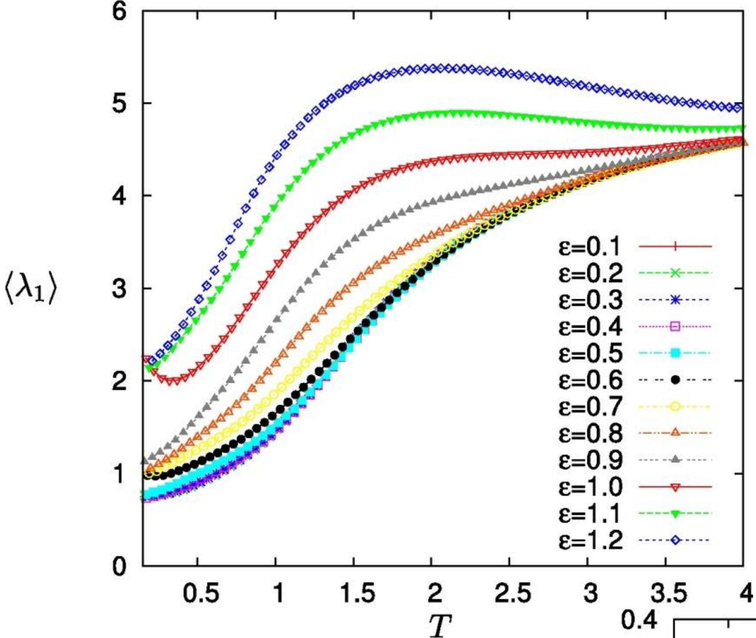
Results: The mean number of adsorbed monomers

