

ON UNIVERSALITY OF THE WRAPPING PERCOLATION TRANSITION

Jiří ŠKVR^{a,*} and Ivo NEZBEDA^{a,b}^a Faculty of Science, J. E. Purkinje University, 400 96 Ústí nad Labem, Czech Republic;
e-mail: jskvor@physics.ujep.cz^b E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals,
Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchbát, Czech Republic;
e-mail: ivonez@icpf.cas.cz

Received January 2, 2008

Accepted March 13, 2008

Published online April 24, 2008

Dedicated to Professor William R. Smith on the occasion of his 65th birthday.

The hypotheses of the scaling universality of the wrapping probability at the percolation threshold and of the critical exponent ν have been examined for the PM/TIP4P primitive model of water. The obtained results confirm the validity of the recently proposed method of determination of the percolation threshold in fluids and its characteristics, supporting further the hypothesis of universality, and efficiency and accuracy of the method.

Keywords: Percolation threshold; Wrapping probability; Spanning probability; Scaling laws; Clusters.

The percolation theory¹ is widely used in a number of branches of science. It deals with the formation and disruption of clusters which may have different interpretation depending on various applications. In molecular science, cluster is a group of particles that are connected by an unbroken path of interparticle bonds. The occurrence of such clusters affects substantially the properties of fluids; particularly, the formation or disruption of an infinite cluster via percolation transition. However, studies of the percolation transition on 3D continuous systems are very time-consuming. As a result, only rough (and sometimes contradicting) estimations of the percolation threshold have been made for fluids.

There are two main concepts of defining spanning clusters for bulk fluids simulated in a (cubic) box with periodic boundary conditions identified as wrapping (having an infinite extent within the framework of the periodically repeating cells) and crossing (determined by spatial extension only) clusters. Moreover, one can consider wrapping or crossing in one, two or

three directions – distinguished henceforth by superscripts (e), (2), and (3), respectively. The probability of a spanning cluster to be found in the system is described by a function $R(\rho, L)$, where L is the length of the edge of the cubic simulation box and ρ is the number density. In the thermodynamic limit ($L \rightarrow \infty$, $\rho = \text{const.}$), $R(\rho, L)$ approaches a step function with $R = 0$ below and $R = 1$ above the percolation threshold ρ_c . Near the percolation threshold and for large L , function $R(\rho, L)$ is supposed to exhibit the universal behavior as a function of the scaling variable $(\rho - \rho_c)L^{1/\nu}$ (and other irrelevant variables^{1,2}).

In a recent paper³ we have examined various wrapping (R_w) and crossing (R_{cr}) probability functions in the bulk fluid at several supercritical temperatures and used finite-size scaling to determine their values at the percolation threshold in infinite systems. We have considered a simple square-well fluid and found that in the bulk fluid the wrapping probabilities do exhibit highly universal behavior. The finite-size corrections for R_w at the percolation threshold have been found to be negligible even in a relatively small system of 500 molecules. We have obtained the scaling functions for wrapping probabilities $R_w^{(e)}$, $R_w^{(2)}$, and $R_w^{(3)}$, and the respective values $R_{w,c}$ at the percolation threshold in particular. On the other hand, for the crossing probabilities, finite size corrections to scaling are large and the use of R_{cr} for the localization of the percolation threshold does not seem suitable at all.

If the above mentioned finding regarding the wrapping probability is proved to be universal, it may be used for the determination of the percolation threshold in complex fluid systems because the obtained scaling functions should not be very different from those for other fluids. A reasonable estimate of the percolation threshold may thus be obtained even from one simulation on a single system by using the critical values of the wrapping probabilities.

Since in a recent paper³ the behavior of the spanning probability function has been examined for and the hypothesis drawn from results for one model only, a simple square-well fluid, we examine in the present note the wrapping probability function for a qualitatively very different model, a primitive model of water, to further examine the hypothesis of the scaling universality. Molecular simulations have been performed on the model over a wide range of supercritical temperatures and the obtained results show that even in this case the scaling universality holds true.

THEORY AND SIMULATION DETAILS

The model considered in this paper is a primitive model⁴ PM/TIP4P descending from the parent TIP4P model of water⁵.

