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CRYSTALLIZATION NUCLEI IN LIQUID IN A SOUND FIELD

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Abstract—This paper is concerned with the theoretical investigation of crystallization nuclei undergoing radially symmetric oscillations in supercooled liquids and supersaturated solutions exposed to a sound field. Periodic crystallization and melting processes occurring in the course of these oscillations are shown to result in higher amplitudes. This enhances the nonlinear interaction of sound with an oscillating nucleus which results in the phenomenon of rectified heat transfer, i.e. a slow (as against the sound cycle) process of heat pumping into a nucleus. Another peculiar feature of the nonlinear interaction between the sound and the nuclei is evidenced by the fact that the location of nucleation sites in a standing sound wave depends on the dimensions of nuclei and the sound frequency—a situation differing substantially from the case of solid particles without phase transformations. It is shown that phase transformations may markedly increase the absorption and dispersion of the speed of sound propagating in crystallizing liquids as compared with liquids containing solid particles without phase transformations. It is also shown that an increase in the amplitude of the oscillations of crystallization nuclei enhances their interaction with each other.

NOMENCLATURE

a,	crystal lattice constant;
c,	solution concentration;
c_1,	sound speed in a liquid, $(\gamma/\rho\beta)^{1/2}$;
c_2,	thermal wave speed, $(-i\omega D)^{1/2}$;
C_p,	specific heat at constant pressure;
C_σ,	specific heat along the phase equilibrium curve;
d_σ,	crystallization curve slope, $(\partial T/\partial P)_\sigma$;
$\Delta_\sigma^{(c)}$,	slope of the curve of equilibrium solubility;
$\Delta_\sigma^{(2)}$,	quantity characterizing nonlinearity of the crystallization curve, $(\partial^2 T/\partial P^2)_\sigma$;
Δ_S,	slope of adiabatic curve, $(\partial T/\partial P)_S$;
D,	thermal diffusivity;
D_c,	diffusion coefficient;
f_1, f_2,	scattering amplitudes;
I,	mass flux through unit surface of nucleus;
k_B,	Boltzmann's constant;
k_1,	sound wavenumber, ω/c_1;
k_2,	wavenumber of thermal wave, $\omega/c_2 = (i\omega/D)^{1/2}$;
k_c,	wavenumber of diffusional wave, $(i\omega/D_c)^{1/2}$;
K,	intrinsic nuclear compressibility;
$\lvert\mathcal{K}\rvert$,	module of complex compressibility $\mathcal{K}$;
L,	heat of melting;
L_c,	heat of dissolution;
m_1, m_2,	mass of molecules of a solvent and solute, respectively;
n_1, n_2,	number of particles of a solvent and solute, respectively;
N_A,	Avogadro's number;
n,	number of nuclei of the same radius per unit volume of liquid;
P,	pressure;
P_0,	pressure in unperturbed liquid;
P_m,	pressure in a sound wave;
$\tilde{P}r$,	modified Prandtl number, $[(4\eta/3) + \zeta]/\rho D$;
P_k,	sound pressure at which $d\bar{R}/dt = 0$;
Q,	factor accounting for the relationship between external pressure and that inside a nucleus, dP/dP';
r,	space-dependent (radial) variable;
R,	nucleus radius;
S,	entropy;
T,	temperature;
T_0,	temperature in unperturbed liquid;
T_σ,	equilibrium temperature of pure liquid crystallization;
$T_\sigma^{(c)}$,	equilibrium temperature of crystallization of a liquid with impurity;
ΔT_0,	supercooling of pure liquid, $T_\sigma(P_0) - T_0$;
t,	time;
u,	radial displacement;
U,	velocity at the interface;
$\mathbf{v}$, v,	velocity and radial velocity component, respectively;
ΔV_c,	volume change on dissolution.

Greek symbols

α,	thermal coefficient of volumetric expansion;
β,	coefficient of isothermal compressibility;

γ,	specific heat ratio;
δ,	symbol which indicates that a small variation about a mean value of the quantity is considered (δp, δR etc.);
ε,	volumetric concentration of solid phase, $4\pi n R^3/3$;
ζ,	coefficient of volumetric viscosity;
η,	coefficient of shear viscosity;
θ,	phase of complex compressibility $\mathscr{K}$;
κ,	thermal conductivity;
λ_T,	thermal wave length, $(2D/\omega)^{1/2}$;
Λ, $\Lambda^{(c)}$,	kinetic coefficients determining non-equilibrium condition of crystallization of pure liquid and liquid with an impurity, respectively;
$\Lambda_\sigma^{(c)}$,	kinetic coefficient characterizing decomposition of supersaturated solution;
μ',	Lamé coefficient;
ρ,	density;
σ,	surface tension coefficient;
ω,	circular frequency of sound.

Subscripts

σ,	indicates that the values taken along the phase equilibrium curve;
R,	the value of the quantity taken at $r = R$;
S,	the value of the quantity taken at S = const.

Superscripts

$\langle\ \rangle$ or $\bar{\ }$,	means averaging over the sound cycle (e.g. $\langle R\rangle \equiv \bar{R}$);
$'$,	quantity refers to a nucleus;
$\dot{}$,	denotes a time derivative ($\dot{R} \equiv \mathrm{d}R/\mathrm{d}t$ etc.).

1. INTRODUCTION

INTEREST in the study of the dynamics of solid phase nuclei in a sound field has been engendered by the problem of the effect of sound on the structure of substances crystallizing out of liquid phase [1–5] and by the studies of sound propagation in a crystallizing liquid [5, 6]. Numerous experiments show that the exposure to sound of the process of crystallization promotes appreciable decomposition of the substance forming from a melt and the attainment of its uniform structure. Possible mechanisms for this effect have been suggested [1–5]. However, as yet no theory of this phenomenon has been advanced and the mechanism of sound interaction with a separate nucleus of a solid phase is as yet unknown [3]. There is also a distinct lack of theoretical work on the mechanism of sound speed absorption and dispersion in a crystallizing liquid containing solid phase nuclei [5, 6]. The problems mentioned above are the concern of this contribution.

A characteristic feature of the behaviour of solid phase nuclei in a sound-exposed liquid, distinguishing them from ordinary solid particles, is the existence on their surface of periodically alternating processes of melting and crystallization. This causes an additional change in the nuclear volume as a consequence of mass transfer during phase transformations. As will be shown below, this eventually leads to an additional change in compressibility and to an increase of the amplitude of radially symmetric oscillations of nuclei, as well as of the sound energy dissipation near it. As a result, abnormal absorption and dispersion of sound speed might be expected. Higher sound absorption, causing the acceleration of acoustic flows, promotes the attainment of a uniform structure of substances crystallizing out of a liquid state in a sound field [5]. The growth of radially symmetric oscillations of nuclei due to mass transfer may also lead to an increase in the forces of interaction between the nuclei, e.g. the Bjerkness forces [7, 8]. This, in particular, may be a very important factor in the formation of the fine stucture of substances crystallizing from melts under the effect of sound.

