CAN SMALL FREE METHANE CLUSTERS EXHIBIT PHASE-LIKE TRANSITIONS?

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Abstract

Low-temperature (< 60K) phase changes of free clusters containing 50, 137, and 229 CH$_4$ molecules have been observed in isoenergetic Molecular Dynamics computations. Bulk solid methane exhibits structural phase transformation at 20.4 K. However, clusters of 50 molecules already melt at $\sim$ 25 K, which makes the observation of solid-solid transformations rather challenging.

1 Introduction

Small free clusters of molecules with very high symmetry (octahedral) have been found to resemble bulk of the same substance even in the case of small number of ingredients (30 to 80) [1]. The number of particles (molecules or/and atoms) that mimics bulk properties like phase transitions is strongly dependent on the range of the potential. The effect of decreasing the range of the potential is to destabilize strained structures [2]. In the case of long-range potentials (Coulomb [1]) one detects structures, determined by the co-operative (collective) interaction - the system is expected to transform easier than in the case of short-range interactions. On the other side, the surface of free clusters plays much more important role for long-range potentials. Various parameters of the potential, for instance electric charge value, govern the cluster response to external changes. An example is the melting temperature increase for higher charge values [3].

In the present work we study clusters consisting of less symmetrical molecules (tetrahedral) in order to check how the lower symmetry of the ingredients influences cluster’s behavior at different temperatures. The interacting potential contains a long-range term (Coulomb), which makes it necessary to study the size influence - clusters of 50, 137, 229 methane molecules have been simulated with the help of the isoenergetic Molecular Dynamics method described in the next section. Simulations of methane clusters have been performed more than two decades ago [4]. They showed that the lower limit of the classic approach is $\sim$10K. In those days the computers were less fast and the researchers tended to go for cheap rather than reliable potentials. Nowadays
more sophisticated potentials are available and better results could be obtained [5]. This justifies re-visiting the problem of how the cluster size influences the structural phase changes. Another intriguing question is how a free cluster, e.g. a cluster at zero external pressure, behaves when the temperature is rather close to the ultimate low limit of the classic mechanics calculations.

Solid (bulk) methane exhibits several crystalline phases based mainly on the difference in the orientation of molecules in the unit cell. Infrared investigation of solid methane performed by Bini and co-workers [6] let him propose a phase diagram, which has been additionally elucidate by Nakahata et al. with a help of optical and X-ray diffraction studies [7]. The liquid methane freezes at 90.6 K and $p = 0.1$ MPa [8] into a fcc orientational disordered phase I [9], characterized with rotational diffusion of the molecules. A transition to the orientational ordered phase II occurs at 20.4 K [10] at zero pressure. The phase II is the James-Keenan cubic structure, in which one out of four molecules ($O_h$) is undergoing a weakly hindered rotation, while the other three molecules ($D_2d$) have an anti-ferro order [11].

The state of orientational disorder takes place for the systems of spherically-symmetric molecules ($CH_4$) with a symmetry lower than the site in the crystal structure [9]. At cooling such systems could undergo phase transitions to a partially-ordered or fully ordered state. Hindered rotations occur because of weakly angular-dependent intermolecular forces and a large rotational energy as it is in methane [11].

Is such a behavior inherent for small systems as well? This is the question we study in the current work.

2 The model

Due to their spherical symmetry methane molecules resemble in many aspects the noble gases (Ar, Kr, Xe). The intra-molecular frequencies ($\sim 4 \times 10^{13}, \sim 9 \times 10^{13}$ Hz) are one order of magnitude higher than the frequency of the intermolecular vibrations. That is why, we consider the molecules as rigid bodies (C-H distance $b=1.094 \, \text{Å}$). Suitable intermolecular potentials for regarding molecular space orientations could be the Lenard-Jones potential [5] or a more sophisticated 3-body RMK potential [12]. In both approaches complicated procedures had been followed to obtain parameters’ values. Needless to say, these parameters are not entirely satisfactory. In our study, the total potential is a sum of pair atom-atom potentials $U_{pw}(i, j)$:

$$U_{pw}(i, j) = \sum_{\alpha, \beta=1}^{5} \left[ 4 \epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j \epsilon_{\alpha\beta}}{4\pi\varepsilon_0 r_{ij}^3}$$

$$U_{pot} = \sum_{i, j=1}^{N} U_{pw}(i, j)$$

where $\alpha, \beta$ denote either a carbon or a hydrogen atom; $r_{ij}$ is the distance between the $i$-th and the $j$-th atom; $q_i, q_j$ is either $q_C = -0.572$ or $q_H = 0.143$ in elementary charge units.

The parameters have been obtained in a way to fit experimental data. For instance, the charge and the bond-length are determined from the octopole moment value. $\sigma_{\alpha\beta}$ in $\text{Å}$, $\epsilon_{\alpha\beta}$ in $\text{meV}$ are

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Figure 1: Lindemann index for clusters of 50 and 229 molecules; a bcc-starting configuration.

