

Methane Clusters at Low Temperatures

Ana Proykova and Evgeniya Daykova

University of Sofia

Abstract

Free methane clusters containing up to 250 molecules adopt local icosahedral-like structures at low temperatures (10-50 K). The long-range order is lost and the cluster state could be attributed to a liquid-like state even if it is 'frozen'.

MOTIVATION

- Fundamental properties of symmetrical molecules in (a)symmetrical environment
- Greenhouse effect & hydrogen storage
- Clathrate [2, 3]
- Beauty

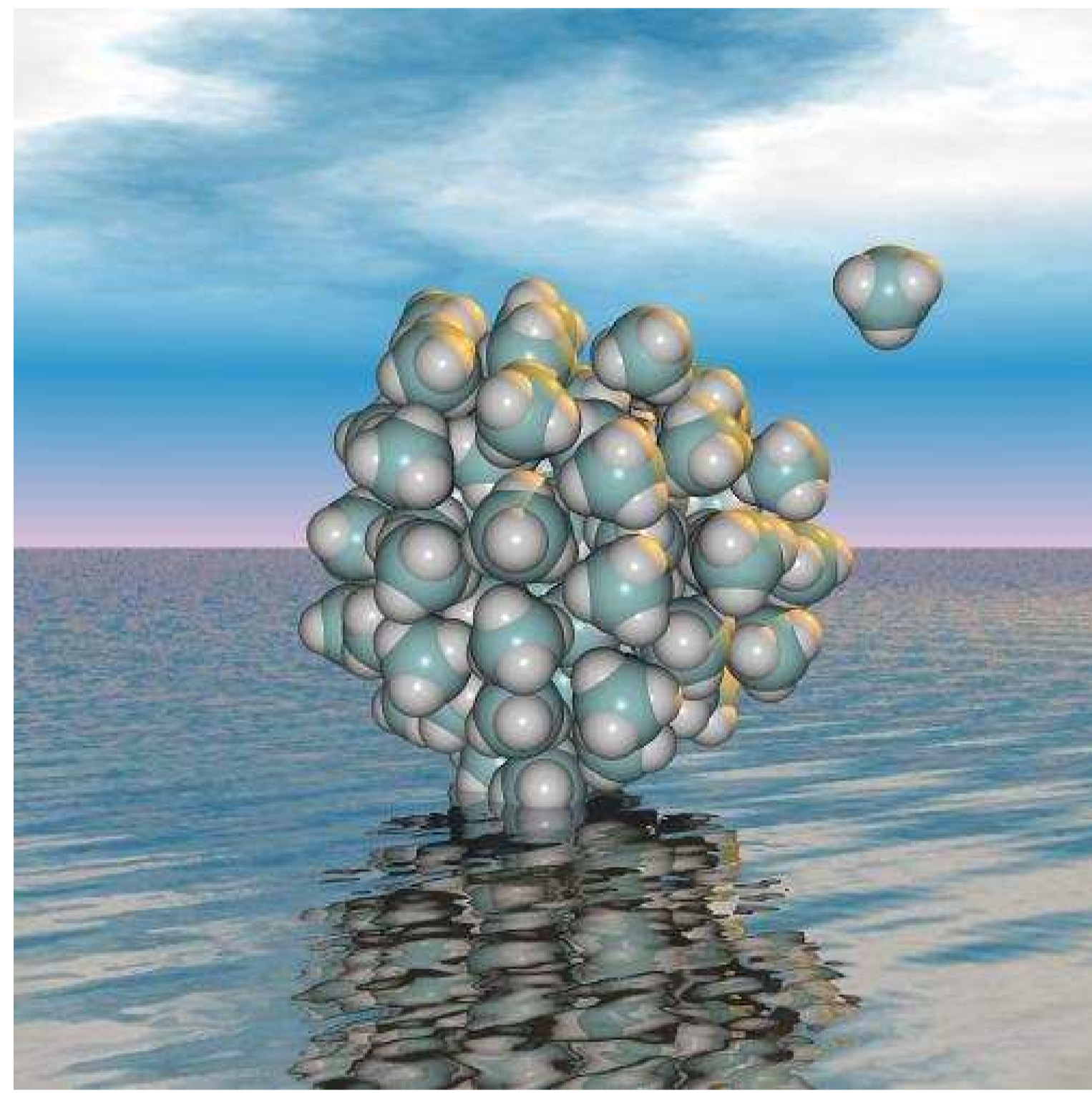


Figure 1. Evaporation of a molecules: Rossen Radev's vision. Monte Carlo simulations of 59 methane cluster at 50K.