Physically, sound interaction with crystallizing nuclei can be explained as follows. For simplicity, let us assume that the nucleus is spherical with radius R. Suppose an harmonic sound wave $P_m \exp(-i\omega t + ik_1 r)$ is incident on it. The temperature of the nuclear surface T_R at each time instant during a quasi-equilibrium phase transition is shown in Fig. 1 by points on the phase equilibrium curve 1. The temperature of the liquid near the nucleus surface follows the sound pressure along the adiabatic curve 2. Periodically the liquid adjacent to the nucleus surface is locally supercooled or superheated by the amount $\Delta T_0 = T_\sigma - T_S$, which leads to the alternating processes of crystallization and melting. The resulting mass transfer causes an additional change in the nuclear volume. The liquid starts to crystallize on a rise of pressure—an additional change in the volume is positive, i.e. it competes with a decrease in the nuclear volume as a result of mechanical compression. One can readily conceive a situation when a change in the nuclear volume due to mass transfer becomes larger than that produced by mechanical compression only. Then an effective negative compression of the nucleus

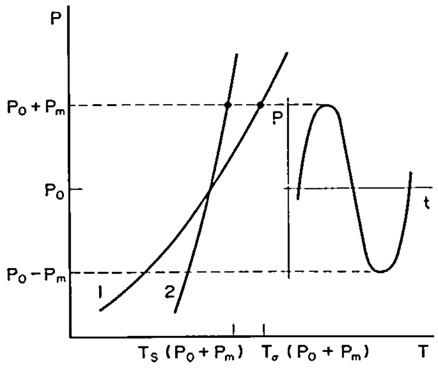

FIG. 1. Schematic representation of the phase state of a crystallization nucleus in a sound field.

will appear to have occurred. Since mass transfer occurs on the surface of the nucleus, while compression takes place throughout its volume, the case described may arise only at sufficiently small radii when the surface effect is appreciable. Under these conditions a substantial increase in the amplitude of nuclear oscillations in a sound field is to be expected. It is evident that the heat transfer processes near the nuclear surface should also be considered, since the crystallization and melting phenomena are very sensitive to the conditions of phase transition heat removal from the interface. Thus, the oscillations of crystallization nuclei in a sound field may be considered by simultaneously solving the hydrodynamic equations and the equations that describe the kinetics of phase transitions. The system of equations obtained is solved below using perturbation theory.

2. BASIC ASSUMPTIONS AND INITIAL SYSTEM OF EQUATIONS

If the size requirement for the nucleus compared with the wavelength in a liquid is met, $k_1 R \ll 1$, then the temperature and pressure distribution far from the nucleus can be written as

$$\begin{aligned} P(x,t) &= P_0 + P_m e^{-i\omega t}, \\ T(x,t) &= T_0 + d_S P_m e^{-i\omega t}. \end{aligned} \tag{1}$$

These boundary conditions represent perturbations, in response to which the nucleus undergoes radially symmetric oscillations about some radius $\bar{R}$ which, in turn, can vary with time as

$$R(t) = \overline{R(t)} + \delta R(t),\ \overline{R(t)} = \langle R(t)\rangle = \frac{\omega}{2\pi}\int_t^{t+2\pi/\omega} R(t)\mathrm{d}t. \tag{2}$$

Henceforth, only forced oscillations of frequency ω will be considered, then $\delta R(t) = R_m \exp(-i\omega t)$. In doing so, the following relationships will be assumed

$$|\delta R| \ll \bar{R}, \quad |\dot{\bar{R}}| \ll |\delta\dot{R}| = \omega |R_m|. \tag{3}$$

The quantity δR is assumed to be linear in amplitude P_m and the quantity $\dot{\bar{R}}$ to be quadratic in P_m. We may assume that similar relationships hold for other physical quantities: pressure, temperature and density. These assumptions allow one to separate the equations for linear oscillating values of the quantities from those for averaged values.

A spherical system of coordinates locating the origin at the nuclear center is used. For mean values of quantities in the quadratic approximation of the perturbation theory we may write the following hydrodynamic equations:

$$\rho\langle\nabla \mathbf{v}\rangle + \nabla\langle\delta\rho\delta\mathbf{v}\rangle = 0, \tag{4}$$

$$\nabla\bar{P} = \left(\frac{4}{3}\eta + \zeta\right)\nabla\langle\nabla\mathbf{v}\rangle - \frac{\rho}{2}\nabla\langle\delta v^2\rangle + \nabla\langle\delta P(\delta\rho/\rho)\rangle, \tag{5}$$

$$\nabla\langle\kappa\nabla T\rangle = \nabla\mathbf{q},\ \mathbf{q} = \rho C_P\langle\delta\mathbf{v}(\delta T - d_S\delta P)\rangle + \left\langle\delta\mathbf{v}\left[\delta P - \left(\frac{4}{3}\eta + \zeta\right)\nabla\delta\mathbf{v}\right]\right\rangle. \tag{6}$$

Linear perturbations in the liquid are described by the linearized hydrodynamic equations:

$$\delta\dot{\rho} + \rho\nabla\delta\mathbf{v} = 0, \tag{7}$$

$$\rho\delta\dot{\mathbf{v}} + \nabla\delta P = -\eta\{\nabla[\nabla\delta\mathbf{v}]\} + \left(\frac{4}{3}\eta + \zeta\right)\nabla(\nabla\,\delta\mathbf{v}), \tag{8}$$

$$\delta\dot{T} - d_S\delta\dot{P} = D\nabla^2\delta T, \quad D = \kappa/\rho C_p. \tag{9}$$

The spherical solid nucleus is assumed to be isotropic. Taking into account the condition $k_1 R \ll 1$, the pressure inside the nucleus may be considered the same everywhere,

$$P'(r,t) = P'(R,t) = P'_R(t), \quad r \leqslant R. \tag{10}$$

The remaining equations for the isotropic nucleus coincide with equations (4), (6), (7) and (9) provided that $\eta = \zeta = 0$.

For the above equations to be solved, it is necessary to formulate the boundary conditions. The conditions far from the nucleus are expressed by equations (1). At the center of the nucleus the absence of any singularity is assumed: $T'(0,t) < \infty$, $\nabla T'|_{r=0} = 0$. In a general case, the joining of solutions at the interface of the nucleus requires five boundary conditions [the pressure and temperature in the nucleus and liquid as well as the radius $R(t)$ are unknown quantities].

The first three boundary conditions can be obtained from the general mass, momentum and energy conservation laws [7, 9, 10]. The mass and momentum conservation equations yield

$$\rho(\dot{R} - U) = \rho'(\dot{R} - U') = J, \tag{11}$$

$$P'_R = P_R + \frac{2\sigma}{R} + J^2\frac{\Delta\rho}{\rho'\rho} + \left[4\eta\frac{U}{R} - \left(\frac{4}{3}\eta + \zeta\right)(\nabla v)_R\right] - 4\mu'\left[\frac{u'_R}{R} - \frac{(\nabla u')}{3}R\right]. \tag{12}$$

The energy conservation equation can be written in the linear and quadratic approximations as

$$L\delta J = \kappa'(\nabla\delta T')_R - \kappa(\nabla\delta T)_R, \tag{13}$$

$$\bar{J}L - \left\langle\delta J\left\{(C'_P - C_P)\delta T_R - \frac{\Delta\rho}{\rho'\rho}\delta P_R - \frac{1}{\rho'}\frac{2\sigma}{R}\frac{\delta R}{R} - \frac{\Delta\rho}{\rho'\rho} \times \left(4\eta\frac{\delta U}{R}\right) - \left(\frac{4}{3}\eta + \zeta\right)(\nabla\,\delta v)_R\right\}\right\rangle = \langle\kappa'(\nabla T')_R\rangle - \langle\kappa(\nabla T)_R\rangle. \tag{14}$$

The remaining boundary conditions follow from the relations established experimentally. The fourth boundary condition accounts for the continuity of temperature on the nucleus surface [12, 13]

$$T'(R, t) = T(R, t) = T_R. \tag{15}$$

The fifth boundary condition is the equation of crystallization kinetics [12, 13]

$$J = \rho'\Lambda(T_\sigma - T_R), \quad \Lambda = aL\rho/(\eta T_\sigma). \tag{16}$$

This equation holds for a large number of substances (metals, cryogenic liquids, a large class of inorganic liquids) that satisfy the condition $L/k_B T N_A \lesssim 2$ [5, 12, 13].