The total intermolecular interaction consists of a hard-sphere core of diameter σ_{OO} (mimicking oxygen), and three imbedded sites of two kinds: Two sites, denoted as X, mimic the hydrogen atoms and one M-site mimics the negatively charged site (the reader is referred to ref.⁴ for further details). The attractive interaction between the unlike sites at a distance r apart is represented by a square-well potential, u_{SW} ,

$$\begin{aligned} u_{\text{SW}}(r, \lambda) &= -\varepsilon, & \text{for } r < \lambda \\ &= 0, & \text{for } r \geq \lambda \end{aligned} \quad (1)$$

and the repulsive interaction between the like sites is represented by a hard-sphere potential, u_{HS} ,

$$\begin{aligned} u_{\text{HS}}(r, \sigma) &= \infty, & \text{for } r < \sigma \\ &= 0, & \text{for } r \geq \sigma. \end{aligned} \quad (2)$$

Thus, the considered model assumes the form

$$u_{\text{PM}}(1,2) = u_{\text{HS}}(r_{\text{OO}}, \sigma_{\text{OO}}) + \sum_{i \in \{1\}, j \in \{2\}} u_{\text{HS}}(r_{ij}, d_{ij}) + \sum_{i \in \{1\}, j \in \{2\}} u_{\text{SW}}(r_{ij}) \quad (3)$$

where the summation in the second term of Eq. (3) runs over the pairs of like sites and in the third term of unlike sites. The potential parameters σ_{OO} and ε are conveniently used to scale distances and energies, respectively, and we therefore set, without loss of generality, $\sigma_{\text{OO}} = 1$ and $\varepsilon/k_{\text{B}} = 1$, where k_{B} is the Boltzmann constant. The simplicity of the attractive interaction makes it also possible to define uniquely the criterion of bonding: Two particles create a bond whenever their interaction energy equals $-\varepsilon$ (we note in passing that the model does not allow creation of more than one bond between a pair of particles).

We carried out common Metropolis Monte Carlo (MC) simulations⁶ and analyzed the configurations with respect to the presence of clusters using the wrapping definition: The cluster wraps the system if it is possible to get, starting from any particle of the cluster and moving along interparticle bonds, to an image of that particle in another replica⁷. The parameters of

the simulations were set so as to maintain the acceptance ratio, around ca. 1/3. All the systems were equilibrated by performing $10^5 N$ particle displacement steps where N is the total number of particles in the simulation cell. To keep the development of the simulated systems under control, various control quantities were monitored⁸. Configurations used for the evaluation of the presence of the wrapping cluster were separated by $4N$ attempted displacement steps, and the total number of analyzed configurations was $4 \times 10^9/N$.

With respect to the previous results³ we focus in this note only on clusters wrapping at least in (any) one direction, $R_w^{(e)}$. For a given temperature, $T = 1/\beta$, and number of particles, we obtain the wrapping probabilities $R_w^{(e)}$ as a function of density ρ . These functions should cross very close to ρ_c which naturally depends on T . From this characteristic we can then get a first estimate of ρ_c . A convenient function providing a very good fit to $R(\rho)$ is

$$f(\rho) = \frac{1}{1 + \exp(a_0 + a_1\rho + a_2^2\rho_2 + a^3\rho_3)} \quad (4)$$

where a_i are numerical parameters. As noted above, the probability R as a function of the scaling variable $(\rho - \rho_c)L^{1/\nu}$ is supposed to be universal near the percolation threshold and for large L , where ρ_c and ν are the parameters we want to determine. Considering that the probability R is expressed as a function of density ρ for a set of system sizes (characterized, equivalently, by the number of particles N rather than the box length L) then

$$R\left((\rho - \rho_c)\left(\frac{N}{\rho}\right)^{1/3\nu}\right) \neq f(N). \quad (5)$$

Thus, a second estimate of ρ_c and the critical exponent ν and, consequently, also $R_{w,c}^{(e)}$, are determined by trial and error to minimize the differences in $R_w^{(e)}$ as a function of scaling variable in Eq. (5) for various N . The obtained critical exponent ν as well as the probability R at the percolation threshold (R_c), in an infinite system should be universal for a given dimensionality of the system, definition of the infinite cluster, and boundary conditions².