OBJECTS - SMALL

Size is always a special-case experience (Fuller)

Why 'small is different'?

Number of connections - a basis for the phenomenon of vastly different properties exhibited by systems with identical constituents

Dimers - Role in Nanomaterials

- Clusters containing $N = 2, 13, 50, 55, 137, 229$ molecules: magic numbers for closed shells in different structures

- Classical trajectories - solutions of

$$\frac{dp_i}{dt} = -\frac{\partial}{\partial r_i} H(p_1, r_1, \dots, p_N, r_N) \quad (1)$$

$$\frac{dr_i}{dt} = \frac{\partial}{\partial p_i} H(p_1, r_1, \dots, p_N, r_N) \quad (2)$$

p_i and r_i - the momentum and the position of the molecule: $i = 1, 2, \dots, N$ with $H = U(r) + E_{kin}$

- Interaction potential $U(r)$: to account for various mutual orientations of the molecules, a pair-wise atom-atom interaction is considered

$$U = \sum_{i,j=1}^N \sum_{\alpha,\beta=1}^5 \left[4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^6 \right] + \frac{q_{i\alpha} q_{j\beta}}{4\pi\epsilon_0 r_{ij}^2} \right] \quad (3)$$

$r_{ij} = |r_i - r_j|$ is the distance between i^{th} and j^{th} atom, α and β denote either a carbon or a hydrogen atom, the parameters fit experimental data.

