

Cluster Mechanism of Homogeneous Crystallization (Computer Study)

D. K. Belashchenko

Published online: 20 November 2008
© Springer Science+Business Media, LLC 2008

Abstract A molecular dynamics (MD) study of homogeneous crystallization of liquid rubidium is conducted with an inter-particle pair potential. The equilibrium crystallization temperature of the models was 313 K. Models consisted of 500, 998, and 1968 particles in a basic cube. The main investigation method was as follows: to detect (along the MD run) the atoms with Voronoi polyhedrons (VP) of 0608 type (“0608-atoms,” as in a bcc crystal) and to detect the bound groups of 0608-atoms (“0608-clusters”) that could play the role of the seeds in crystallization. Full crystallization was observed only at temperatures lower than 185 K with the creation of a predominant bcc crystal. The crystallization mechanism of Rb models differs drastically from the mechanism adopted in classical nucleation theory. It consists of the growth of the total number of 0608-atoms on cooling and the formation of 0608-clusters, analogous to the case of coagulation of solute for a supersaturated two-component solution. At the first stage of the process the clusters have a very loose structure (something like medusa or octopus with many tentacles) and include inside atoms with other Voronoi polyhedron types. The dimensions of clusters quickly increase and approach those of the basic cube. 0608-atoms play the leading role in the crystallization process and activate the transition of the atoms involved in the 0608-coordination. The fast growth of the maximum cluster begins after it attains a critical size (about 150 0608-atoms). The fluctuations of cluster sizes are very important in the creation of a 0608-cluster of critical (threshold) size. These fluctuations are especially large in the interval from 180 K to 185 K.

D. K. Belashchenko (✉)
Moscow State Institute of Steel and Alloys (Technological University),
Leninskij prospect 4, Moscow 119049, Russian Federation
e-mail: dkbel@mail.ru

Keywords Clusters · Crystallization · Molecular dynamics · Rubidium · Supercooling

1 Introduction

The phenomenon of homogeneous crystallization of a liquid metal model was first discovered in [1–5] using molecular dynamics (MD). The models consisted of 108, 256, 500 [2], and 500 [3, 4] particles. In [2, 5] the Lennard-Jones inter-particle potential was used, in [3] a pseudo-potential for Rb was used, and in [4] both of these potentials were used in full or truncated form. For rather long MD runs, the crystallization of the liquid was observed with the formation of bcc or fcc crystals and their dependence on the form of inter-particle potential used. Voronoi polyhedrons (VP) of the 0-6-0-8 and 0-4-4-6 types prevailed in the case of bcc crystallization.

It is proposed in the classical nucleation theory that for a supercooled liquid crystal seeds of different sizes must constantly appear and disappear (hetero-phase fluctuations). The possibility to create a seed is determined by the Gibbs energy of formation ΔG . One commonly considers a spherical seed of radius r and expresses ΔG as for macroscopic phases:

$$\Delta G = 4\pi r^2 \sigma_{ls} + (4/3) \pi r^3 (\mu_l - \mu_s) \quad (1)$$

Here σ_{ls} is the inter-phase tension and μ_l and μ_s are the Gibbs free energies of the liquid and solid phases for unity volume. Then, the possibility of the seed creation is

$$W = A \exp(-\Delta G / (kT)) \quad (2)$$

Here A is the frequency factor. The value of ΔG increases up to some maximum with the growth of the radius but then begins to diminish to negative values. The critical seed radius is determined by the maximum of ΔG . The growth of the seed becomes thermodynamically favorable after this maximum is reached.

It follows from these assumptions that, in a supercooled liquid, seeds of different sizes must exist and the concentration of pre-critical seeds must diminish with their size. These conclusions must be true for a stable and metastable liquid and do not correlate with the mechanism of the creation and growth of seeds.

However, there are rather little data on the real mechanism of liquid crystallization, especially at the first stages and at strong supercooling. The computer simulation method is very suitable for observing processes in supercooled liquids at the atomic scale. Therefore, in this study the processes of crystallization in supercooled liquid Rb were studied by the MD method to verify, in particular, the basic concepts of classical nucleation theory. In pioneering works [1–5] it was shown that, in a supercooled Rb model at 70 K to 80 K, the process of solidification begins after a rather long MD run and it then takes only 1,000 to 2,000 time steps for the transformation from liquid to crystal. The current work considers their results from the point of view of classical nucleation theory. But a more careful study shows that the real mechanism of

solidification of Rb at conditions used in [1–5] differs drastically from the classical one (see below).