RESULTS AND DISCUSSION

We carried out simulations on the PM/TIP4P model for five supercritical isotherms and for each isotherm we considered a series of the number of particles within the range $N \in \langle 500, 16000 \rangle$. As a first estimate of the percolation threshold we used the crossing point of the wrapping probabilities $R(\rho)$ for various N . That such a point may exist is demonstrated (using different zoom) in Figs 1 and 2. Figure 1 indicates the validity of the given approximation, Eq. (4); Fig. 2 includes also the limiting case of $R(\rho, N \rightarrow \infty)$ as a step function with the step at the percolation threshold ρ_c . It is worth noting the obvious fact: the higher the number of particles N in the system, the sharper increase in wrapping probabilities $R(\rho)$. The upper panel of Fig. 3 then indicates the precision with which the percolation threshold can be determined; in this case it is 0.3095 ± 0.01 .

In Fig. 4 we show the wrapping probability as a function of the scaling variable $(\rho - \rho_c)L^{1/\nu}$. As it is seen, all results fall on a single curve. This means that it is possible to find values of ρ_c and ν such that the wrapping probabilities can be described by universal functions of the scaling variable. This finding holds over a wide range of the system sizes represented by N (see also the lower panel of Fig. 3 for inverse temperature $\beta = 6.0$ with N ranging from 500 to 16000). This fact makes it possible to specify the value of percolation threshold density ρ_c . Consequently, the system of only 500 molecules is sufficiently large for the proposed method to be used for the percolation threshold location.

The respective values of ρ_c , R_c and ν for all temperatures considered are summarized in Table I. This table also includes the value of the average energy per particle U_c/N which corresponds, for the given model, to the average number of bonds per particle $n_{b,c}$ in the system. As one may intuitively expect, the higher temperature, the higher the percolation threshold density ρ_c ; this temperature dependence is shown in Fig. 5 (upper panel). The temperature dependence of $n_{b,c}$ is similarly distinctive; see the lower panel of Fig. 5. We remark that the presence of the (critical) wrapping cluster then requires a higher fluid density but a lower number of bonds per particle with increasing temperature, which seems to be related to the change of the structural properties of the system and the clusters. In contrast to this fact, the parameters R_c and ν are not so strongly temperature dependent and they are in reasonable agreement with the values obtained for the supercritical square-well fluid³.

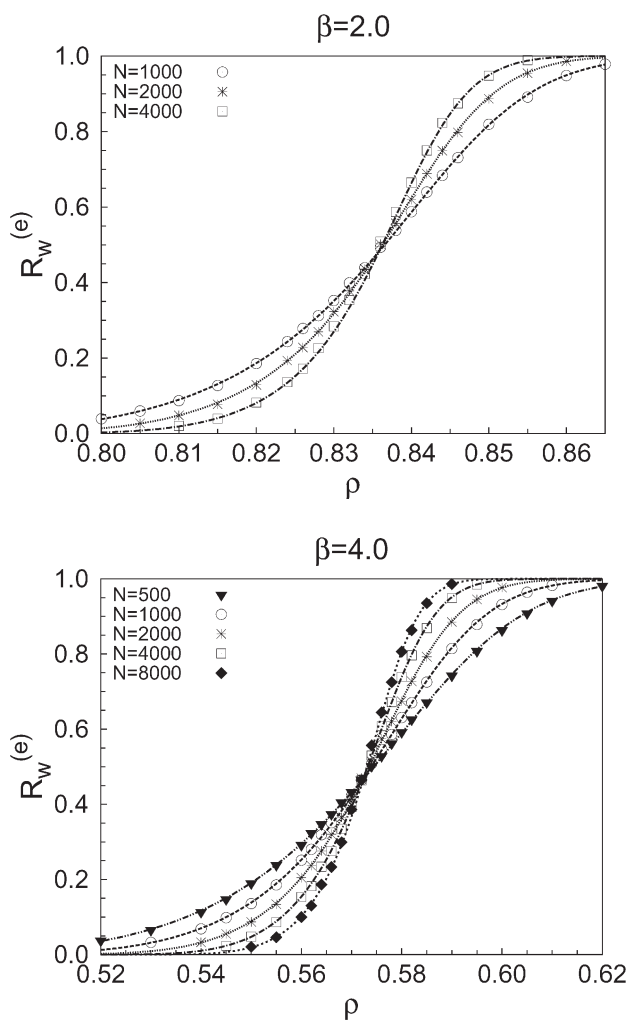


FIG. 1

Wrapping probability as a function of the number density; symbols are simulation data and the curves have been obtained from the fit (Eq. (4))

