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DEFECTS AND LIQUID STRUCTURE BY HIGH TEMPERATURES

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НОВОСИБИРСК

Defects and Liquid Structure by High Temperatures[1)]

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ABSTRACT

A system of atoms is considered close to the high temperature boundary of locally ordered liquid. The size of a defect and the role of extended defects in the local structure breakdown is discussed.

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In the crystal state, defects of packing are well known. A defect is defined by mending the defect configuration starting from the appropriate ideal lattice. The lattice realize the stable configuration of atoms witch is an absolute or relative minimum of the interaction energy $U\{r\}$. The configuration corresponding to a defect is also a relative minimum of the energy $U\{r\}$, but the energetic barrier that divide this minimum from a neighboring one is too low to hold the configuration local by high temperatures.

As an example let us consider a vacancy in a two dimensional system of classical particles (see Fig.1) interacting via the Lennard-Jones potential

$$U\{r\}= \sum_{i\,j} U(r_i - r_j), \tag{1}$$

$$U\{r\}=A\,[(a/r)^{12} - 2\,(a/r)]^6. \tag{2}$$

For pressure $P=0$ the inter atomic distance is equal to a. The change ΔU of the energy due to a displacement x along AO of the atom A from a site in the first coordination shell of the vacant site O is schematically drawn in Fig.2. Positions of atoms at infinity are fixed. The concrete form of $DU(x)$ and the barrier energy ε depend upon the trajectories of surrounding particles. One easy found $\varepsilon=7A$ by moving only one particle A.For few particles allowed to move one easy gets $\varepsilon=4A$.

The energy of a small displacements x of one regular

atom in the lattice one gets from (1), (2) has the form

$$\Delta U_r(x) = 142 \cdot A \cdot (x/a)^2 \ . \qquad (3)$$

One see from (3) that ε is comparable with the energy ΔU_r of a displacement x=0.15a. It is known from experiment (the Lindemann criterion) that the mean square relative displacement $\xi^2=(x/a)^2$ at the melting temperature T_m is close to ξ_m^2=0.01 for 3D systems and to a higher value ξ_m^2=0.02 for D=2.

For the general case of an atomic system with nonzero pressure and thermal motions the barrier energy ε depends on the state of the system as well as the mean thermal displacement of an atom. The geometrical nature of Lindemann criterion leads to the relation

$$\varepsilon = p \cdot T_m \ . \qquad (4)$$

In (4), p is a dimensionless characteristics of the system and of the defect. One expects p to be of the order of unit, as shown above. A system of few vacancies situated along a line is a configuration associated with a dislocation dipole. For that configuration parameter p is relatively small. For temperatures $T \ll \varepsilon$ the most probable position of atom A is located near points of minimal energy $\Delta U(x)$, the vacancy can only jump with frequency proportional to $\exp(-\varepsilon/T)$. For higher temperatures $T \geq \varepsilon$ atom A is no more localized in a small vicinity of a site, as well as other atoms surrounding the vacant site. The vacancy become extended, it occupies a region of a size $l(T)$ that increases with the temperature. The estimation of the barrier energy ε in two and three dimensions shows that the effect is rather to be expected above the melting temperature, in the liquid state. In the solid state extended defects where discussed by Seeger and Shik [1] and by Pokorny and Grimwall [2] in connection with experimental data. For solids the defect may involve only nearest coordination shells.

In the melt close to the melting line the local crystalline order is expected to exist. It means that the most part

of the system is occupied by a multi connected cluster of "good material", every small volume of the last can be treated as a part of an ideal lattice-for more details see Refs [3, 4]. The equivalence of the local structure of the liquid (melt) and those of a crystal in a volume including few coordination shells allows one to define corresponding defects of packing in the melt.

The level of thermal fluctuations ξ_m=0.01 at the melting line of a three dimensional system does not destroy the local order. For fluctuating small clusters of dense packed structures ensembles are studied (see Ref [5]) of configurations one gets for each cluster by independent particle displacements with given ξ. The potential energy $U\{r\}$ of a many particle system with interaction like (1)-(2) may have a number of minima corresponding to different local structures. In harmonic approximation ξ^2=const·T. For high enough ξ (ξ>0.02 for D=3) ensembles of configurations essentially overlap. The mean energy of thermal motion pro degree of freedom (the temperature) for that level of fluctuations reaches the energy ε_{S1} of a barrier that divide different structures. One is unable to speak about some definite structure of a cluster for temperatures $T > \varepsilon_{S1}$.