2 Procedures

In this work a pair potential that was calculated for liquid Rb in previous studies [6,7] was used. This potential is shown in Fig. 1. The minimum is located at 4.4048 Å; its depth is equal to 0.0347 eV. A model for liquid Rb was created at 313 K and a real density of $1.476 \text{ g} \cdot \text{cm}^{-3}$ was realized using the MD method with this potential. The pair correlation function (PCF) of the liquid Rb model at 313 K is shown in Fig. 2 in comparison with diffraction data [8]. They agree well, with a standard deviation of 0.061. Hence, the potential [6,7] is reasonable for the simulation of liquid Rb.

Our models consisted of $N = 500, 998, \text{ or } 1968$ particles in a basic cube at a density of $0.011116 \text{ at}/\text{Å}^3$, as was used in [3]. It differs only slightly from the real value at 313 K ($0.01040 \text{ at}/\text{Å}^3$). The MD simulation was conducted with the Verlet algorithm

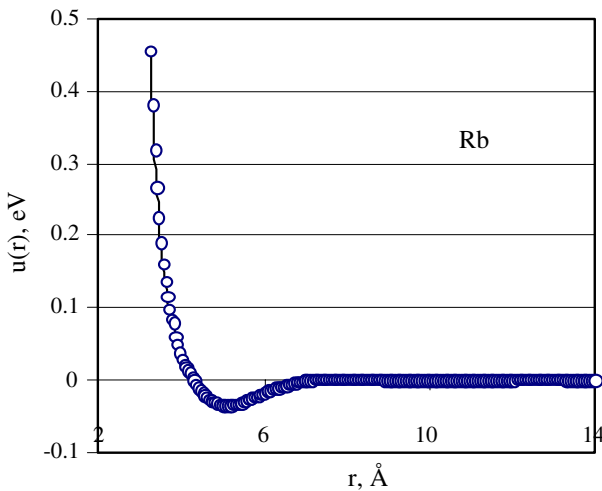


Fig. 1 Inter-particle pair potential of liquid Rb [6,7]

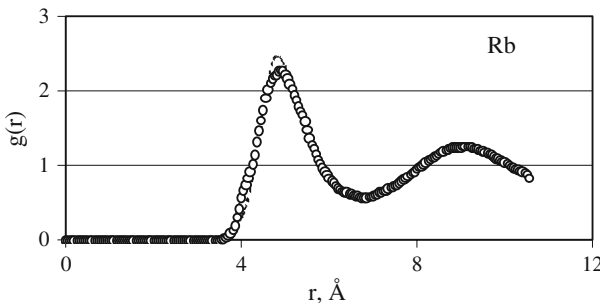


Fig. 2 PCF of liquid Rb at 313 K: *dashed line*—diffraction data, *points*—model

Table 1 Some properties of Rb models

T (K)	$g(r_1)$	$D \times 10^5$ ($\text{cm}^2 \cdot \text{s}^{-1}$)
313	2.25	3.11
200	2.77	1.22
150	3.08	0.74
110	3.43	0.42
100	3.46	0.41
90	3.55	0.13
80	3.71	0.084
70	3.87	< 0.08

at a cutoff radius of 14.35 Å or 10.13 Å. The time step was equal to 4.706×10^{-15} s. The length of one MD run was equal to 1000 time steps. The model was equilibrated at 326 K and then cooled quickly to temperatures from 313 K to 70 K. The subsequent simulations were conducted at a constant temperature and density. Immediately after cooling, all models were liquid or amorphous and it was possible to detect their structure data (the height of the 1st peak of PCF $g(r_1)$) and the self-diffusion coefficient D . These values are shown in Table 1 [9].

For simple liquids the self-diffusion coefficient near the melting point is of the order of $10^{-5} \text{cm}^2 \cdot \text{s}^{-1}$. Hence, at $T < 150$ K, the model liquids are rather viscous, and at $T < 90$ K, they behave as an amorphous substance.

It is known that Rb models crystallize in the bcc structure [3,4]. A Voronoi polyhedron (VP) has the 0-6-0-8 type in this lattice and is stable against small displacements of atoms. Hence, it was decided to investigate the behavior of those atoms that are of the 0-6-0-8 type. Such atoms may be candidates to form a crystallization seed and will be mentioned further as 0608-atoms.