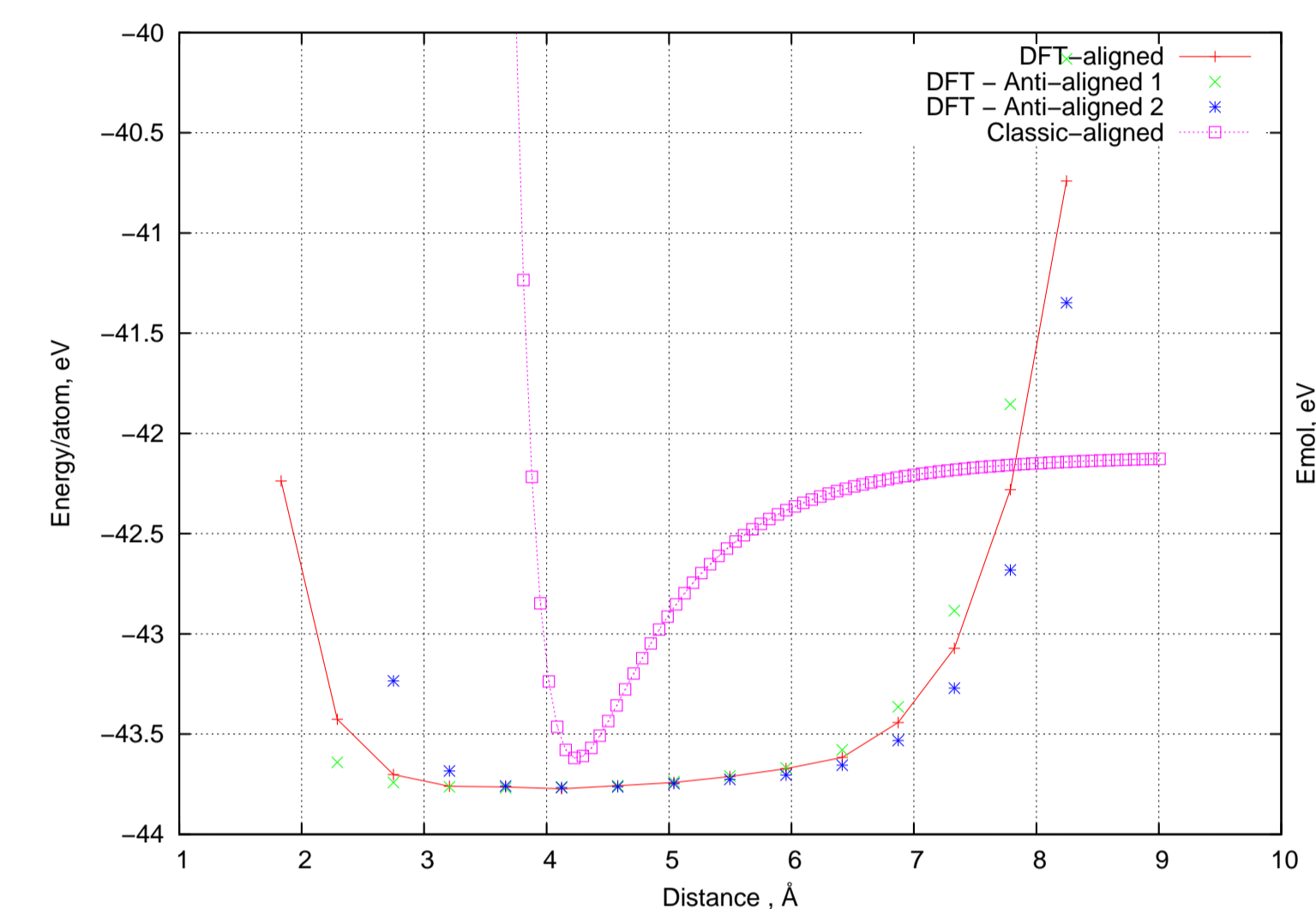


Figure 2. Classical and quantum interaction potential.

- Integration of (1) and (2) at a constant total energy using the velocity Verlet algorithm [1] with a time step of 1 fs that keeps the energy constant up to (10^{-5}) for 1 ns production runs