The quantity $T_\sigma = T_\sigma(P)$ is the temperature corresponding to pressure P along the phase equilibrium curve; it can be found, for example, from the requirement for the equality of chemical potentials of liquid and nucleus [14]. In the quadratic approximation of the perturbation theory the quantity T_σ can be written as

$$\begin{aligned} T_\sigma = T_0 + \Delta T_0 + d_\sigma \Big\{ &(P_R - P_0) \\ &\times \left[1 - \frac{\rho}{\Delta\rho}\frac{d_\sigma^{(2)}}{d_\sigma}(P'_R - P_R)\right] \\ &- \frac{\rho}{\Delta\rho}(P'_R - P_R)\Big\} + \frac{1}{2} d_\sigma^{(2)}(P_R - P_0)^2. \end{aligned} \tag{17}$$

Here it is necessary to note the difference in methods of averaging the boundary conditions and hydrodynamic equations. The averaging of boundary conditions is carried out on the moving surface of the nucleus which oscillates with the sound frequency, while the hydrodynamic equations are averaged at a fixed point in space. For these averaging operations to be matched, the function $\psi(R) \doteq \psi(\bar{R} + \delta R)$, prescribed at the nucleus surface, is expanded as a Taylor series in the neighbourhood of the point $\bar{R}$ and averaged in the quadratic approximation [9]

$$\langle\psi_R\rangle = \langle\psi_{\bar{R}}\rangle + \langle(\delta R\nabla)\delta\psi\rangle_{\bar{R}}. \tag{18}$$

Note that within the quadratic approximation the value of $\langle\psi_{\bar{R}}\rangle$ coincides with the corresponding value of $\langle\psi\rangle$ at the fixed point of space. Equation (18) completes the formulation of the initial system of equations.

3. FORCED LINEAR OSCILLATIONS OF NUCLEI

The forced radially symmetric vibrations or oscillations of nucleation centers in a pure liquid were first considered in detail in [14]. We shall limit our discussion to some basic concepts which will be required later. The scattering of a plane sound wave on a spherical nucleus in the monopolic approximation is considered, so that pressure and temperature distributions in a liquid can be written as

$$\begin{aligned} \delta P(r) = \delta P_0 \Big\{ &\frac{\sin k_1 r}{k_1 r} + f_1 \frac{e^{ik_1 r}}{r} \\ &+ f_2 \frac{e^{ik_2 r}}{r}\Big\}, \quad \delta P_0 = P_m e^{i\alpha}, \end{aligned} \tag{19}$$

$$\begin{aligned} \delta T(r) = d_S \delta P_0 \Big\{ &\frac{\sin k_1 r}{k_1 r} + f_1 \frac{e^{ik_1 r}}{r} \\ &- \frac{f_2}{\alpha\rho c_2^2 d_S(1 - \bar{P}r)} \frac{e^{ik_2 r}}{r}\Big\}. \end{aligned} \tag{20}$$

The liquid velocity field can be determined with the aid of equations (7) and (8) subject to the conditions (19) and (20). The temperature distribution inside the nucleus can be found from the solution of the heat conduction equation (9) inside the nucleus. Then

$$(\nabla\delta T')_R = -\frac{i\omega R}{3D'}(\delta T'_R - d'_S \delta P'_R)\varphi(k'R) \tag{21}$$

where $\varphi(z) = 3(z \operatorname{cth} z - 1)/z^2$, $k' = (-i\omega/D')^{1/2}$. The velocity of nuclear particles on the interface is determined by integrating the continuity equation (7) taking into account the state equation $\delta\rho'/\rho' = \beta'\delta P' - \alpha'\delta T'$

$$\delta U' = \frac{i\omega R}{3}[\tilde{\beta}\delta P'_R - \alpha'\varphi\delta T'_R], \tag{22}$$

$$\tilde{\beta} = \frac{\beta'}{\gamma'} + \alpha'\varphi d'_S.$$

The nuclear radial fluctuations can be written then as

$$\begin{aligned} &\frac{\delta R}{R} = -\frac{K}{3Q}\delta P_0, \\ &Q = 1 - \frac{K}{3}\frac{\rho\omega^2 R^2}{1 - ik_1 R} - \frac{G}{3}\left(\frac{2\sigma}{R} + 4\eta i\omega\right), \end{aligned} \tag{23}$$

$$\begin{aligned} K &= \beta_0 - \frac{C'_\sigma}{L}\left(\varphi - \frac{C_\sigma}{C_P}\frac{C'_P}{C'_\sigma}\Phi\right)d_\sigma\xi, \\ G &= \frac{\beta'}{\gamma'} + \frac{C'_P}{L}\Phi\xi\frac{\rho}{\Delta\rho}d_\sigma, \end{aligned} \tag{24}$$

$$\begin{aligned} \beta_0 &= \frac{\beta'}{\gamma'} + \alpha'(d_S - d'_S)\frac{\varphi\Phi}{\varphi - \Phi}, \\ \Phi &= 3\frac{\rho C_P}{\rho' C'_P}\frac{1 - k_2 R}{(k_2 R)^2}, \end{aligned} \tag{25}$$

$$\xi = (1 - i\omega\tau)^{-1}, \quad \tau = \frac{C'_P}{L}\frac{R(\varphi - \Phi)}{3\Lambda}. \tag{26}$$

As is shown in ref. [14], K is the intrinsic compressibility of the nucleus, $K = -(1/V)(dV/dP')$, while the quantity $\mathscr{K} = K/Q$ is the compressibility of the nucleus considered as an element of a two-phase medium or $\mathscr{K} = -(1/V)(dV/dP)$. The parameter ξ characterizes the non-equilibrium nature of phase transformation. For a quasi-equilibrium phase transformation $\xi = 1$, which, at small field frequencies, is also the case for liquids having a high enough kinetic coefficient Λ. Conversely, the assumption that $\Lambda = 0$ yields the case of solid particles without phase transformations.

Figures 2 and 3 show the relation $\mathcal{K}(R) = |\mathcal{K}|\,\mathrm{e}^{-i\theta}$ for hydrogen and water. It can be seen that at small nuclear radii the absolute value of compressibility $|\mathcal{K}|$ is much greater than the value of $|\mathcal{K}|$ which is observed at large R and which is asymptotical to the adiabatic compressibility β'/γ'. This increase in $|\mathcal{K}|$ is associated with an additional change in the nuclear volume due to phase transformations on its surface [9, 14]. The occurrence of a maximum and the subsequent decrease in the function $|\mathcal{K}(R)|$ are attributed to the damping effect of surface tension forces on the sound pressure [14].

The analysis of the compression phase $\theta(R)$, presented in Figs. 2 and 3, shows the nuclear compressibility as having a negative sign. For substances with a positively sloped phase equilibrium curve ($d_\sigma > 0$) this property is associated with a change in the nuclear volume due to crystallization-induced mass transfer competing with the change caused by mechanical compression. At large R, when the surface effect is small, the nuclear compressibility is positive, but at small R, this effect becomes significant and results in a negative compressibility due to the prevailing influence of mass transfer. In particular, the minimum in the curve $|\mathcal{K}(R)|$ for hydrogen is caused by competing mechanical compression and mass transfer. In the case of water, for which $d_\sigma < 0$, this minimum is absent since the effect of mass transfer and mechanical compression on a change in the nuclear volume is of the same sign.

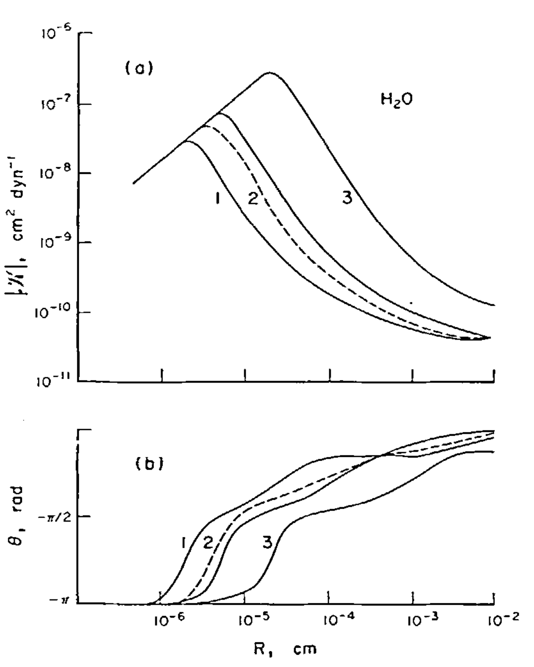

FIG. 2. Compressibility $\mathcal{K}(R)$ in the case of a crystallization nucleus in water at different sound frequencies: 1, 410 kHz; 2, 26 kHz; 3, 0.4 kHz. (a) the function $|\mathcal{K}(R)|$. (b) the function $\theta(R)$. Solid curves correspond to the liquid without an impurity; dashed curves relate to the liquid with an impurity having $\bar{c}_0 = 1\%$.