Some methods were used for a more detailed structure study. First, we determined the dependence of the concentration of 0608-atoms on temperature (before the beginning of solidification). Then, we detected the existence of bound groups of 0608-atoms (0608-groups or 0608-clusters) where each atom has one or more neighbors from the same group (neighbor atoms lay not more than 6.55 Å from each other—coordinate of 1st minimum of PCF). We calculated the number of groups of different sizes and the dependence of the mean group size with time along the MD simulation runs. The mean size was determined as the 2nd moment,

$$M_2 = \frac{\sum_i i^2 m(i)}{p}, \quad (3)$$

where i is the number of atoms in a group, $m(i)$ is the number of groups with size i , and p is the total number of 0608-atoms in a model.

Also, we calculated the structure factors of a model $S(\mathbf{K})$ for a number of scattering vectors \mathbf{K} in different directions:

$$S(\mathbf{K}) = \frac{1}{N} \left| \sum_j \exp(i \mathbf{K} \mathbf{R}_j) \right|^2 \quad (4)$$

Here \mathbf{R}_j is the radius vector of the j -th atom, and the sum is taken over all atoms of a model. For an ideal crystal, $S(\mathbf{K}) = N$ if \mathbf{K} is the vector of an inverse lattice and $S(\mathbf{K}) = 0$ if not. For the case of periodic boundary conditions, the components of the \mathbf{K} vector must be equal to $(2\pi/l)m$ where l is the edge length of the basic cube and m is an integer or zero.

The beginning of crystallization was revealed when a large 0608-cluster appeared with a threshold size N_c that did not diminish for the following simulation and could only grow. In this case, the structure factor also exceeded some threshold value S_c at some K values. The values of N_c and S_c are determined very roughly.

3 Results

The equilibrium melting temperature of Rb models with the potential of [5,6] was determined in [9] as (313 ± 1) K using the “back-heating method.” The fully crystallized model was heated to different temperatures, and the point at which the crystal structure disappears was detected in the MD runs. For the case of $N = 1968$, the 0608-cluster size distribution at 326 K was near $1^{23}2^63^14^2$ (23 monomers of isolated 0608-atoms, 6 dimers, etc.) and the maximal $S(K)$ module was 23.80 (i.e., only 1.2 % from a maximal value of 1968). The maximal 0608-cluster consisted of four 0608-atoms. After fast cooling to some temperature, the simulation was conducted with many 1000-step runs and the total duration was more than 10^5 steps. The concentration of 0608-atoms steadily increased with cooling following

$$\theta = p/N = 0.00924 \exp(2442.7/(RT)) \quad (5)$$

The value of $-2.4427 \text{ kJ} \cdot \text{mol}^{-1}$ can be considered as the heat of transformation of a common Rb atom in a 0608-atom. The heat of crystallization of our Rb model is equal to $-1.73 \text{ kJ} \cdot \text{mol}^{-1}$ [9]. Therefore, we may consider the 0608-atoms as “the component of solution of crystalline Rb in liquid Rb.” This concentration grows from 2.3 % at 326 K to 6 % at 150 K. At 100 K, Eq. 5 gives a value of 17 % but this concentration cannot be realized because of the rather fast crystallization process described by the model.

It was established that at temperatures higher than 185 K the crystallization of the model never happens. The mean and maximal 0608-cluster sizes were fluctuating with an amplitude that increased with supercooling. The typical dependence of the 0608-cluster size from the step number at $N = 1968$ and $T = 185$ K is shown in Fig. 3. These fluctuations are too small to cause crystallization. A run length of 10^6 to 10^7 time steps is necessary to observe several events of such type. The fluctuations are especially strong in the region of 180 K to 185 K.

The temperature of 185 K is the definite threshold. At $T > 182.5$ K, our models did not crystallize, even for 101000 time steps. The maximum size of a 0608-cluster did

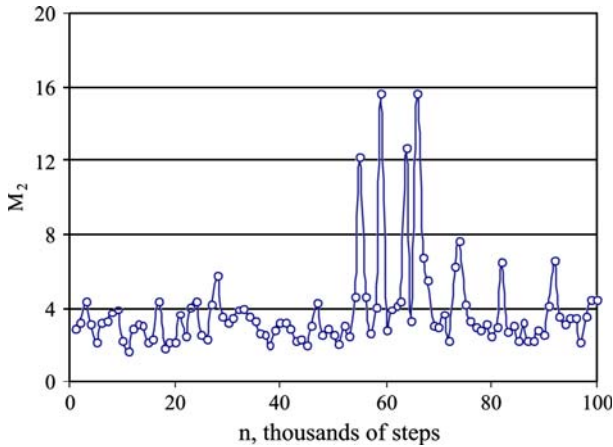


Fig. 3 Fluctuations of mean 0608-cluster size along MD run at 185 K

not exceed 16 atoms, and small clusters dominated. The size distribution was equal to $1^{32}2^63^54^210^113^1$ at 200 K and $1^{26}2^74^15^1$ at 313 K. These distributions are rather constant along an MD run. But at $T < 185$ K, all our models showed crystallization after a sufficiently long simulation.