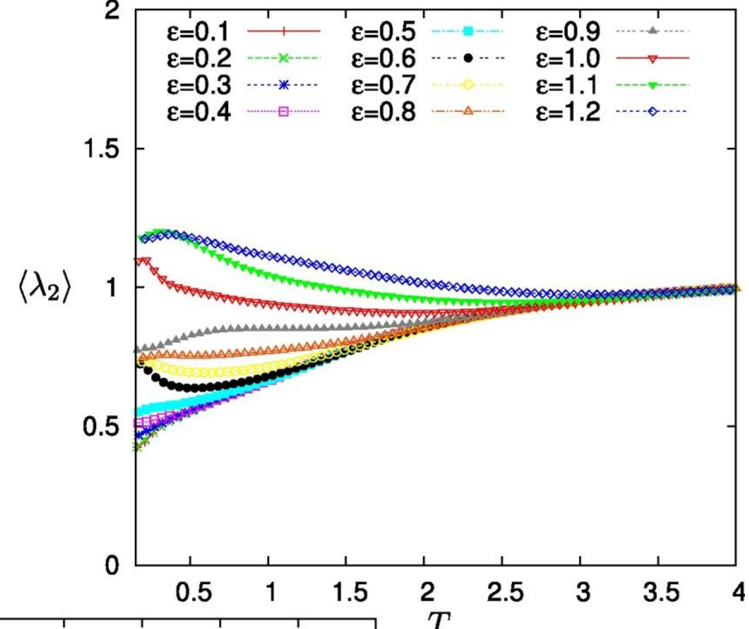


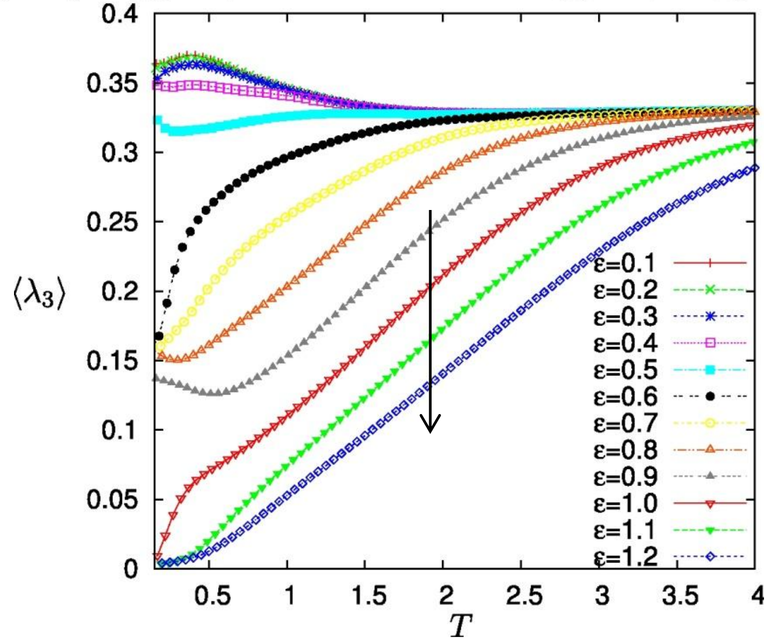
Results: Relative Shape Anisotropy



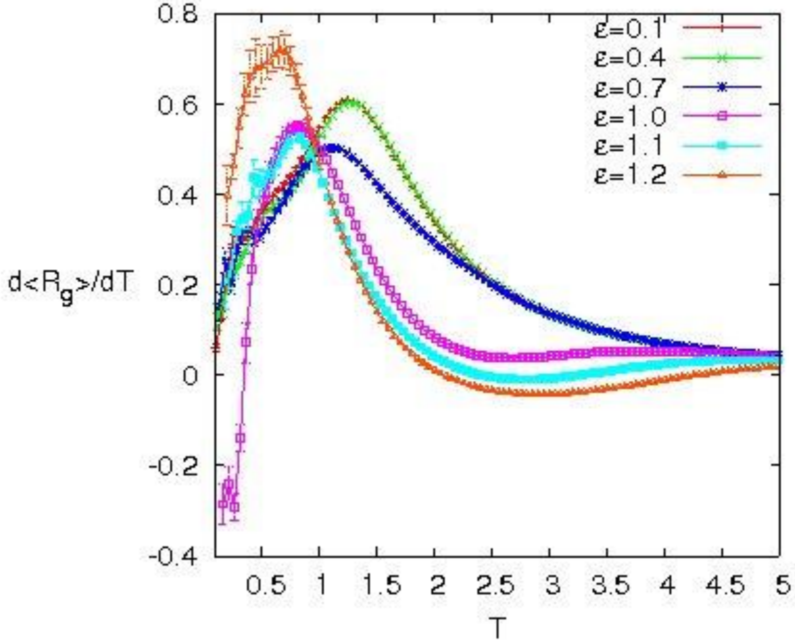
Results: The eigenvalues of the Gyration tensor