4. THE EFFECT OF RECTIFIED HEAT TRANSFER IN OSCILLATIONS OF NUCLEI

In order to determine the behaviour of the mean radius $\overline{R(t)}$, it is necessary to consider the averaged hydrodynamic equations (4)–(6) subject to boundary conditions (11), (12) and (14)–(16).

Integration of the Navier–Stokes equation (5) taking account of the continuity equation (4) and equations (7), (8) and (18) yields the following result:

$$\langle P_R\rangle = P_0 + \langle \delta R(\nabla\delta P)_R\rangle - \rho\langle\delta U^2\rangle - 2\rho\int_{\infty}^{R}\langle\delta v^2\rangle\frac{\mathrm{d}r}{r}. \quad (27)$$

On integrating the continuity equation (4) over the nuclear volume and applying equation (18), we obtain

$$\overline{U'} = -\left\langle\frac{\delta\rho'}{\rho'}\delta U'\right\rangle + \left\langle\delta R\left(\frac{\partial\delta v'}{\partial r}\right)_{\bar{R}}\right\rangle = \left\langle\frac{\delta J}{\rho'}\left(\frac{\delta\rho'}{\rho'} + 2\frac{\delta R}{R}\right)\right\rangle. \quad (28)$$

The integration of the heat conduction equation (6) from r to ∞ and from $\bar{R}$ to ∞ gives

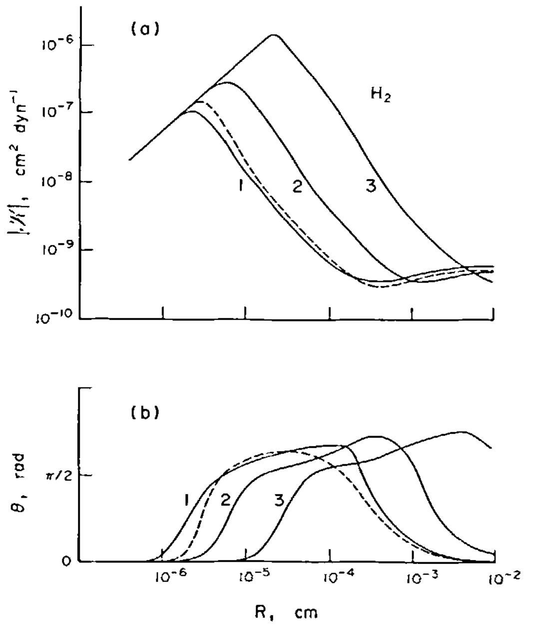

FIG. 3. Compressibility for crystallization nuclei in hydrogen at different sound frequencies. Details as Fig. 2.

$$\langle\kappa(\nabla T)_R\rangle = -\frac{\kappa}{R}[\bar{T}_R - T_0 - \langle\delta R(\nabla\delta T)_{\bar{R}}\rangle] + \frac{1}{R}\int_{\infty}^{\bar{R}} q\,\mathrm{d}r + q_R, \quad (29)$$

where q is given by equation (6). The expression $\langle\kappa'(\nabla T')_R\rangle$ is found by integrating equation (6) with the condition $\nabla T'|_{r=0} = 0$,

$$\langle\kappa'(\nabla T')_R\rangle = -C'_P\langle\delta J(\delta T_R - d'_S\delta P'_R)\rangle + \langle\delta U'\delta P'_R\rangle - 2\kappa'\left\langle\frac{\delta R}{R}(\nabla\delta T')_R\right\rangle. \quad (30)$$

With the help of the expressions obtained we can determine the mean rate of crystallization nucleus growth in a supercooled liquid

$$\dot{\bar{R}} = A(R)\left[\Delta T_0 - d_\sigma\frac{\rho}{\Delta\rho}\frac{2\sigma}{R} - \Delta T\right],$$
$$A(R) = \frac{\kappa}{\rho' LR}\left[1 + \frac{\kappa}{\rho' LR\Lambda}\right]^{-1} \quad (31)$$

where the quantity ΔT is

$$\Delta T = \sum_{l=1}^{5}\Delta T_l, \quad \Delta T_1 = -d_\sigma^{(2)} \times\left[\frac{1}{2}\langle\delta P_R^2\rangle - \frac{\rho}{\Delta\rho}\langle\delta P_R\delta(P'_R - P_R)\rangle\right],$$
$$\Delta T_2 = d_\sigma\left[\rho\langle\delta U^2\rangle + 2\rho\int_{\infty}^{R}\langle\delta v^2\rangle \times\frac{\mathrm{d}r}{r} + \frac{1}{\rho'}\langle\delta J^2\rangle - \langle\delta R(\nabla\delta P)_R\rangle\right], \quad (32)$$
$$\Delta T_3 = \langle\delta R(\nabla\delta T)_{\bar{R}}\rangle,$$
$$\Delta T_4 = \frac{1}{\kappa}\int_{\infty}^{\bar{R}}\langle\delta v\delta P\rangle\,\mathrm{d}r,$$
$$\Delta T_5 = \frac{1}{D}\int_{\infty}^{\bar{R}}\langle\delta R(\delta T - d_S\delta P)\rangle\,\mathrm{d}r.$$

All of the terms constituting the sum ΔT have a clear physical meaning. The first term is associated with the nonlinearity in the phase equilibrium curve. For most substances $d_\sigma^{(2)} < 0$, therefore, this term leads to a decrease in $\dot{\bar{R}}$. The term ΔT_3 is due to the surface effect described for the first time by Hsieh and Plesset [7, 15] with reference to the dynamics of gas bubbles in a sound field. The term ΔT_4 accounts for the absorption of sound energy as a consequence of the work done by the field on the liquid flows set in motion by this field. The quantity ΔT_5 is the mean convective heat flux from the liquid to the nucleus caused by the motion of liquid particles under the action of sound. As a whole, the quantity ΔT depends on the work of the field and therefore $\Delta T = B(R, \omega)P_m^2$, where $B > 0$. The appearance of a temperature difference is associated with a peculiar phenomenon of heat pumping into the nucleus. Similar to the case of vapour bubbles [7], this effect has been termed the effect of rectified heat transfer [9].

Next the sound pressure amplitude at which $\dot{\bar{R}} = 0$ will be determined. This case occurs at a certain threshold pressure P_k determined from

$$P_k = \left[\left(\Delta T_0 - d_\sigma\frac{\rho}{\Delta\rho}\frac{2\sigma}{R}\right)\Big/B(R, \omega)\right]^{1/2}. \quad (33)$$

The function $B(R, \omega)$ can be found by the following approximate equation:

$$B(R, \omega) = -\frac{d_\sigma^{(2)}}{4}\left[1 - 2\frac{\rho}{\Delta\rho}\frac{2\sigma}{R}|\mathscr{K}|\cos\theta\right] + \frac{|\mathscr{K}|}{6\rho C_P}\left\{d_\sigma\rho C_\sigma\left[1 + \frac{R}{\lambda_T} + 2\frac{\Delta\rho}{\rho}F''_3\left(\frac{R}{\lambda_T}\right)^2\right]\cos\theta + \frac{R}{\lambda_T}\sin\theta\left[d_\sigma\rho C_\sigma + 2\frac{\Delta\rho}{\rho}\frac{R}{\lambda_T}(1 + d_\sigma\rho C_\sigma F'_3)\right]\right\}, \quad (34)$$

where $\lambda_T = (2D/\omega)^{1/2}$, F'_3 and F''_3 are respectively the real and imaginary parts of the integral

$$F_3 = \int_0^{\infty} \mathrm{e}^{-\alpha x}(1 + x)^{-3}\,\mathrm{d}x,$$
$$\alpha = (1 - \mathrm{i})R/\lambda_T.$$

Figure 4 shows the curve $P_k(R)$ at different field frequencies for hydrogen. This figure also contains a schematic representation of the function $P_k(R)$. A straight line corresponding to the magnitude of the sound pressure P_m, will intersect the curve $P_k(R)$ at two points: at $R = R_{\min}$ and $R = R_{\max}$.

