Algorithm for Determining Optimal Configuration of a Three-Dimensional Unit Cell of Nonpolar Liquid

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Abstract

A three-dimensional mathematical model is represented for a unit cell of nonpolar liquid. On its basis algorithm to determine the optimal configuration of cells for different numbers of molecules with regard to their uniform distribution by sphere is designed and implemented.

Keywords: liquid structure, nonpolar liquid, optimal configuration.

Introduction

Description of the liquid state at the molecular level refers to the fundamental tasks of modern physics. A variety of liquid types and qualitative differences in their properties significantly complicate solving this problem. And as a consequence is a variety of existing theories used to describe the liquid state. In recent times special attention is paid to the cluster theory of liquids [1-7,13].
In the most general case, clusters are the assembly of homogeneous elements, which are independent units with specific properties. Now this theory is mainly used to describe complex fluids, such as associated liquids (water) [2-4,6,7] and liquid metals melts [1,5,13]. In specified papers the cluster is a molecular complex comprising 100 or more molecules, although consisting of simple elements (dimers, tetrahedra, etc.). The complex has no rigid structure and is a stable formation with dynamically changing components.

Unstable local structures model (ULS) [10, 12] is one of the new models describing liquid state at the molecular level (on the nanometer scale), which allows to describe rheological properties of nonpolar liquids in a wide range of temperatures and pressures [11]. Formally, this model can also be attributed to the cluster type, but it has a number of significant features:

- worked out and most developed for the description of simple liquids;
- a liquid consists of local unstable structures with dimensions comparable to the first coordination zone and a disordered massive of molecules;
- rigid ordering structures with the greatest stability (unit cells) predominantly influence on the properties of the liquid.

The most important task of building the model is to determine the configuration of the unit cells on the basis of the interaction forces between the molecules. A special case of solving this problem is the distribution of molecules in a two-dimensional cell for nonpolar and polar liquids [12, 13]. In these papers it is shown that the most resistant cells should be volume-centered and have a certain arrangement of the points of stability.

However, determining the optimal configuration of a three-dimensional unit cell with the greatest time of stability is still the major problem. The basic principles of its building for the nonpolar liquids are derived from a two-dimensional cell model. Such a cell has the lowest energy of molecules interaction. It is assumed that cell configuration with uniform molecules distribution by sphere corresponds to the minimum of energy.

The solution of this problem involves the following steps:

- physico-mathematical description of the method;
- algorithm design to determine the optimal configuration;
- creation of a simulation program implementing this algorithm.

**Physico-Mathematical Description of an Algorithm**

The determining method base of an optimal molecule configuration in a cell includes the principle of creating conditions for spontaneous molecules
transition into the state corresponding to this configuration. Originally molecules are randomly placed with uniform probability on the sphere surface. For transition it is necessary to select such conditions that potential wells (interaction minima) had been formed in the points of stable molecules arrangement. Central, depended only on the distance between molecules, the Van-der-Waals interaction has obvious potential wells that leads to ease its use in forming the optimal conditions for the transition of molecules into a steady state.

Originally a cell consisting of four molecules was considered. This is the minimum amount that can be distributed by volume. Uniform distribution of the specified number of molecules corresponds to a regular polyhedron with four vertices - tetrahedron. A distinctive feature of this distribution is the lack of cross-links. For molecules transition into steady state we introduce such parameters of the molecules movement, upon which the minima of interaction are located in the vertices of a tetrahedron. Because of the equality of the distances between the vertices of the tetrahedron interaction forces are the same. Consequently, the compensation of the forces acting on the taken separately cell molecule is available only for such fixed positions of the molecules in the cell when the interaction forces are zero. It is this cell is expected to have a minimum energy of the interaction, and hence will be the most stable.

To meet specified conditions a distance between vertices in a tetrahedron is defined by the formula of the circumsphere radius:

\[ a = \frac{4 \cdot R}{\sqrt{6}}, \]

where for ease of calculation the radius of the sphere R is chosen equal to the distance between the cell molecules of the nonpolar liquid [12]. In addition, the Lennard–Jones force constant corresponding to zero potential is given, so that the force of the molecules interaction in a tetrahedron is equal to zero:

\[ \sigma = \frac{a}{\sqrt[4]{2}} \]

In the case of the cell with the molecules number being more than 4, the cross-links influence on the arrangement of the molecules, so that the position of the potential wells corresponding to the minimum of interaction energy is unknown. Proceeding from the assumption that the minimum energy of interaction is achieved when placing the molecules in the potential wells, we select the distance between the molecules, so that the energy of interaction between them is minimal. For this Lennard–Jones force constant is varied:

\[ \sigma = k \cdot \frac{a}{\sqrt[4]{2}} \]
By increasing the number of molecules in a cell, obviously, the distance between them decreases in the steady state, therefore the \( k \)-factor is less than unity.

