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Energy of vacancy formation in the continuum matter model

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The quantum energy spectrum of the oscillating spherical void in solids is calculated within the continuum matter model. It is suggested that the ground state of the oscillating void corresponds to the vacancy in real crystals. The dependence of the vacancy formation energy on the shear modulus, density, pressure and surface tension is determined. The obtained results are used to estimate properties of vacancies in solid Ar. A possibility to use the obtained results to estimate the properties of vacancies in liquid melts is discussed.

PACS: *61.72.jd* Vacancies;
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Many properties of crystals near melting are determined by presence of vacancies [1]. First of all, this concerns the processes of the self-diffusion, the diffusion of impurities, the ion mobility, etc. Vacancies also influence the specific heat and volume thermal expansion of crystals. A number of attempts to construct the vacancy model of melting are known [2–4]. Molecular dynamics studies of melting reveal that an ideal crystal melts at temperatures notably higher than a crystal that contains vacancies [5,6]. The energy of the vacancy formation E_v is the most important characteristic of the vacancies. Experimental values of E_v near the triple point are known for many substances, including series of metals [7] and rare gas solids [8]. Attempts of theoretical determination of E_v are very cumbersome, which makes difficult their extrapolation to the limit of extremely high pressures and temperatures. In the present paper a simple model is suggested, which gives a possibility to obtain an analytical dependence of E_v on the crystal density, external pressure and shear modulus.

Within the model of an isotropic matter, a spherical void formation results in the local change of the crystal potential energy due to the deformation and work against the surface and volume forces:

$$\Delta U = U_d + U_s + U_v = U_d + 4\pi\sigma R^2 + (4\pi/3)pR^3, \quad (1)$$

where σ is the surface tension, p is the external pressure, and R is the void radius. In equilibrium, the energy of deformation is given by [9]

$$U_d = \int \left[\frac{\lambda}{2} u_{ii}^2 + \mu u_{ik}^2 \right] d^3 r \,, \quad (2)$$

where λ and μ are the Lamé coefficients, and u_{ik} is the strain tensor, which (for small deformations) reads

$$u_{ik} \cong \frac{1}{2}\left(\frac{du_i}{dx_k} + \frac{du_k}{dx_i} \right). \quad (3)$$

In the case of a spherical void, the vector of deformation $\mathbf{u}$ depends only on spherical coordinate $\mathbf{r}$

$$\mathbf{u} = u(r)\mathbf{n}_r \quad (4)$$

and nonzero components of the deformation tensor are

$$u_{rr} = \frac{du}{dr}, \quad u_{\theta\theta} = u_{\varphi\varphi} = \frac{u}{r}. \quad (5)$$

The quadratic forms included in Eq. (2) are given by

$$u_{ii}^2 = (u_{rr} + u_{\theta\theta} + u_{\varphi\varphi})^2 = \left(\frac{du}{dr} + 2\frac{u}{r} \right)^2,$$
$$u_{ik}^2 = u_{rr}^2 + u_{\theta\theta}^2 + u_{\varphi\varphi}^2 = \left(\frac{du}{dr} \right)^2 + 2\left(\frac{u}{r} \right)^2. \quad (6)$$

The equation of equilibrium of an isotropic incompressible solid is [9]

$$(\lambda+\mu)\,\mathrm{grad}\,\mathrm{div}\,\mathbf{u}+\mu\Delta\mathbf{u}=0. \tag{7}$$

In the spherically symmetric case $\mathrm{rot}\,\mathbf{u}=0$ and Eq. (7) gets a form

$$\mathrm{grad}\,\mathrm{div}\,\mathbf{u}=0. \tag{8}$$

From this it follows that u satisfies equation

$$\mathrm{div}\,\mathbf{u}=\mathrm{const}, \tag{9}$$

solution of which finite outside the void is

$$u=a/r^2. \tag{10}$$

The constant a is determined from the boundary condition

$$u(R)=a/R^2=R,\quad a=R^3. \tag{11}$$

Thus

$$u(r)=\frac{R^3}{r^2},\quad u_{ii}^2=0,\quad u_{ik}^2=6\frac{R^6}{r^6}. \tag{12}$$