Since a nucleus grows only at $P_m < P_k$, it can be seen that the point $R_{\min}$ is unstable, while the point $R_{\max}$ is

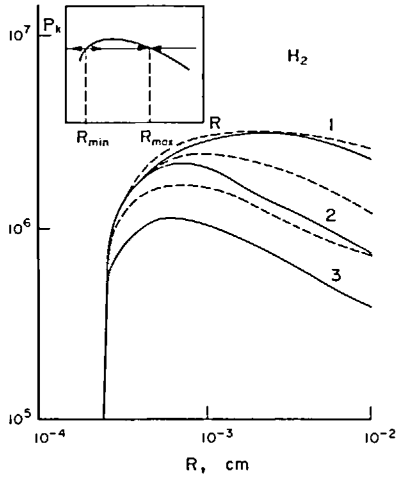

FIG. 4. The function $P_k(R)$ for a supercooled hydrogen ($\Delta T_0 = 10^{-3}$ K) taking account of an impurity with concentration $c_0 = 1\%$ at different frequencies of sound: 1, 0.4 kHz; 2, 26 kHz; 3, 410 kHz. Solid curves, pure liquid; dashed curves, liquid with impurity.

stable with respect to small departures of the radius R from these values. Thus the sound field narrows the wide size distribution of nuclei in the vicinity of the point $R_{\max}$. This provides a principal possibility for the formation of a uniform and fine structure of the solid substance crystallizing in a sound field. It should be noted, however, that substantial amplitudes of the sound pressure are required for the above phenomena to be observed at large supercooling. The analysis shows that the effect of rectified heat transfer is greatest in cryogenic liquids. In such liquids the effect can be recorded by relatively simple methods. In the case of water this effect is less pronounced, due mainly to an increase in the slope of the phase equilibrium curve (decrease of $|d_\sigma|$). For metals, this effect is even weaker than for hydrogen and water.

5. THE EFFECT OF IMPURITIES ON THE DYNAMICS OF NUCLEI IN A SOUND FIELD

In practice a crystallizing liquid always contains impurities of other substances that constitute the solution. The effect of an impurity on nuclei dynamics is qualitatively described below, assuming that the impurities do not interact chemically with the basic liquid (solvent) and that impurity concentration is small. It is known [16] that when an impurity dissolves in a solid phase worse than in a liquid one, its presence in the liquid decreases the equilibrium crystallization temperature. Then, as a nucleus grows, the impurity, displaced from the crystallization front, forms a more concentrated solution near the surface than that of the liquid far from the nucleus. The higher concentration causes a further decrease in the equilibrium crystallization temperature which partially makes up for the supercooling under the action of which the nucleus grows. As a result, the rate of its growth decreases. The opposite effect is observed in melting—a decrease in the concentration of impurity gives rise to an increase of the equilibrium crystallization temperatures. This too leads to a lower rate of radius change. Consequently, the impurity exerts a damping effect on crystallization nuclei oscillations in a sound field. Clearly, this results in a smaller compressibility of the nucleus, as well as in a smaller effect of the rectified heat transfer.

For describing the effect of impurity on the dynamics of nuclei, it is necessary to consider an additional equation, the diffusion equation which governs the distribution of the impurity. It can be shown that the remaining equations presented in Section 1 will retain their forms in the weak impurity concentration approximation. The diffusion equation can be written in the linear and quadratic approximations as

$$\delta\dot{c} = D_c\nabla^2\delta c, \quad \nabla\langle\rho c\mathbf{v}\rangle = \nabla\langle\rho D_c\nabla c\rangle \tag{35}$$

where D_c is the diffusion coefficient, $c = n_2m_2/(n_1m_1 + n_2m_2)$ and n_1 and n_2 are the number of particles of the solvent and solute, respectively. On the assumption that diffusion in a solid phase is neglected, $(\nabla c')_R = 0$, the boundary condition for equation (35) may be written as

$$Jc_R = -\rho D_c(\nabla c)_R. \tag{36}$$

The effect of impurity on the equilibrium crystallization temperature can be related to the condition of equality for the chemical potentials of phases expressed with account taken of the impurity [16]

$$T_\sigma^{(c)} = T_\sigma - \frac{k_BT}{m_2}\frac{\rho'\rho}{\Delta\rho}d_\sigma c_R. \tag{37}$$

The equation for the crystallization kinetics of liquid containing an impurity will change its form compared with that of equation (16). The quantity T_σ will be replaced by $T_\sigma^{(c)}$ determined from equation (37).

The solution of the problem can be obtained as follows. The expression for $(\nabla\delta c)_R$ following from the solution of equation (35) has the form

$$(\nabla\delta c)_R = -\frac{1 - \mathrm{i}k_cR}{R}\delta c_R. \tag{38}$$

Substitution of expression (38) into the boundary condition (36) yields

$$\delta c_R = \frac{Rc_R}{\rho D_c}\frac{\delta J}{1 - \mathrm{i}k_cR}. \tag{39}$$

Then, the oscillations of the equilibrium crystallization temperature of the liquid with an impurity, $\delta T_\sigma^{(c)}$, can be expressed in terms of the oscillations of mass flux δJ. By substituting the resulting value of $\delta T_\sigma^{(c)}$ into the equation for the crystallization kinetics of an impurity-containing liquid, we find that it takes on the form formally coinciding with equation (16) which describes crystallization of pure liquid but with a different kinetic coefficient, i.e. $\Lambda^{(c)}$ determined at $c_0 = c(t, \infty)$ by the following equation:

$$\Lambda^{(c)} = \Lambda\left\{1 + \frac{\rho'}{\rho}\Lambda\frac{c_0R}{D_c}\frac{k_BT^2}{m_2L}\frac{1}{1 - \mathrm{i}k_cR}\right\}^{-1}. \tag{40}$$

By using the relationship for the diffusion coefficient in the form $D_c = k_BT/6\pi\eta a$ [17] and using equation (16) for Λ, the quantity $\Lambda^{(c)}$ can be written as

$$\Lambda^{(c)} = \Lambda\left[1 + \frac{9}{2}\frac{\rho'}{\rho}\frac{\tilde{c}_0R}{a}\frac{1}{1 - \mathrm{i}k_cR}\right]^{-1},$$

$$\tilde{c}_0 = c_0\frac{m_1}{m_2}. \tag{41}$$

In Figs. 2 and 3, the dashed lines show the effect of an impurity on oscillations of the crystallization nuclei in water and hydrogen. We can see that the impurity decreases the value of $|\mathscr{K}|$ and shifts the region in which Re $\mathscr{K} < 0$.

Similar to the case of linear oscillations of nuclei, we can consider the effect of impurity on the mean rate of nuclei growth, $\bar{\dot{R}}$. It can be shown that the effect of an impurity on the mean rate $\bar{\dot{R}}$ is given by the replacement of quantities ΔT_0 and Λ in the function $A(R)$ of equation (31) by the quantities which depend on the impurity concentration

$$\Delta T_0 \rightarrow \Delta T_0^{(c)} = \Delta T_0 - \frac{k_B T}{m_2} d_\sigma \frac{\rho' \rho}{\Delta \rho} c_0, \qquad (42)$$

$$\Lambda \rightarrow \Lambda_2^{(c)} = \Lambda \left[1 + \frac{9}{2} \frac{\rho'}{\rho} \frac{\tilde{c}_0 R}{a} \right]^{-1}.$$

The expression for $B(R, \omega)$ formally remains unchanged, the impurity being accounted for in the expressions for $|\mathscr{K}|$ and θ.

In Fig. 4, the dashed curves show the influence of impurity on the behaviour of the function $P_k(R)$. The impurity is shown to lower the effect of rectified heat transfer.