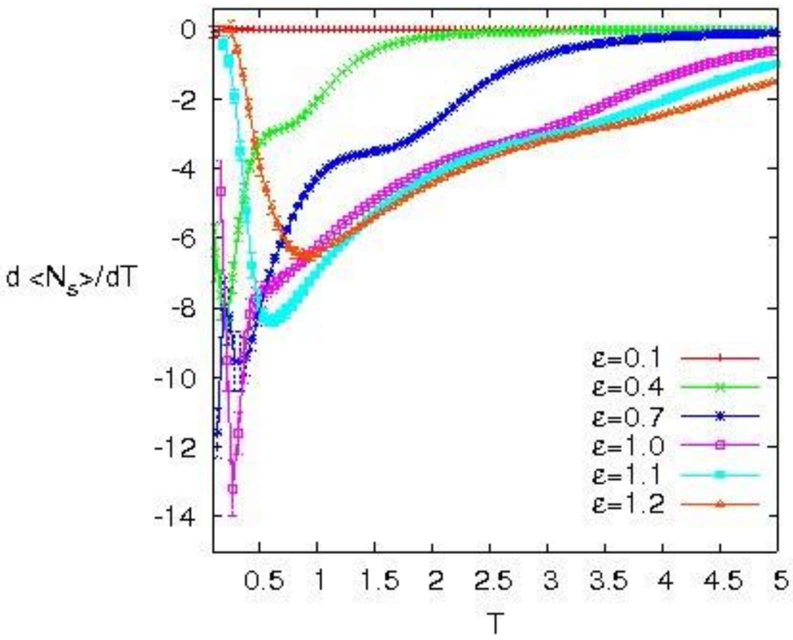


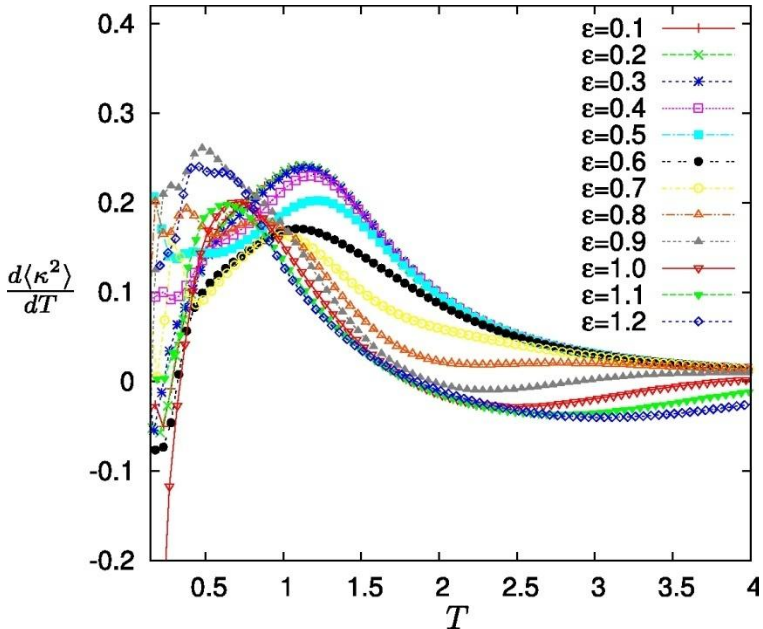




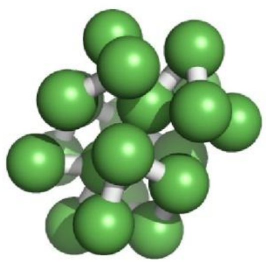
Results: Fluctuations of the Observables



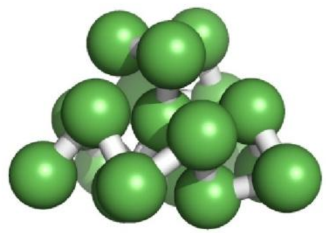




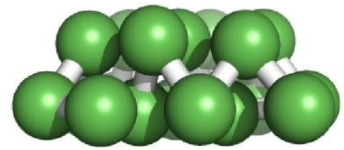
Results: Low Energy Conformations



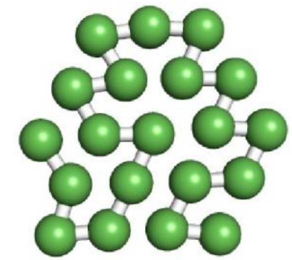
$\varepsilon = 0.1$



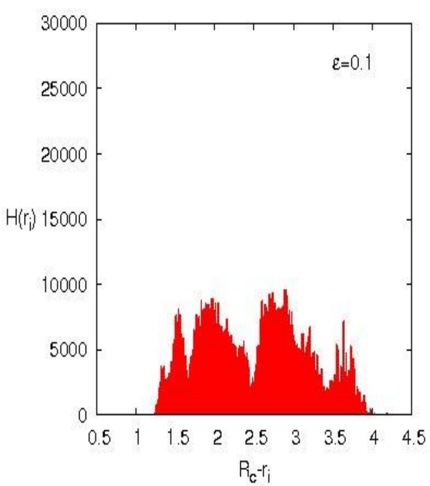
$\varepsilon = 0.4$

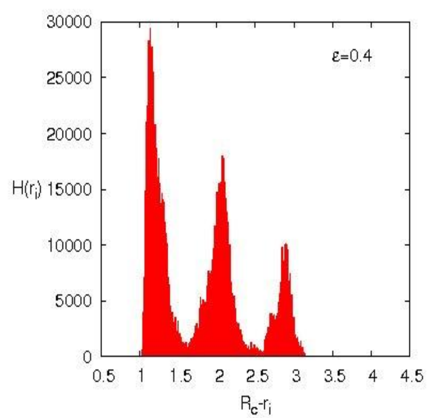


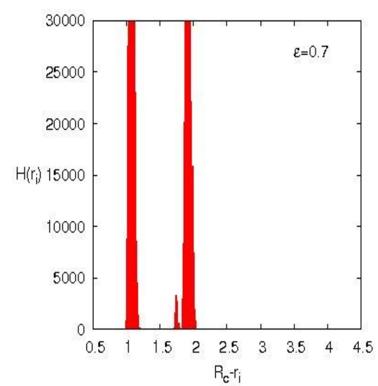
$\varepsilon = 0.7$

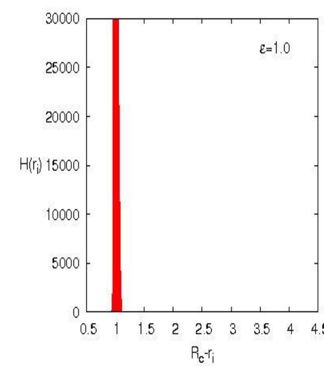


$\varepsilon = 1.0$









Acknowlegments

Unterstützt von / Supported by

Alexander von Humboldt
Stiftung / Foundation

Thanks to ...

CQT Team, Institute of Theoretical Physics, Leipzig

Thank you for your attention.

Results: The ratio of the greatest eigenvalue to the smallest