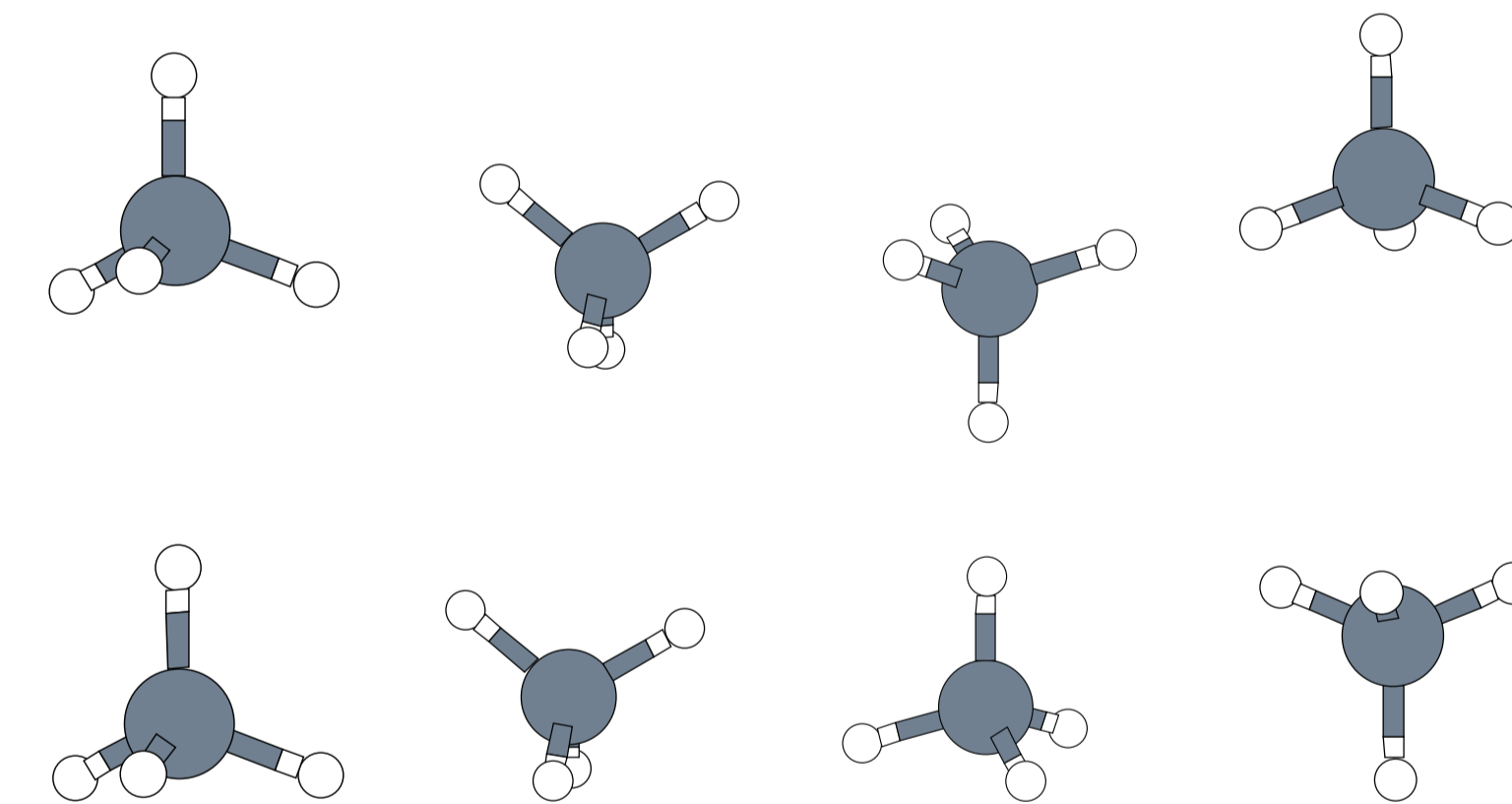


Figure 3. Four specific mutual orientations for 2 CH_4 molecules (from left to right) - aligned, perpendicular, anti-aligned "1" and anti-aligned "2"