Probably the most pronounced influence is exerted by an impurity on the behaviour of the rate $\dot{R}$. Thus, for aluminum the value of A in the presence of an impurity with the concentration $c_0 = 1\%$ decreases by about a factor of 6. Since $R(t) \sim (At)^{1/2}$, it is seen that the impurity will decrease the nuclear radius by 2.5 times relative to the case with no impurity. This effect of impurity on the structure of substances crystallizing out of melt has been noted earlier in a number of works [2-4].

6. DYNAMICS OF NUCLEI UNDER THE ACTION OF SOUND IN CRYSTALLIZING SOLUTIONS

For a supersaturated solution, the phase transformations are periodically alternating processes of pure solid substance dissolution and solution decomposition into a liquid (solvent) and a solid substance, i.e. the essential difference from the cases considered above is in the 'driving force' of phase transformation: oversaturation instead of supercooling of the solution.

The basic hydrodynamic equations given in the previous sections are valid for the present case also. The difference is observed in the boundary condition for the diffusion equation which acquires the form

$$J c_R = J - \rho D_c (\nabla c)_R. \qquad (43)$$

The quantity L is replaced by the heat of dissolution L_c, and for an oversaturated solution the equation of crystallization kinetics (16) is replaced by the relation $c_R = c_\sigma(P, T)$, where the subscript σ means that the quantity is taken along the curve of solution saturation.

The problem of nuclear oscillations in solutions may be solved as follows. The equilibrium concentration oscillations on the nuclear surface are

$$\delta c_R = \frac{\partial c_\sigma}{\partial T} \delta T_R + \frac{\partial c_\sigma}{\partial P} \delta P_R$$

$$= \frac{m_2 c_\sigma}{k_B T^2} L_c (\delta T_R - d_\sigma^{(c)} \delta P_R). \qquad (44)$$

By substituting equation (38) for the concentration gradient, taking account of equation (44), into the boundary condition (43), we obtain the equation for the crystallization kinetics which coincides in form with equation (16) with the sole difference that the quantity d_σ is replaced by $d_\sigma^{(c)}$ and Λ by $\Lambda_\sigma^{(c)}$. These quantities are determined from

$$d_\sigma^{(c)} = \frac{\Delta V_c T}{L_c},$$

$$\Lambda_\sigma^{(c)} = \frac{\rho}{\rho'} \frac{D_c}{1 - c_\sigma} \frac{m_2 c_\sigma}{k_B T^2} L_c \frac{1 - i k_c R}{R}. \qquad (45)$$

All the remaining equations, which are valid for the dynamics of nuclei in a supercooled liquid having no impurities, are also applicable for the analysis of nuclei dynamics in a supersaturated solution provided the quantities d_σ and Λ are replaced by $d_\sigma^{(c)}$ and $\Lambda_\sigma^{(c)}$, respectively.

Figure 5 shows the function $\mathscr{K}(R)$ for a nucleus of potassium bromide in a supersaturated aqueous solution. It is seen that the basic trends typical of the dynamics of nuclei in a supercooled liquid are also observed for the dynamics of nuclei in a supersaturated solution. The difference in the behaviour of the compressibility function is evidenced by a marked shift of the function $\mathscr{K}(R)$ into the region of small dimensions. This is attributed to a substantial difference between thermal diffusivity D and diffusion coefficient D_c that determine the scale lengths for heat and mass transfer (the length of a 'thermal' or 'diffusional' wave).

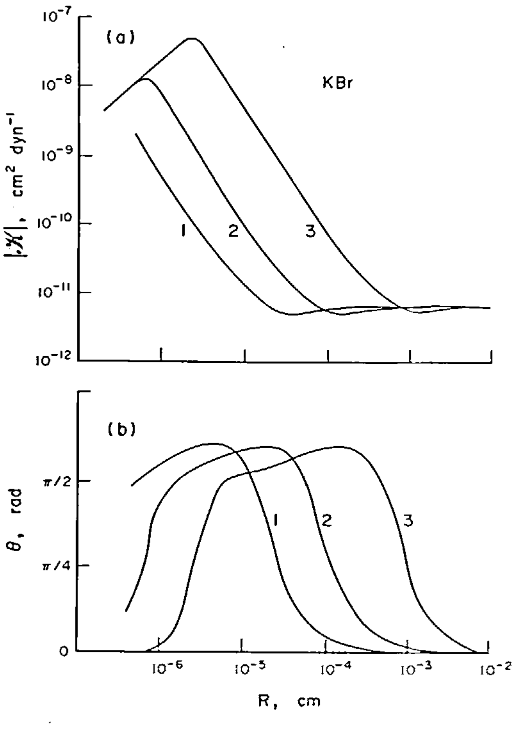

FIG. 5. Compressibility $\mathscr{K}(R)$ in the case of crystallization nuclei of potassium bromide in an aqueous solution at different frequencies of sound: 1, 410 kHz; 2, 26 kHz; 3, 0.4 kHz (a) the function $|\mathscr{K}(R)|$ (b) the function $\theta(R)$.

7. ABSORPTION AND DISPERSION OF THE SPEED OF SOUND IN A CRYSTALLIZING LIQUID

A substantial increase in the absolute value of compressibility $|\mathscr{K}|$, along with the possibility of the real part of nuclei compressibility being negative, may lead to significant anomalies on sound propagation in a crystallizing liquid.

The sound speed absorption and dispersion in a liquid with crystallization nuclei can be calculated using the Foldy dispersion equation [18]

$$k_{1\mathrm{ef}}^2 = k_1^2 + 4\pi n f_1 \tag{46}$$

where n is the number of nuclei of the same radius per unit volume of liquid. Foldy's formula (46) incorporates only the monopoly sound scattering by the nuclei. Account can be taken of higher orders of multipole expansion using the equation given in ref. [19]. It can be shown, however, that the monopoly approximation alone expressed by equation (46) is sufficient for the crystallization nuclei. In fact, even the next dipole term of the expansion that expresses nuclei oscillations as a whole turns to be small owing to the relation $\Delta\rho \ll \rho$. This term should be taken into account only for crystallizing solutions for which ρ' and ρ can differ markedly. But for this case also it is of interest to isolate the region where the contributions due to phase transformations into the sound speed absorption and dispersion become appreciable.

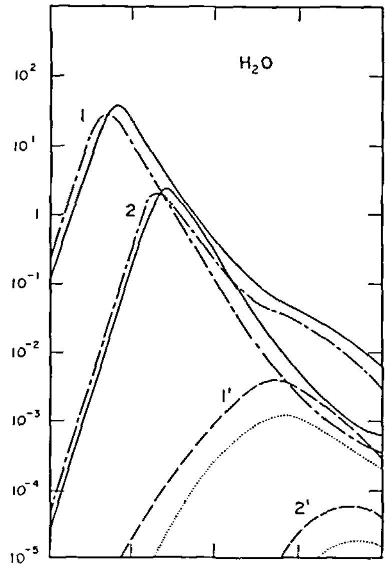

FIG. 6. The dependence of the coefficient of sound absorption of different frequency on the radius R of crystallization nuclei in water: solid and dashed-dotted curves show absorption of sound with account for phase transformations in pure water and in water with an impurity of concentration $\bar{c}_0 = 1\%$, respectively. Dashed curves show sound absorption due to he thermal mechanism [20], dotted curves represent absorption of sound due to the viscous mechanism [21]. Curves 1, 1′ and 2, 2′ correspond to 26 kHz and 0.4 kHz, respectively.