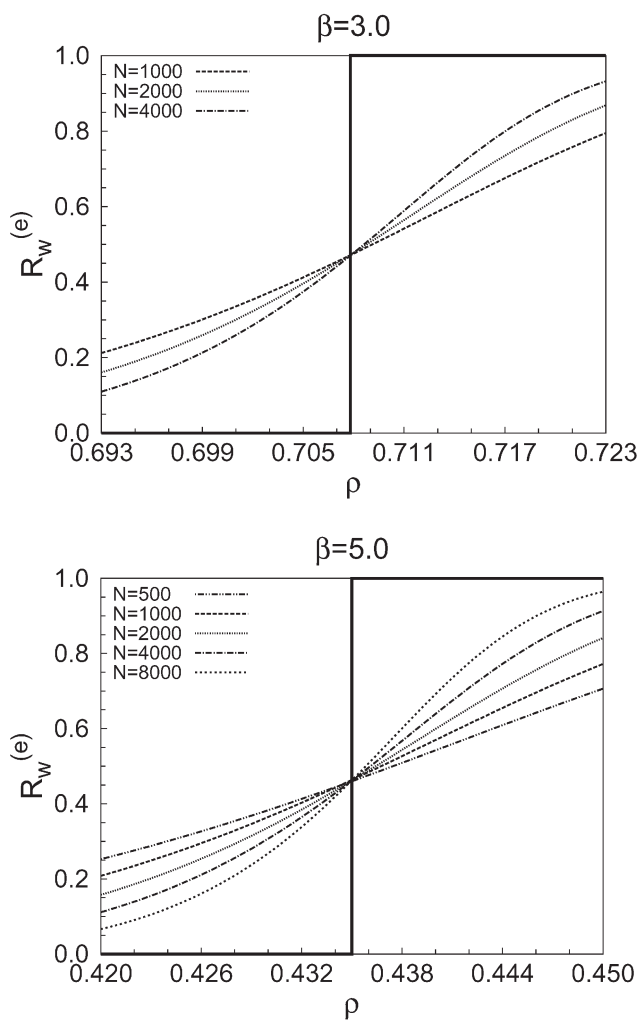


FIG. 2

Detailed course of the wrapping probability as a function of the number density in the vicinity of the crossing point; broken lines are fitting curves and the thick line denotes their limit for $N \rightarrow +\infty$

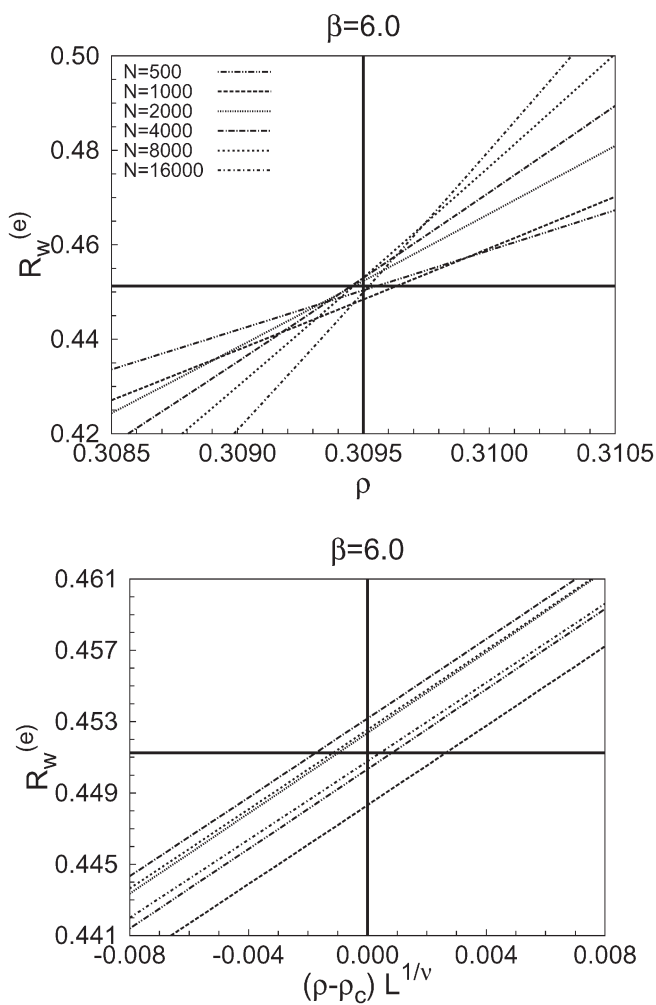


FIG. 3

Detailed course of the wrapping probability as a function of the number density (upper panel) and the scaling variable $(\rho - \rho_c)L^{1/\nu}$ (lower panel) near the percolation threshold (solid lines)