In Table 2 the data that describe the crystallization events are shown. Here n_{total} is the total number of steps, L_C is the step number when the fast growth of cluster size begins (is determined very roughly), N_C is the size of a maximum cluster near the step L_C (is determined also very roughly), S_C is the maximum structure factor value at the step of fast growth, N_{max} and $S(K)_{\text{max}}$ are maximal cluster size and structure factor at the end of simulation (after crystallization), $N(0608)$ and $N(0446)$ are the numbers of 0608- and 0446-atoms in the final state, and Z is the coordination number (CN) in the final state. It is seen that at $T < 185$ K all models begin to solidify for $L_C = 20,000$ th to 70,000th step from the moment of cooling and a critical size of cluster N_C slightly increases at lower temperatures (classical nucleation theory predicts that the critical seed size must diminish with an increase of supercooling). The structure factor S_C in these states differs by only a small amount (110 to 350). The values of N_{max} , $S(K)_{\text{max}}$, $N(0608)$, $N(0446)$, and Z show that the final states at $T < 185$ K are predominantly bcc crystals.

We could observe in detail the solidification mechanism by viewing the configurations of 0608-clusters in the simulation process. The 0608-clusters in the model with $N = 998$ at $T = 100$ K are shown in Fig. 4 at steps 10,000, 20,000, and 30,000. We see that these clusters are very loose and do not resemble regular nanocrystals. In this case the acceleration of cluster growth began in the interval of 60,000 to 100,000 time steps. But the cluster penetrates all of the basic cube area already on the 30,000th step and the CN is near three in this state.

It was implied in [4,5] that the seed of crystallization is a compact nanocrystal. In fact, the crystallization seed is a very loose 0608-cluster whose form resembles a comet, an octopus, or medusa and its linear size reaches the basic cube size. This cluster incorporates atoms of another VP type and stimulates their transformation in

Table 2 Results of the simulations of systems with $N = 1968$

T (K)	n_{total}	L_C	N_C	S_C	N_{max}	$S(K)_{\text{max}}$	$N(0608)$	$N(0446)$	Z
313	4000	—	—	—	5	21.56	—	48	1.60
280	102000	—	—	—	10	45.86	—	42	1.33
250	11000	—	—	—	8	23.70	—	55	2.75
200	44000	—	—	—	8	56.66	—	78	1.75
190	51000	—	—	—	11	32.10	9	74	2.73
185	101000	—	—	—	13	44.35	14	76	2.46
185	101000	—	—	—	30	37.60	8	84	3.33
182.5	91000	73000	123	108.1	1537	1394	1412	125	11.62
180	71000	47000	131	191.6	1409	1415	1112	297	10.98
175	41000	23000	172	353.2	1622	1409	1416	206	11.94
150	52000	22000	202	117.5	1672	1526	1581	91	12.28
100	100000	23000	234	108.7	1746	1687	1693	54	13.11
90	101000	28000	243	120.2	1672	912.6	1358	314	12.38