**Basic Methods of the Algorithm Implementation**

To implement this method the following problems are solved:
• organization of molecules movement strictly over the surface of the sphere;
• determination of an angular molecules displacement sign;
• values limit of angular displacement to prevent molecules rotation in a discrete-time through an angle above \( 2\pi \) radians;

To travel strictly over the sphere we use a spherical coordinate system, while changing only the angles \( \alpha \) and \( \varphi \). Changing the angles is made by the formulas of uniformly variable motion, with initial velocity at every time-moment is re-zeroed for preventing oscillatory motion at the "bottom" of the potential well. For the \( i \)-th cell molecule:

\[
\alpha_i = \alpha_0 + \frac{F_\alpha \cdot N_a}{M \cdot R} \cdot \frac{dt^2}{2},
\]

\[
\varphi_i = \varphi_0 + \frac{F_\varphi \cdot N_a}{M \cdot R} \cdot \frac{dt^2}{2},
\]

where \( M \) - molar mass of a molecule, \( N_a \) - the Avogadro number, \( dt \) – discrete time sampling, \( F_\alpha, F_\varphi \) - projections of forces acting on a molecule on the axis \( \alpha \) and \( \varphi \) defined as

\[
F_\alpha = F_x \cdot \cos\left(\arccos\frac{F_x}{F}\right) \cdot \cos\left(\arccos\frac{F_x}{F_{xy}}\right) + F_y \cdot \cos\left(\arcsin\frac{F_z}{F}\right) \cdot \sin\left(\arccos\frac{F_x}{F_{xy}}\right) - \\
-F_z \cdot \sin\left(\arcsin\frac{F_z}{F}\right),
\]

\[
F_\varphi = -F_x \cdot \sin\left(\arccos\frac{F_x}{F_{xy}}\right) + F_y \cdot \cos\left(\arccos\frac{F_x}{F_{xy}}\right),
\]

where \( F \) - the total force acting on a molecule under consideration from the rest of the cell molecules, \( F_x, F_y, F_z \) – direction force on the axis of \( x, y, z \), \( F_{xy} \) - the projection of force on the plane \( xy \):
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\[ F = \sqrt{F_x^2 + F_y^2 + F_z^2}, \]

\[ F_{xy} = \sqrt{F_x^2 + F_y^2}, \]

where

\[ F_x = \sum_{j \neq i}^{N} F_{xij}, \quad F_y = \sum_{j \neq i}^{N} F_{yij}, \quad F_z = \sum_{j \neq i}^{N} F_{zij} \]

\[ F_{xij} = F_{ij} \cdot \frac{x_{ij}}{r_{ij}}, \quad F_{yij} = F_{ij} \cdot \frac{y_{ij}}{r_{ij}}, \quad F_{zij} = F_{ij} \cdot \frac{z_{ij}}{r_{ij}} \]

where \( x_{ij}, y_{ij}, z_{ij} \) - difference of coordinates on axes \( x, y, z \) between the \( i \)-th (under consideration) and \( j \)-th molecules, \( r_{ij} \) - distance between the \( i \)-th and \( j \)-th molecules, \( F_{ij} \) - the force of pair-wise interaction, defined by the Lennard-Jones potential:

\[ F_{ij} = 24 \cdot \varepsilon \cdot \left[ \frac{\sigma^6}{r_{ij}^6} - \frac{2\sigma^{12}}{r_{ij}^{13}} \right] \]

Angular displacements sign is determined by the sign of the angular acceleration without regard to the initial velocity influence, since it is assumed to be zero.

To avoid too significant angular displacement at a discrete-time (> 2 \( \pi \) radians) a maximum angle of the molecule rotation is limited. This is accomplished as follows. For each cell molecule the angular acceleration on the axes \( \alpha \) and \( \varphi \) are determined. Sampling discrete times are defined according to the obtained accelerations by the formula of uniformly variable motion for a fixed value of the rotation angle (0.01 rad). Minimum of all calculated time of molecules rotation on the axes \( \alpha \) and \( \varphi \) sets the sampling discrete time at which the angles are recalculated.

The Results of the Simulation Program

The optimal cell configuration consisting of 4 molecules has been derived as a result of simulation program work based on the described algorithm. The tetrahedron corresponds to such arrangement and this confirms the correctness of the algorithm (Fig. 1).
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Fig. 1. Optimal configuration for a four-molecule cell corresponding to the tetrahedron.

In the case of the cell containing 5 or more molecules, we have obtained plots of interaction energy of the cell molecules against a multiplier of the Lennard–Jones constant $k$-factor (Fig. 2, 3).

Fig. 2. Plot of minimal interaction energy against a multiplier of the Lennard–Jones constant $k$-factor for a five-molecule cell.

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As seen from the graphs, several local minima may correspond to each number of molecules in the cell, indicating the presence of a few stable cell configurations. For each value of $\sigma$, corresponding to the energy minimum, steady positions of the cells molecules are identified. If the number of molecules in the cell is equal to the number of vertices of regular polyhedra, as one of the stable states configurations corresponding to regular polyhedra (Fig. 4, 5) are obtained, this confirms the applicability of the algorithm.

Fig.3. Plot of minimal interaction energy against a multiplier of the Lennard–Jones constant $k$-factor for a six-molecule cell.

Fig.4. Optimal configuration for a five-molecule cell.
Fig.5. Optimal configuration for a six-molecule cell corresponding to the octahedron.

The optimum configurations of cells are obtained for cases where the number of molecules is from 4 to 15.

Conclusion

Determining the best configuration of nonpolar liquid cells allows to find out the longest stability time of the cell for different numbers of molecules and to select the cells with the optimal number of molecules. On the basis of these cells a model can be built that allows the properties of nonpolar liquids to be described at the molecular level. In the case of more complex fluids the problem becomes considerably complicated due to the presence of other than the van der Waals interaction forces between molecules.

References


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