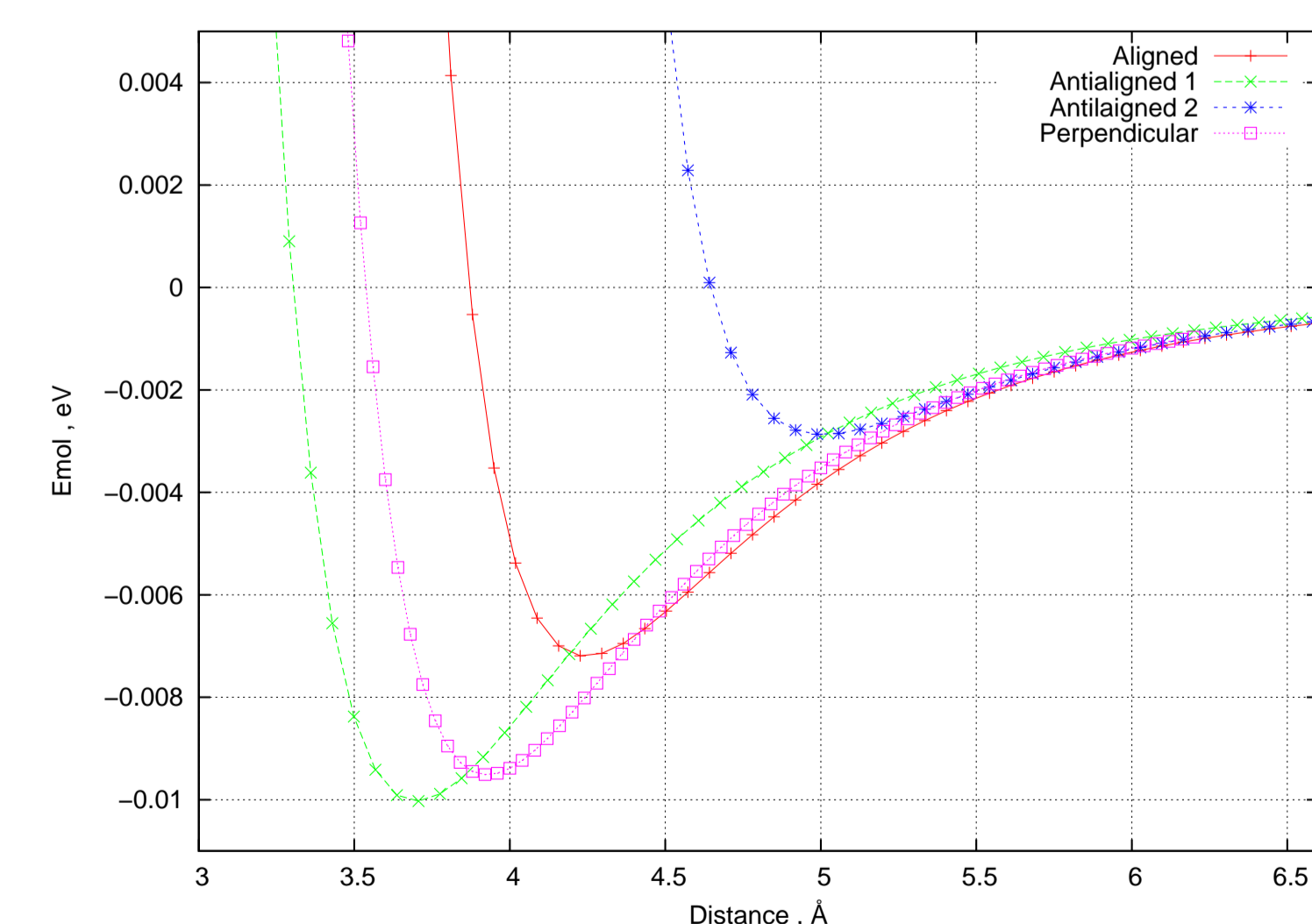


Figure 4. Potential energy per molecule for a methane dimer at 4 different mutual orientations.

The cluster state - liquid or solid - is determined by the radial distribution function $g(r)$:

Department of Atomic Physics

Faculty of Physics

5 James Bourchier Blvd.

Sofia 1126, Bulgaria

email: anap@phys.uni-sofia.bg

http://cluster.phys.uni-sofia.bg:8080/



$$g(r) = \frac{V}{N^2} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta(r - r_{ij}) \right\rangle \quad (4)$$

Clusters of 55 molecules at 10 K have well resolved doublets at the closest distance, however they do not have a long-range order like liquids.