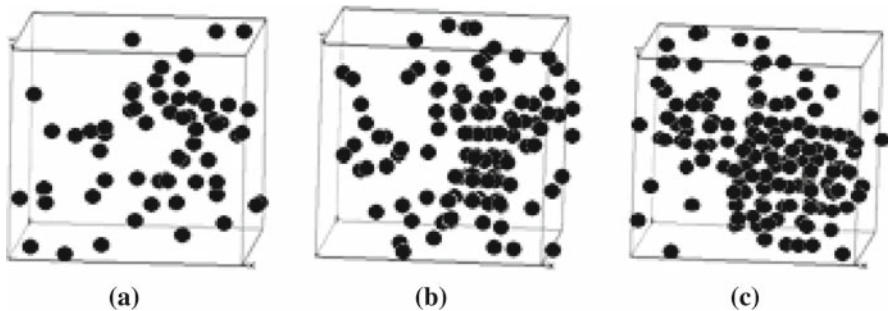


Fig. 4 Disposition of 0608-atoms in a model with $N = 998$ at $T = 100$ K in the solidification process: (a) step 10000, cluster distribution $1^{20}2^35^18^234^1$, mean CN of all 0608-atoms is 2.22, mean CN of maximal cluster is 3.47; (b) step 20000, cluster distribution $1^{10}2^13^17^1121^1$, mean CN of all 0608-atoms is 4.61, mean CN of maximal cluster is 5.36; and (c) step 30000, cluster distribution $1^92^1188^1$, mean CN of all 0608-atoms is 4.96, mean CN of maximal cluster is 5.24

0608-atoms. The ability for this stimulation appears when the size of a cluster reaches some critical value (“critical size” in cluster mechanism of solidification). Namely, this is the mechanism of growth of clusters after they reach the critical size. So this mechanism differs drastically from the adopted one in classical nucleation theory where the seed is a true nanocrystal.

For the case of strongly supercooled Rb, the description of the solidification process is as follows. The atoms in a liquid persistently change their VP types. Atoms having a VP of the 0-6-0-8 type appear in a supercooled metal having some energetic preference before other atoms and behave as a moving force in the rubidium crystallization process. At first, they are distributed chaotically but steadily aggregate together. This process is accompanied by an energy gain. The growth of 0608-clusters is continuing via the accommodation of small particles by bigger ones as in the process of

coagulation of solute from a supersaturated solution [10]. Atoms with different coordination numbers captured in a 0608-cluster may transform themselves into the 0608-type. The growing 0608-clusters have a loose, non-regular form and, already at the first stages, penetrate the entire volume of the liquid (or amorphous phase). The following cluster growth consists of the transformation of foreign atoms (inside and near the cluster) in 0608-atoms. It is important that the growing 0608-clusters are not crystals initially and transform to a crystal structure only after reaching some critical size. We did not observe any qualitative difference between the crystallization of liquid and amorphous models.

4 Why the Models Do Not Solidify above 185 K?

One must explain why there is a very sharp threshold between temperatures at which the system can solidify via a cluster mechanism or cannot. Classical nucleation theory does not work with loose, non-regular clusters that really are the important factors of this process. A solution can be obtained by consideration of the equilibrium (or quasi-equilibrium) between clusters of different sizes in the liquid metal. The reaction between clusters may be expressed as

$$nA_1 = A_n \quad (6)$$

The equilibrium constant of this reaction is

$$K_n = \frac{c(A_n, T)}{C^n(A_1, T)}, \quad (7)$$

where $c(A_1, T)$ and $c(A_n, T)$ are the concentrations of monomers A_1 and clusters A_n . The dependence of K_n on temperature is described by $\ln K_n/dT = \Delta U_n/RT^2$ where ΔU_n is the internal energy difference in the reaction of Eq. 6. Assuming that ΔU_n does not depend on the temperature, we get

$$\ln \frac{K_n(T)}{K_n(T_m)} = \frac{\Delta U_n}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \quad (8)$$

where T_m is the melting temperature. It follows from Eqs. 7 and 8 that

$$\ln c(A_n, T) = \ln c(A_n, T_m) + n \ln \frac{c(A_1, T)}{c(A_1, T_m)} + \frac{\Delta U_n}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \quad (9)$$

If the concentrations $c(A_n, T)$ decrease monotonically with n , the growth of big clusters is not possible and solidification does not take place. However, if the derivative $\ln c(A_n, T)/dn$ appears to be positive at $n > n_c$, then the continuous growth of clusters

will take place at $n > n_c$. The monomer concentration will be constant because 0608-monomers are in equilibrium with all atoms of the liquid. The derivative is equal to

$$\frac{d \ln c(A_n, T)}{dn} = \frac{d \ln c(A_n, T_m)}{dn} + \ln \frac{c(A_1, T)}{c(A_1, T_m)} + \frac{d\Delta U_n}{dn} \frac{1}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \tag{10}$$