Now Eq. (2) gets a form

$$U_d=8\pi\mu R^3. \tag{13}$$

Taking into account the kinetic energy of the radial motion, the change of the full energy of the deformed isotropic matter is given by

$$\Delta E=\int\frac{\rho\dot{\mathbf{u}}^2}{2}d^3r+4\pi\sigma R^2+\frac{4\pi}{3}pR^3+8\pi\mu R^3=$$
$$=6\pi\rho R^3\dot{R}^2+4\pi\sigma R^2+\left(8\pi\mu+\frac{4\pi}{3}p\right)R^3, \tag{14}$$

where ρ is the matter density and $\dot{u}=3R^2\dot{R}/r^2$. In the case of $\Delta E\neq 0$ this equation describes an oscillatory motion of the void wall under the action of the elastic forces, surface tension and pressure. The energy of any oscillation is quantized. The dispersion law of these oscillations can be determined from the Bohr–Sommerfeld quantization conditions

$$\oint P_R dR=2\pi\hbar\left(n+\frac{3}{4}\right),\quad n=0,1,..., \tag{15}$$

where $P_R=4\pi\rho R^3\dot{R}$ is the generalized momentum of the surrounding matter. Substitution of $\dot{R}$ from Eq. (14) into Eq. (15) gives an integral equation for determination of the void creation energy ΔE_n

$$\int_0^{R_n}R^{3/2}\left[\Delta E_n-4\pi\sigma R^2-\frac{4\pi}{3}(6\mu+p)R^3\right]^{1/2}dR=$$
$$=\left(\frac{3\pi}{8\rho}\right)^{1/2}\hbar\left(n+\frac{3}{4}\right), \tag{16}$$

where the maximum size of the void R_n is determined by

$$\Delta E_n-4\pi\sigma R_n^2-\frac{4\pi}{3}(6\mu+p)R_n^3=0. \tag{17}$$

In two limiting cases, solution of Eqs. (16) and (17) can be obtained analytically. When $(6\mu+p)R_n/3\sigma\gg 1$ the surface force can be neglected and we get

$$\Delta E_n\cong\frac{[8\pi\mu+(4\pi/3)p]^{5/8}}{I^{3/4}}\left(\frac{3\pi}{8\rho}\right)^{3/8}\hbar^{3/4}\left(n+\frac{3}{4}\right)^{3/4},$$
$$R_n^3\cong\frac{\Delta E_n}{8\pi\mu+(4\pi/3)p}, \tag{18}$$

where

$$I=\int_0^1 x^{3/2}(1-x^3)^{1/2}dx\cong 0.28\,.$$

In the opposite limit $(6\mu+p)R_n/3\sigma\ll 1$ the energy spectrum of the void is determined by

$$\Delta E_n\cong 2^{12/7}3^{2/7}\pi\frac{\sigma^{5/7}}{\rho^{2/7}}\hbar^{4/7}\left(n+\frac{3}{4}\right)^{4/7},$$
$$R_n^2\cong\frac{\Delta E_n}{4\pi\sigma}. \tag{19}$$

A spectrum similar to Eq. (19) was obtained by Lifshitz and Kagan [10] for the energy of quantum nuclei and by Khrapak [11,12] for the energy spectrum of microscopic bubbles (bublons) in ideal incompressible liquids.

From Eqs. (16) and (17) it follows that the creation energy and size of the voids are quantized and can not be arbitrary small. Ground state with minimal values of the E_n and R_n are realized for $n=0$. Owing to their quantum nature, the zero-oscillations of voids cannot decay, for example, as result of the acoustic radiation. This gives reason to think that within the continuum matter model, the ground state of voids corresponds to the vacancies in real crystals.

Below we estimate some properties of vacancies in solid Ar using the proposed model. At $T=0$ the density of solid Ar is $\rho_s=1.77$ g/cm^3 and the shear modulus is $\mu=14.6$ kbar [13]. Assuming that at $T=0$ a contribution of the surface force can be neglected, then for $p=0$ the vacancy ground state energy and radius are given by

$$\Delta E_0=\frac{3^{9/8}\pi}{2^{3/4}I^{3/4}}\frac{\mu^{5/8}\hbar^{3/4}}{\rho_s^{3/8}}\cong 1290\ \mathrm{K}\,,$$
$$R_0=\left(\frac{3^3\hbar^2}{2^{10}I^2\mu\rho_s}\right)^{1/8}\cong 0.8\cdot 10^{-8}\ \mathrm{cm}\,. \tag{20}$$

This value of ΔE_0 is in qualitative agreement with theoretical and experimental estimations of the monovacancy formation energy $E_v\cong 905$ K (see, for example, [1]). Equation (20) is valid when $2\mu R_0/\sigma_s\gg 1$. To check the validity of this inequality one has to know the surface ten-