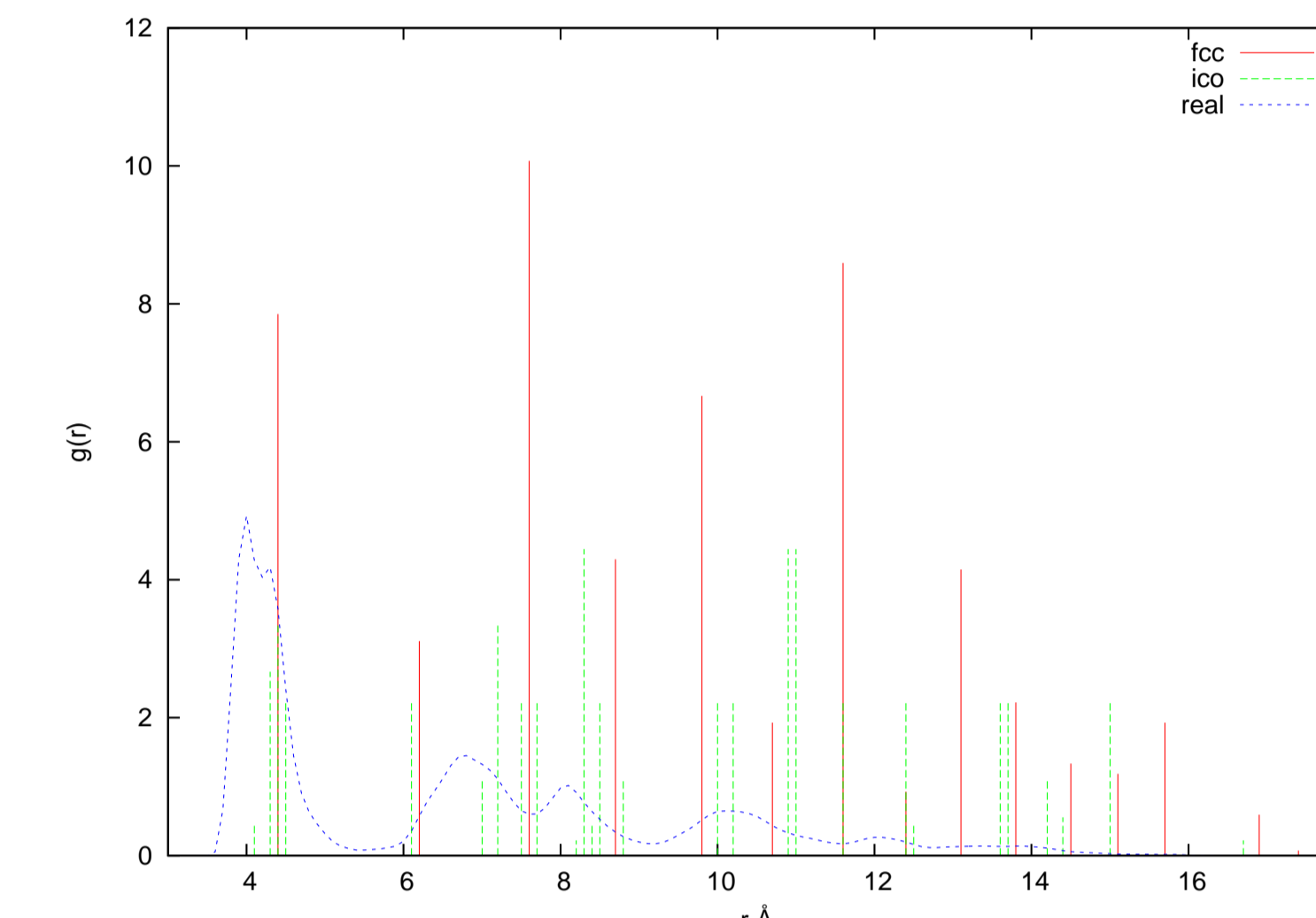


Figure 5. Radial distribution function for 55 molecules arranged in a static fcc, a static ico, and a 'real' structure at T = 10 K.

The peak located in the (3.5-4.1)Å region contains mainly 'anti-ferro' dimers retrieved by a comparison of the dimer potential energy and the doublet in $g(r)$. The table contains the distribution of the neighbors as a function of the distance between the molecular center of mass. Various techniques can be used to compute the nearest-neighbors with different accuracy [4]. We integrate $g(r)$.

Table 1. NN=Nearest-Neighbors; NNN=Next-to-the-Nearest-Neighbors.

number of neighbors	NN (3.5-4.1)Å	NNN (4.1-4.5) Å	NN + NNN (3.5-4.5) Å
1	2	4	11
2	12	11	0
3	13	13	0
4	9	13	0
5	9	7	9
6	5	4	14
7	4	2	12
8	1	1	5
9	0	0	4
10	0	0	3
11	0	0	5
12	0	0	3
mean	3.85	3.6	7.56

Liquid/solid- like phases are usually distinguishable via the value of the modified Lindemann index δ_{lin} (the cluster is solid if $\delta_{lin} < 0.08$) [5]:

$$\delta_{lin} = \frac{2}{N(N-1)} \sum_{i,j(i < j)=1}^N \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle} \quad (5)$$