The value of $\delta U_n = d\Delta U_n/dn$ is the energy change for the reaction $A_n + A_1 = A_{n+1}$. At large n , it must be close to the heat of crystallization. MD simulation gives the formula for the concentration of 0608-monomers in liquid Rb at different temperatures [9]:

$$\frac{c(A_1, T)}{c(A_1, T_m)} = \exp \left[\frac{\Delta L}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \tag{11}$$

with $\Delta L = 698\text{J} \cdot \text{mol}^{-1}$. Let's denote $\gamma_n(T_m) = d\ln c(A_n, T_m)/dn$. Then, having in mind Eq. 5, we obtain

$$\frac{d \ln c(A_n, T)}{dn} = \gamma_n(T_m) + \frac{\Delta L - \delta U_n}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \tag{12}$$

For the case of Rb models, $\gamma_n(T_m)$ is close to -1.5 for small clusters ($n < 5$) and increases to -0.75 for $5 < n < 8$ [9] (the clusters of larger size did not exist in models at T_m). Very likely $\gamma_n(T_m)$ increases monotonically with n approaching an asymptotic value γ_{inf} . The value of δU_n also does not depend on n at large n . Then one can determine the critical value $\gamma_c(T)$ at a temperature T by the condition

$$\gamma_c(T) = \frac{\Delta L - \delta U_n}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \tag{13}$$

Then $d\ln c(A_n, T)/dn = \gamma_n(T_m) - \gamma_c(T)$. This derivative will be positive if $\gamma_n(T_m) > \gamma_c(T)$. Evidently, if $\gamma_c(T) > \gamma_{inf}$, then $\gamma_n(T_m) < \gamma_{inf} < \gamma_c(T)$ for all n . Then $d\ln c(A_n, T)/dn < 0$ for all n , and clusters cannot grow. Let us determine the threshold temperature T_{max} by using $\gamma_c(T_{max}) = \gamma_{inf}$. Therefore, at $T > T_{max}$, solidification via a cluster mechanism is not possible.

Taking the values $\gamma_n(T_m) = -0.75$, $\Delta L = 698$, and $\delta U_n \cong -1730\text{J} \cdot \text{mol}^{-1}$, we define from Eq. 12,

$$\frac{d \ln c(A_n, T)}{dn} = -0.75 + 292 \left(\frac{1}{T} - \frac{1}{T_m} \right) \tag{14}$$

Here $T_m = 313\text{K}$ and the derivative will be positive for $T < 173.5\text{K}$. Hence, this calculation gives the threshold solidification temperature of Rb models very near to the established result in MD simulations. Taking $\gamma_n(T_m) = -0.646$, we obtain the correct crystallization threshold $T_{max} \cong 185\text{K}$.

The condition $\text{d} \ln c(A_n, T) / \text{d}n = \gamma_n(T_m) - \gamma_c(T) = 0$ determines the critical cluster size n_c at temperature T . The smaller is T , the smaller is n_c because $\gamma_n(T_m)$ increases with n . The critical seed size in classical theory must also behave in a similar manner. We could not observe this effect because of a rather rough estimate of the moment when fast solidification begins.

At temperatures $T > T_{\text{max}}$, solidification using the rubidium model may occur, in principle (at the condition $\text{d} \ln c(A_n, T) / \text{d}n < 0$), but it requires the creation of rather large 0608-clusters via fluctuations, as in classical nucleation theory. The observation of such events in the MD run is very time consuming because of their very small possibility.

Acknowledgment This work was supported by the Ministry of Education of Russian Federation.

References

1. A. Rahman, M.J. Mandell, J.P. McTague, *J. Chem. Phys.* **64**, 1564 (1976)
2. M.J. Mandell, J.P. McTague, A. Rahman, *J. Chem. Phys.* **64**, 3699 (1976)
3. C.S. Hsu, A. Rahman, *J. Chem. Phys.* **70**, 5234 (1979)
4. C.S. Hsu, A. Rahman, *J. Chem. Phys.* **71**, 4974 (1979)
5. M.J. Mandell, J.P. McTague, A. Rahman, *J. Chem. Phys.* **66**, 3070 (1977)
6. D.L. Price, *Phys. Rev. A* **4**, 358 (1971)
7. D.L. Price, K.S. Singwi, M.P. Tosi, *Phys. Rev. B* **2**, 2983 (1970)
8. Y. Waseda, *The Structure of Non-crystalline Materials. Liquids and Amorphous Solids* (McGraw-Hill, New York, 1980)
9. D.K. Belashchenko, *Russ. J. Phys. Chem.* **80**, 1968 (2006)
10. D.K. Belashchenko, E.S. Lobanov, G.F. Syrykh, *Russ. J. Phys. Chem.* **79**(1), S135 (2005), Suppl. 1