By using equation (46) it is possible to obtain the following expressions determining the absorption and dispersion of sound speed in a liquid with nuclei

$$\alpha = \frac{3}{2}\varepsilon\frac{c_1}{\omega R^3}\,\mathrm{Im} f_1, \quad \frac{\Delta c_1}{c_1} = -\frac{3}{2}\varepsilon\frac{c_1^2}{\omega^2 R^3}\,\mathrm{Re} f_1, \tag{47}$$

where $\Delta c_1 = c_{1\mathrm{ef}} - c_1$, $c_{1\mathrm{ef}}$ is the speed of sound in a liquid with nuclei. The expression for f_1 can be determined using the above results

$$f_1 = f_1^{(0)} + f_1^{(\Lambda)}, \tag{48}$$

where $f_1^{(0)}$ is the amplitude of sound scattering by nuclei without account for the effects of phase transformations, $f_1^{(\Lambda)}$ is an additional contribution into the scattering amplitude f_1 due to the effects of phase transitions alone. The quantities $f_1^{(0)}$ and $f_1^{(\Lambda)}$ are defined by the following expressions:

$$f_1^{(0)} = \frac{\rho\omega^2 R^3}{3Q}\left[\frac{\beta'}{\gamma'} - \frac{\alpha'}{d'_S}(d_S - d'_S)^2\,\frac{\varphi\,\Phi}{\varphi - \Phi}\right] - \frac{k_1^2 R^3}{3}, \tag{49}$$

$$f_1^{(\Lambda)} = -\frac{K - \beta_0}{3Q}\,\Delta\rho\omega^2 R^3. \tag{50}$$

Equation (49) allows the determination of the excessive absorption and dispersion of sound speed occurring due to a thermal mechanism which was first considered by Isakovich for liquids with inclusions and without phase transformations [20].

For an equilibrium phase transformation ($\Lambda = \infty$), the expression for f_1 can be written as

$$f_1 = -\frac{K}{3Q}\,\Delta\rho\omega^2 R^3\left[1 - \frac{\beta_0}{K}\frac{\rho'}{\Delta\rho}\right] - \frac{k_1^2 R^3}{3}. \tag{51}$$

The absorption coefficient α and sound speed dispersion $\Delta c_1/c_1$ can then be determined as

$$\alpha = -\frac{\varepsilon}{2}\,\Delta\rho\omega c_1\,\mathrm{Im}\,\mathscr{K}, \tag{52}$$

$$\frac{\Delta c_1}{c_1} = \frac{\varepsilon}{2}\left[1 + \Delta\rho c_1^2\,\mathrm{Re}\,\mathscr{K}\left(1 - \frac{\beta_0}{K}\frac{\rho'}{\Delta\rho}\right)\right]. \tag{53}$$

When $\Lambda = \infty$, the sound propagation in a liquid with crystallization nuclei can also be examined using equations (51)–(53), but then it is necessary to take into account that in the expressions for K and Q the quantity $\Lambda \neq \infty$ in contrast to the equilibrium case.

The effect of impurities on sound propagation in a crystallizing liquid can be taken into account, just as in the case of oscillations of crystallization nuclei, through a formal change-over $\Lambda \rightarrow \Lambda^{(c)}$ by equation (41).

Sound propagation in crystallizing solutions can also be studied by equations (51)–(53) with the sole difference that the quantities Λ and d_σ in the expressions for K and Q should be replaced by $\Lambda_\sigma^{(c)}$ and $d_\sigma^{(c)}$ according to equation (45).

In Figs. 6–8 the solid curves show the calculated values of sound speed absorption and dispersion for water, while the dashed and dotted curves show the effect of impurities. The dashed curves in Fig. 6 show the contribution of a thermal mechanism into sound absorption [20]. The dotted curves correspond to the case of viscous sound absorption [21].

Figures 6–8 show a marked effect of phase transformations on the absorption and dispersion of sound speed. It is seen that the impurities that damp the oscillations of crystallization nuclei decrease the sound speed absorption and dispersion. Regions of negative dispersion of sound speed are shown in Fig. 8 for water. A similar phenomenon is also the case for other substances for which $d_\sigma > 0$. As seen from equation (53), the region of negative dispersion appears because of a substantial increase in the absolute value (and a change in the sign of the real part) of nuclear compressibility. For solid particles without phase transformations this effect is absent. The mechanism of sound speed absorption and dispersion is a mechanism of non-local relaxation type suggested, probably, for the first time by Mandelshtam [22].

The above anomalies in sound propagation in ice-containing water are of interest for the study of sound propagation in polar regions of the ocean where the underwater sound channel is restricted to the ocean surface [23], i.e. to the layer filled with sludge ice.

Higher sound absorption in a crystallizing liquid induces stronger acoustic flows, since $v_{\text{fl}} \sim \alpha$ [24]. These are of interest for the analysis of methods used to obtain uniform and fine structure of substances crystallizing out of a liquid phase in a sound field [5].

8. LOCALIZATION AND INTERACTION OF NUCLEI IN A SOUND FIELD

The appreciable effect of phase transformations on the behaviour of nuclei compressibility is of interest in regard to the question of nuclei localization in a sound field. It is known [25, 26] that foreign particles occupy different positions in a sound field depending on the sign of the quantity ζ in the expression for the force F acting on the particle in a field which, in the case of a standing sound wave, may be written in the form [26]:

$$F = 4\pi R^2 (k_1 R) \frac{P_{\text{m}}^2}{2\rho c_1^2} \zeta \sin 2k_1 x,$$

$$\zeta = \frac{\rho' + 2\Delta\rho/3}{2\rho' + \rho} - \frac{\mathscr{K}\gamma}{3\beta}. \tag{54}$$

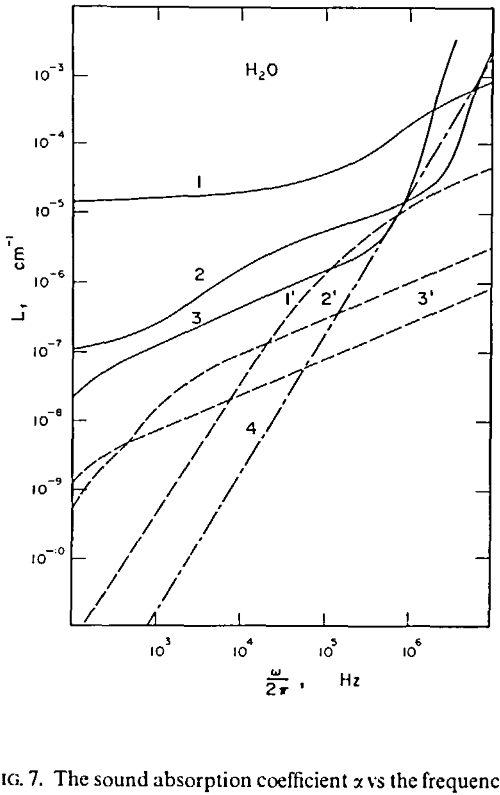

FIG. 7. The sound absorption coefficient α vs the frequency ω in water containing crystallization nuclei of different radii R: 1, 1', $R = 1.3 \times 10^{-4}$ cm; 2, 2', $R = 2 \times 10^{-3}$ cm; 3, 3', $R = 8 \times 10^{-3}$ cm. Solid curves correspond to the contribution to sound absorption of the mechanism of phase transformations; dashed curves, to the thermal mechanism [20]; dashed-dotted line corresponds to $\alpha(\omega)$ in the case of pure water. Concentration $\varepsilon = 10^{-5}$.

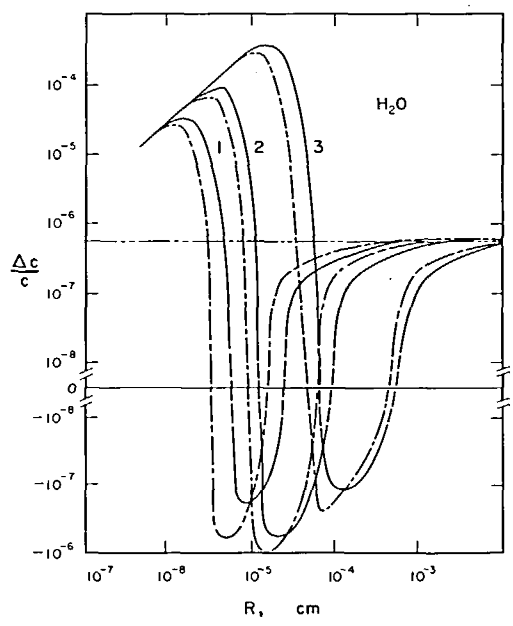

FIG. 8. The sound speed dispersion $\Delta c_1/c_1$ of different frequency depending on the radius R of the crystallization nuclei in water: 1, 410 kHz; 2, 26 kHz; 0.4 kHz. Solid curves correspond to water without an impurity; dashed-dotted curves, to water with an impurity of concentration $\tilde{c}_0 = 1\%$. The value of $\Delta c_1/c_1$ is calculated with account for the phase transformations. The horizontal dashed-dotted line corresponds to the dependence of $\Delta c_1/c_1$ on the nuclei radius with account for the thermal mechanism alone [20]. The concentration $\varepsilon = 10^{-6}$.