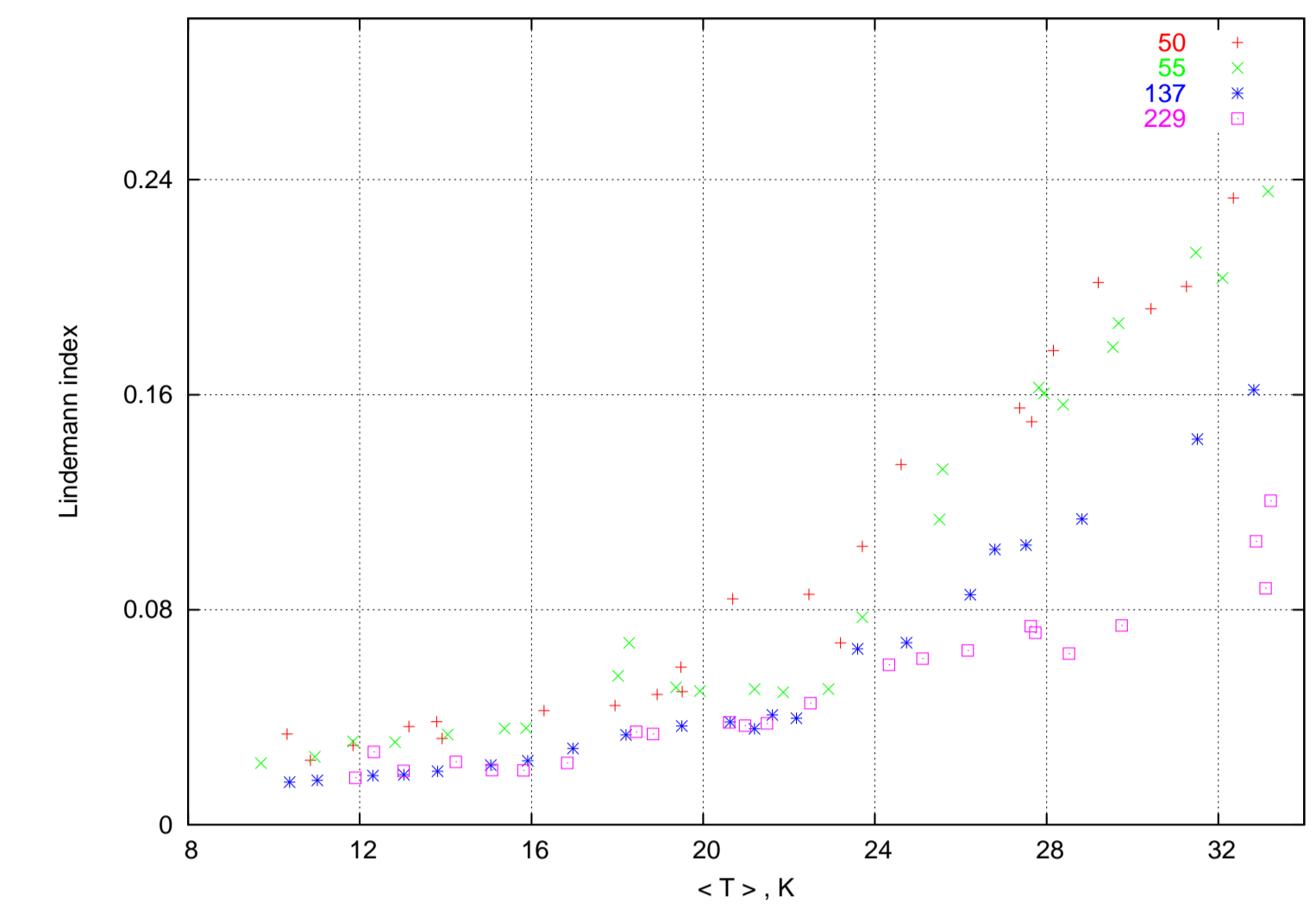


Figure 6. Lindemann index - size effect.

The low-frequency peak in the vibrational spectra at T=10K corresponds to a collective surface wave.