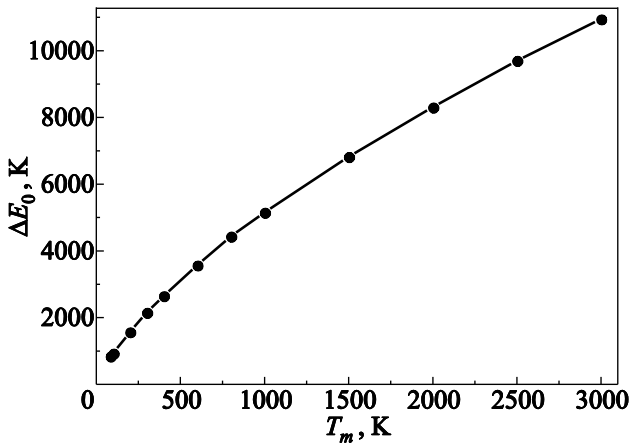

Fig. 1. The energy of the vacancy creation in solid Ar as a function of the melting temperature.

sion σ_s of the solid Ar. It can be estimated by means of the parachore formula [14] according to which $\sigma \sim \rho^4$. Using well known surface tension of liquid Ar at the triple point $\sigma_l = 13.4$ dyn/cm and density $\rho_l = 1.42$ g/cm^3 we get

$$\sigma_s \cong (\rho_s / \rho_l)^4 \sigma_l \cong 32.4 \text{ dyn/cm}. \quad (21)$$

This gives $2\mu R_0 / \sigma_s \cong 11$ and thus the neglect of the surface energy is justified.

At the Ar triple point $T = T_t = 83.8$ K, $\rho_s = 1.62$ g/cm^3, $\mu \cong 6.00$ kbar [13], $\sigma_s \cong 22.7$ dyn/cm. According to Eqs. (16) and (17) $\Delta E_0 \cong 880$ K (contribution to ΔE_0 from the surface energy amounts to $\sim 15\%$). The shear modulus $\mu = \rho_s c_t^2$ (c_t is the transverse sound velocity) increases with the melting temperature T_m and density ρ_m. In Ar c_t was measured along its solidus in of relatively wide temperature region, from T_t to 205.6 K [15,16]. Corresponding values of μ were reported by Burakovsky *et al.* [13] together with an analytical formula for $\mu(T_m)$, which permits an extrapolation to extremely high temperatures $T_m \sim 3000$ K. In Fig. 1 the dependence of ΔE_0 on T_m, following from Eqs. (16) and (17), with $\mu(T_m)$ from [13] and ρ_m, p_m from [17] is shown. One can see that with a good accuracy $\Delta E_0 / T_t \cong 10.5$ which is in reasonable agreement with the approximate relation $E_v / T_t \cong 9.4$ obtained by Bhatia and March [18] for monovacancies in solid Ar. The ratio $\Delta E_0 / T_m$ decreases with the melting temperature. Direct comparison with experiments, where the constancy of the ratio E_v / T_m is peculiar to classical rare gas crystals, a number of metals [19] and even for quantum crystals [20,21] is problematic for (at least) two reasons: First, the enthalpy of the vacancy formation is usually measured instead of E_v and the contribution of the nonconfigurational entropy (which has to grow with T_m) is difficult to detach. Second, the shear modulus increases with the frequency of an external force (see, for example, [22]). The frequency of the void wall oscillations $\omega_0 = \Delta E_0 / \hbar \sim 10^{14}$ Hz at the triple point, and it increases with T_m. This effect was not taken into account in calculating $\mu(T_m)$ [13]. Unfortunately, the dependence $\mu(\omega)$ at very high frequencies is unknown.

The local undamped oscillations of matter surrounding the vacancy are not artifacts of the continuum matter model. In real crystals the vacancy formation has to result in reconstruction of the oscillation spectrum and in appearing of a new quantized mode. This effect may be important for development the vacancy theory of melting. The existing theories interpret the melting as the first order phase transition in the vacancy subsystem: At the melting line the equilibrium between crystalline system with relatively low concentration of vacancies, $c = n_v / n_a \sim 10^{-3}$, and quasi-crystalline system (liquid melt) with relatively high $c \sim 10^{-1}$ takes place. However, properties of vacancies in the melt are unknown. We suppose that owing to the high frequency of the vacancy wall oscillations, the shear modulus does not change significantly upon melting and vacancies in a liquid preserve main properties of vacancies in a solid.

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