When $\zeta > 0$, the particles occupy pressure nodes. he quantity $\mathscr{K}$ is usually taken to be the adiabatic ompressibility β'/γ' [26]. However, it is not difficult to tend a generalization to an arbitrary compressibility . The quantity ζ will then have the form

$$\zeta = \frac{\rho' + 2\Delta\rho/3}{2\rho' + \rho} + \frac{\Delta\rho c_1^2}{3} \operatorname{Re}\left[\mathscr{K}\left(1 - \frac{\beta_0}{K}\frac{\rho'}{\Delta\rho}\right)\right]. \tag{55}$$

Taking into account that in the absence of phase ansformations $K = \beta_0 \simeq \beta'/\gamma'$ and assuming that Q 1, we may obtain equation (54) from equation (55). the presence of crystallization nuclei it is also ecessary to account for the inequality $\Delta\rho \ll \rho$. Then e quantity ζ becomes

$$\zeta = \frac{1}{3}\left[1 + \Delta\rho c_1^2 \operatorname{Re}\mathscr{K}\left(1 - \frac{\beta_0}{K}\frac{\rho'}{\Delta\rho}\right)\right]. \tag{56}$$

Comparing equations (56) and (53) we can see that e sign of the quantity ζ coincides with that of the und speed dispersion $\Delta c_1/c_1$. As has been noted ove, the sound speed dispersion can be negative in e case of crystallization nuclei. Simultaneously, the antity $\zeta < 0$, so that the nuclei change their location d move into the anti-nodes of the pressure wave. The terval of radii and frequencies at which this phenomon is observed for water can be determined from ig. 8. It should be emphasized that such solid particles ithout phase transformations are always located in e nodes of pressure wave, i.e. always at $\zeta > 0$.

It should be noted that a change in the location of ystallization nuclei in a sound field depending on eir radius and the field frequency bears a remblance to the behaviour of bubbles [7, 27]. Howcr, these phenomena are of different origin. In the se of bubbles, the reason for such behaviour is traced the resonance character of their vibrations, while in e case of nuclei it is due to an increase in the absolute lue, and a change in the sign of the real part, of mpressibility owing to phase transformationduced mass transfer.

Stronger oscillations of crystallization nuclei may ad to an increase of the forces of their interaction. he most substantial of these are the forces of Bjerkess and the forces of König [7]. The former are ssociated with the oscillations of inclusions, the latter ith the oscillating vibrations as a whole. The Bjerkess forces are mainly typical of well-compressible clusions such as bubbles. In the case of solid articles, the most substantial are the König forces 28]. However, in the case of crystallization nuclei for hich $\Delta\rho \ll \rho$, their oscillations as a whole relative to e liquid may be neglected. Therefore, for these nuclei, contrast to solid particles without phase transforations, the main interaction forces are the Bjerkness rces [7]

$$F_B = \frac{8\pi\rho}{r^2}\bar{R}_1^2\bar{R}_2^2\langle\dot{R}_1\dot{R}_2\rangle$$

$$= \frac{4\pi\rho\bar{R}_1^3\bar{R}_2^3\omega^2}{9r^2}\operatorname{Re}(\mathscr{K}_1\mathscr{K}_2^*)P_m^2 \tag{57}$$

where $\mathscr{K}_1$ and $\mathscr{K}_2$ are compressibilities of two different nuclei. For nuclei of the same radius, the Bjerkness forces are

$$F_B = \tfrac{4}{9}\pi\rho\omega^2 R^6 |\mathscr{K}|^2 P_m^2/r^2. \tag{58}$$

It follows from the formulae and results given in Figs. 2 and 3 that the Bjerkness forces for nuclei increase sharply as compared with the case of solid particles without phase transformations.

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NOYAUX DE CRISTALLISATION DANS UN LIQUIDE SOUMIS A UN CHAMP SONORE

Résumé—On étudie théoriquement les noyaux de cristallisation soumis à des oscillations radialement symétriques dans des liquides sous-refroidis et des solutions sursaturées avec un champ sonore. Une cristallisation et une fusion périodiques se produisent pour les plus grandes amplitudes. Il en résulte une interaction non-linéaire du son avec le noyau oscillant et un transfert thermique modifié, par exemple un lent (par rapport au cycle sonore) pompage de chaleur dans le noyau. Un autre aspect de cette interaction non-linéaire est dans le fait que la place des sites de nucléation dans une onde sonore dépend des dimensions des noyaux et de la fréquence du son — situation qui diffère fortement du cas des particules solides sans transformation de phase. On montre que ces transformations de phase peuvent accroître l'absorption et la dispersion du son dans les liquides par rapport aux liquides contenant des particules solides sans transformation de phase. On montre aussi que l'accroissement d'amplitude des oscillations des noyaux de cristallisation augments les interactions avec les autres.

KRISTALLISATIONSKERNBILDUNG IN FLÜSSIGKEITEN IN EINEM SCHALLFELD

Zusammenfassung—Der Bericht handelt von der theoretischen Untersuchung der Kristallisationskernbildung unter radialsymmetrischen Schwingungen in unterkülten und übersättigten Lösungen, die einem Schallfeld ausgesetzt sind. Im Verlauf der Schwingung treten periodisisch Kristallisations- und Schmelzprozesse auf, was sich in höheren Amplituden ausdrückt.

Dies steigert die nichtlineare Wechselwirkung des Schalls mit einem schwingenden Kern, was einen gerichteten Wärmetransport bewirkt. Dabei wird Wärme vergleichsweise langsam in den Kern gepumpt. Ein weiteres besonderes Merkmal der nichtlinearen Wechselwirkung zwischen dem Schall und dem Kern ist von besonderer Bedeutung; die Lage des Kerns in einer stehenden Welle hängt von der Größe des Kerns und der Schall-Frequenz ab ein grundlegender Unterschied zu Feststoffen ohne Phasentransformation. Es wird gezeigt, daß die Phasenverschiebung in kristallisierenden Flüssigkeiten merklich die Absorption und die Streuung der Schallausbreitung vergrößert, verglichen mit Flüssigkeiten, die Feststoffpartikel enthalten und keine Phasenverschiebung haben. Es wird auch gezeigt, daß eine Erhöhung der Schwingungsamplitude des kristallisierenden Kerns die Wechselwirkung der Kerne untereinander verstärkt.

ЗАРОДЫШИ КРИСТАЛЛИЗАЦИИ В ЖИДКОСТИ В ЗВУКОВОМ ПОЛЕ

Аннотация—Теоретически исследованы радиально-симметричные колебания зародышей кристаллизации, происходящие в звуковом поле в переохлажденных жидкостях и пересыщенных растворах. Показано, что существование периодических процессов кристаллизации и плавления при колебаниях зародышей приводит к увеличению амплитуды этих колебаний. Это обстоятельство способствует усилению нелинейного взаимодействия звука с пульсирующим зародышем. Оно приводит к явлению выпрямленной теплопередачи при колебаниях зародышей – медленному по сравнению с периодом звука процессу накачивания тепла внутрь зародыша. Другая особенность нелинейного взаимодействия звука с зародышами выражается в зависимости места локализации зародышей в стоячей звуковой волне от их размеров и частоты звука, что существенным образом отличается от случая твердых частиц без фазовых превращений. Показано, что из-за наличия фазовых превращений поглощение и дисперсия скорости звука, распространяющегося в кристаллизующихся жидкостях, содержащих твердые частицы без фазовых преращений. Показано также, что увеличение амплитуды колебаний зародышей кристаллизации приводит к повышению сил взаимодействия их друг с другом.