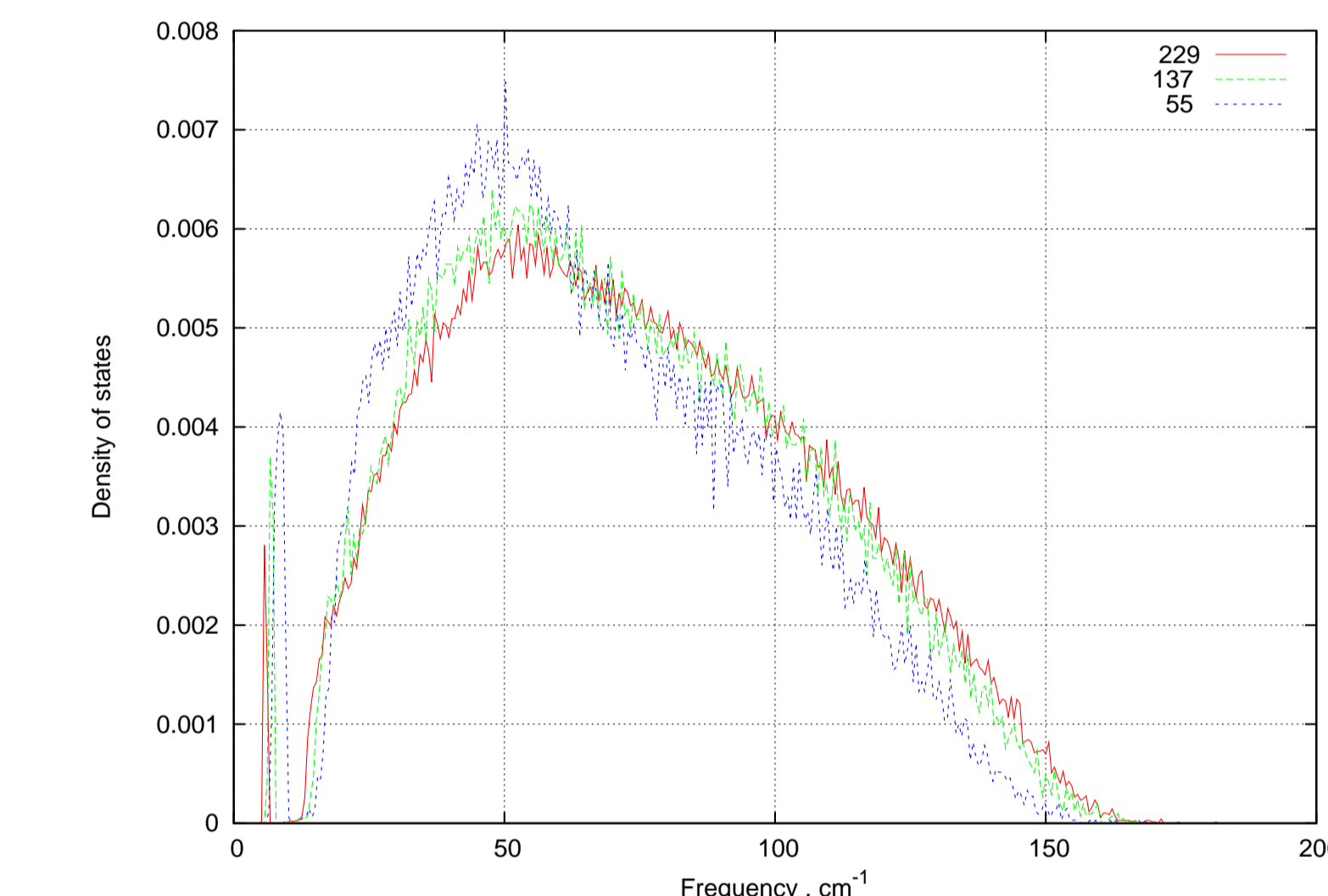


Figure 7. Vibrational spectra at 10K - size effect.

At T=30K all clusters are liquid-like and the low-frequency peak disappears in the vibration spectra.

CONCLUSION

The most important finding in this study is that dimers of molecules with a specific mutual anti-ferro ordering determine the cluster structure at low temperatures. Obviously, the angular dependence of the classical interaction causes a specific alignment of molecular axes even if the external pressure is zero. The topography of the potential energy surface of clusters of various sizes must be studied as well.

Acknowledgements

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Production runs: Monte Carlo - Rossen Radev

DFT calculations: Stoyan Pisov

References

- [1] M. P. Allen and Tildesley, *Computer simulation of Liquids* (Clarendon, Oxford, 1994).
- [2] E. Dendy Sloan, Jr. *Clathrate Hydrates of Natural Gases*, (Second edition, Revised and Expanded), (Marcel Dekker Inc., New York 1998).
- [3] E. Daykova, A. Proykova and I. Ohmine, *Meetings in Physics@University of Sofia* 2,p.44 (Sofia, Heron Press, 2002).
- [4] B.O'Malley and L.Snook, *Phys. Rev. Lett.* **90**, 085702-1 (2003).
- [5] A. Proykova, S. Pisov and S. Berry (2001) *J. Chem. Phys.* **115**, 8583.