Figure 2: Lindemann index for clusters of 50 and 229 molecules; a fcc-starting configuration.

\[ \sigma_{CC} = 3.35, \sigma_{HH} = 2.81, \sigma_{CH} = 3.08; \]
\[ \epsilon_{CC} = 4.257, \epsilon_{HH} = 0.715, \epsilon_{CH} = 1.7447. \]

Two starting configurations with randomly oriented molecules have been designed: 1) a bcc lattice, which resembles the most spherically-symmetric shape of a cluster and 2) fcc, which is a possible lattice for a bulk methane. We execute the velocity Verlet algorithm \[5, 13\] for numerical integration of classic equations of motion in a special micro-canonical ensemble - \( N, E, p=0 \) (free clusters) at temperatures above 10\( K \) to avoid quantum effects. The integration step of \( dt = 1\)\( fs \) guarantees an accuracy greater than 0.003\% of the energy conservation for runs up to \( \sim 0.5\)\( ns \); the records are taken every 100\( fs \).

3 Results

Liquid- and solid-like phases can be distinguished with the help of a specially constructed formula, which is an extension of the Lindemann index \( \delta_{lin} \) \[14]:

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

where \( r_{ij} \) is the distance between molecular centers of mass. In bulk, the Lindemann index is computed on the basis of the mean deviation of the \( i \)-th atom from its ideal lattice position and \( \delta_{lin} < 0.1 \) indicates a solid state. In a free cluster the surface plays a destabilizing role and the cluster is solid if \( \delta_{lin} < 0.08 \) \[15\].

The Lindemann index, plotted in the Figs.\[11 - 3\], shows three distinguishable phases: two solid-like phases below 30\( K \) and a liquid-like phase above 30\( K \) for all three sizes and both starting configurations.

The caloric curves (total energy per particle as a function of temperature) are given in the Fig.\[5\]
and Fig.6. Although the caloric curves are too smooth (a change of the slope is hardly seen, no more than 6%), we observe a region of frustration in the temperature interval (18, 25) K. In our computations the average temperature of the system is computed from its average kinetic energy: \( < E_{\text{kin}} > = \frac{3}{2} k_B T \), with \( k_B \) - the Boltzmann constant. Analyzing the trajectories at different total energies, we see that the system temperature jumps unevenly in the above interval. This is an indication for changes much more clearly seen with the help of the Lindemann index. There is no hysteresis on 'heating-cooling' of the system - Fig.4.

The different phase structures are distinguished on the basis of their radial distribution functions - Eq. 2: the radial distribution of molecular centers of mass shows the structure of the cluster at a specific temperature, while the atom-atom radial distribution reveals orientational order (disorder) of the molecules.

\[
g(r) = \frac{V}{N^2} \left( \sum_{i=1}^{N} \sum_{j \neq i} \delta(r - r_{ij}) \right)
\] (2)

Fig.7 shows the existence of a solid-like structure below 30 K and the absence of that structure above 30 K. The volume of the cluster enlarges at heating as well. Fig.8 shows typical distribution of the atoms for the oriented (solid line in the figure) and disoriented (dashed line in the figure) solid-like phases. The first peak of the distribution correspond to the H-H neighbors, the second peak corresponds to the C-H neighbors, and the third one is for the C-C neighbors. The same maximum of the H-H and C-H peaks indicates a unique mutual orientation of the molecules, e.g. the cluster is orientationally ordered. The phase transition at \( \sim 20 \)K causes disorientation of the molecules as it is seen in the Fig.8 - the dotted curve.

Finally, we present the Density of States (DOS) function obtained by a normal mode analysis of the quenched system [16]. The Fig.9 shows evidently the existence of a rovibrational coupling
Figure 5: Caloric curves at heating of clusters containing 50, 137, and 229 molecules, a bcc-starting configuration.

Figure 6: Caloric curves for the same cluster sizes with a fcc-starting configuration.

Figure 7: Radial distribution of the molecular centers of mass for a 50 CH₄ cluster; a fcc-starting configuration.

Figure 8: Atom-atom radial distribution for 50 CH₄ cluster, fcc-start.
Figure 9: The DOS for a 229 $CH_4$ cluster, a
$fcc$-starting configuration at 11 $K$ - the total spectrum is indicated with 'all' in the figure inlet; 'rot' is the rotational and 'vib' is the vibrational spectrum.

[9] The Fig.10 shows broadening of the vibrational spectrum at heating.

4 Conclusion

Implementing Molecular Dynamics method to a microcanonical state of free methane clusters, we show that they exhibit transformations between an orientationally-ordered (at $\sim 10K$) and disordered phase (above 20K). The lack of hysteresis in the cooling-heating regime indicates a continuous transition. However, such a statement can be confirmed either by studying infinite systems (i.e. periodic boundary conditions) or by applying the finite-size scaling theory [17].

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