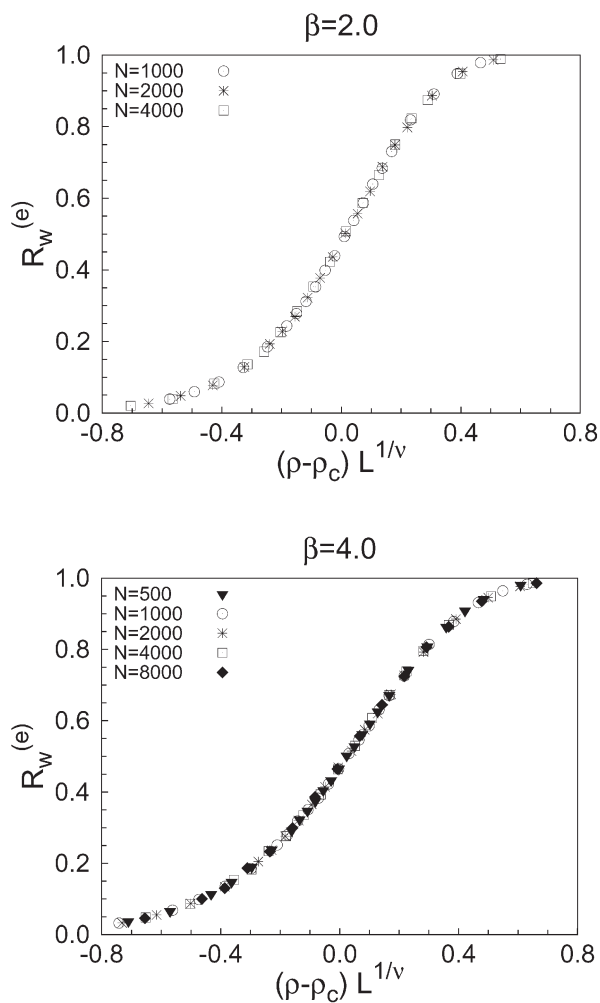


FIG. 4

Simulation results for the wrapping probability as a function of the scaling variable $(\rho - \rho_c)L^{1/v}$ for different system size

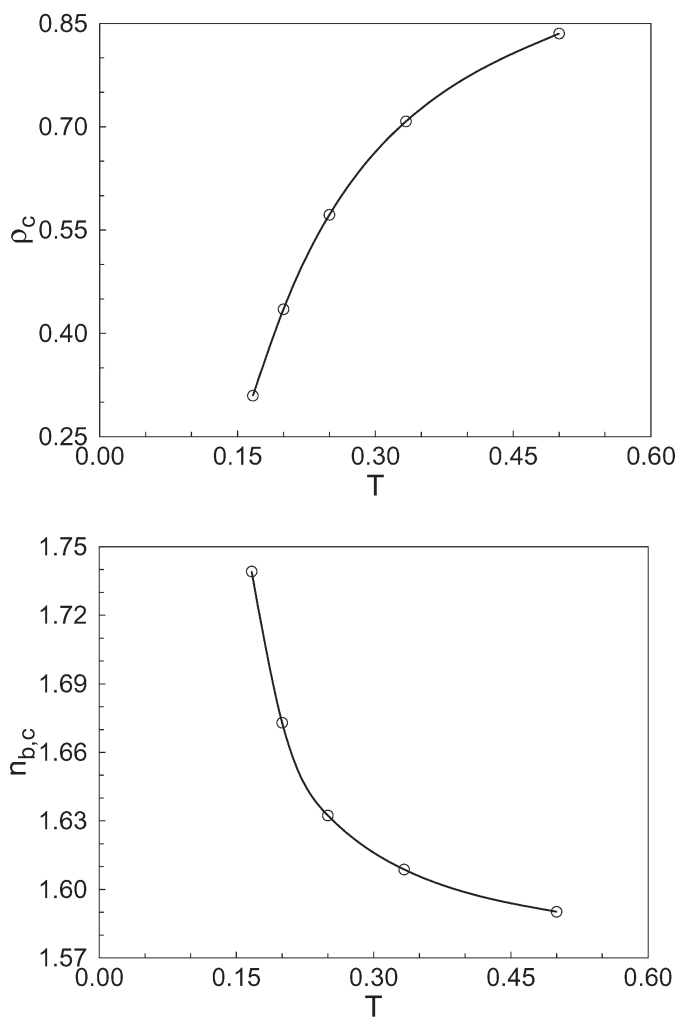


FIG. 5
Temperature dependence of the percolation threshold density ρ_c and the average number of bonds per particle, $n_{b,c}$. Open circles are simulation results, the solid line serves as a guide for eye