Let me suggest that for every system of atoms there is a level of fluctuations ξ_{S1} and a corresponding temperature $T_{S1}(P)$ where the local structure is lost. A vicinity of the line $T=T_{S1}$ is the boundary of condensed (locally structured) state of the matter in the thermodynamic (P-T) plane.

Close to $T=T_{S1}$ the extended defect is a cluster of size $l(T)$. The number of atoms in this cluster is $N=V/v_0$, $V=l(T)^3$, v_0 is the volume per particle. The free volume of the defect $v_d \sim v_0$ is distributed over N particles so that the mean relative displacement in the cluster increases from the bulk value $\xi=\xi(T)$ to the value $\xi=\xi_{S1}$ for witch the local structure is lost. Of course our restrictions are rather of geometrical origin as well as the Lindemann criterion. Rece-

ntly the stability of the Lindemann criterion were proved under nonthermal displacements of atoms (see Voronel and oth. [6]).

From the condition that the free volume of the defect v_d is distributed over N particles adding to the volume $v_0\xi(T)^3$ of bulk particle thermal motion the complement to the critical value $v_0\xi_{S1}^3$ one obtains

$$\frac{v_d}{N} = \frac{v_d\, v_0}{l^3} = v_0\xi_{S1}^3 - v\xi(T), \quad l(T)=\left[\frac{v_d}{\xi_{S1}^3 - \xi(T)^3}\right]^{1/3},$$

$$l(T) \sim (T_{S1}-T)^{-1/3}. \qquad (5)$$

For a two dimensional system instead of (5) one gets

$$l(T)=\left[\frac{s_d}{\xi_{S1}^2 - \xi(T)^2}\right]^{1/2} \sim (T_{SL} - T)^{-1/2}. \qquad (6)$$

In (6) s_d is the free surface due to defect.

Let me describe a typical configuration of the liquid. At the melting line it is assumed to be locally crystalline. With increasing temperatures the concentration and the size of defects increases. The percolation of defects close to $T=T_{S1}$ leads to the rather smooth transition to structureless (dense gas) state. In some sense the line $T=T_{S1}(P)$ plays the part of the continuation of the line of liquid-gas transition where the local structure is lost due to the decrease of density. A typical configuration described above resembles a two phase system - a part of the system is in structureless (dense gas) state ($\xi=\xi_{S1}$), the rest is locally structured ($\xi=\xi(T)<\xi_{S1}$). For some types of defects, especially for dislocations, the effect of extension may occur due to merging of the defect and vacancies.

Defect extension can be studied in computer simulations, especially in two dimensional systems. The smoothed transition from liquid to gas and the temperature T_{S1} one hopes to see by studying heat capacity, compressibility and kinetic coefficients as functions of the temperature.

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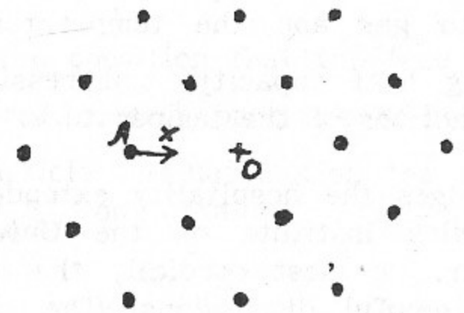

Fig. 1.

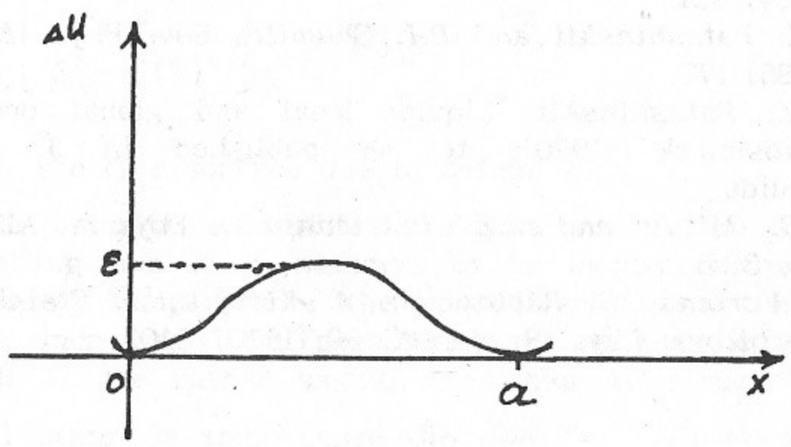

Fig. 2.

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