TABLE I

Parameters of the wrapping probability function and the internal energy at the percolation threshold for the supercritical PM/TIP4P model of water in dependence on the inverse temperature

β	ρ_c	$R_{w,c}^{(e)}$	ν	U_c/N
2.0	0.835	0.472	0.85	-0.795
3.0	0.708	0.471	0.89	-0.804
4.0	0.572	0.465	0.88	-0.816
5.0	0.435	0.462	0.91	-0.837
6.0	0.309	0.451	0.91	-0.870

CONCLUSIONS

In the present note we have examined the hypothesis on universality of the spanning probability function for a continuous system – fluid. Unlike the previous paper³ where a simple fluid, the square-well model, was considered, in this paper we have considered a model with strong and strongly orientation-dependent attractive interactions mimicking water with all its anomalies. It is shown that even for this qualitatively quite different system the universality seems to hold. To be specific, the results may be summarized as follows:

1. There exists the crossing point of the wrapping probabilities $R_w^{(e)}(\rho)$ for different (but sufficiently large) N ; this point provides a very good estimate of the percolation threshold. This means that only two simulations on systems of two sizes may be sufficient for quite an accurate percolation threshold determination.

2. It has been confirmed that the wrapping probabilities can be described by a universal function of scaling variable $(\rho - \rho_c)L^{1/\nu}$. A more accurate estimate of ρ_c can thus be obtained by minimizing the difference according to Eq. (5) if more simulation data are available.

3. The system of 500 particles seems to be sufficiently large for the determination of the percolation threshold; a higher number of particles, however, improves the accuracy taking into account that the density dependence of the wrapping probability $R_w^{(e)}(\rho)$ for higher N is stronger and its variance for the same number of analyzed configurations near the percolation threshold is smaller.

4. The critical value of the wrapping probability $R_{w,c}^{(e)}$ does not seem to be a universal constant; however, it is not very much different from 0.45. Thus, if the probability $R_w^{(e)}$ in the system is about this value, we can expect that its density ρ is also near the percolation threshold density ρ_c .

Because of yet unsettled problem of the determination of the percolation threshold in continuous systems, we have focused rather on the mathematical aspect of percolation leaving physical consequences aside. Issues as, e.g., a link of the percolation to the remarkably strong dependence of the properties of water on the thermodynamic conditions in supercritical states, breakage of the infinite hydrogen-bond network via percolation in supercritical water, or a relation of the percolation density to the critical density can be addressed only after the percolation identification in the system has been properly clarified and will be the subject of the subsequent research.

This research was supported by the Czech National Research Program "Information Society" (project No. 1ET400720409) and by the Grant Agency of the Academy of Sciences of the Czech Republic (project No. IAA400720710).

REFERENCES

1. Stauffer D., Aharony A.: *Introduction to Percolation Theory*. Taylor & Francis, London 1992.
2. Hovi J. P., Aharony A.: *Phys. Rev. E* **1996**, *53*, 235.
3. Škvor J., Nezbeda I., Brovchenko I., Oleinikova A.: *Phys. Rev. Lett.* **2007**, *99*, 127801.
4. Vlček L., Nezbeda I.: *Mol. Phys.* **2004**, *102*, 485.
5. Jorgensen W. L., Chandrasekhar J., Madura J. D., Impey R. W., Klein M. L.: *J. Chem. Phys.* **1983**, *79*, 926.
6. Allen M. P., Tildesley D. J.: *Computer Simulation of Liquids*. Clarendon Press, Oxford 1987.
7. Seaton N. A., Glandt E. D.: *J. Chem. Phys.* **1987**, *86*, 4668.
8. Nezbeda I., Kolafa J.: *Mol. Simul.* **1995**, *14*, 153.