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# Theory of melting and crystallization in small specimens with surface coating

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A theory of melting and crystallization in small specimens with surface coating is developed. The basic idea is that both transitions may be described within the framework of a strongly coupled system of dislocations and vacancies (free volume). The configurational integral of the dislocations is calculated by taking the dislocation-vacancy interaction for the mobility of the dislocations (absorption and emission of vacancies) and directly over their conservative interaction into account. Integrating out the configurations of the dislocations generates an induced and attractive interaction between vacancies. The solid-liquid transition is then studied via a gas-liquid—type transition in the vacancy system, where it is assumed that the number of unpaired vacancies (or free volume) is a conserved quantity, due to the surface coating. Under reasonable assumptions it is shown that melting proceeds within a temperature interval as observed by Gleiter, Perepezko, and Smidoda. Within the same theory, crystallization of supercooled samples is studied.

## I. INTRODUCTION

Recently the experimental study of superheating[1] and supercooling[2] phenomena in specimens of a size in the order of microns and provided with a surface coating has received much attention. The surface coating of these specimens is supposed to inactivate the nucleation processes starting mainly at the open surfaces of the system and should therefore allow the study of their physical properties in the usually inaccessible domains of metastability. In these regimes the transition into the thermodynamically stable phases is of particular interest. For supercooled specimens the theoretical prediction by Schneider *et al.*[3] is that a soft relaxational mode drives the system into the solid phase continuously, implying the divergence of the structure factor $S(\vec{q}_0)$ at $T_1^*$, where $\vec{q}_0$ is a reciprocal-lattice vector of the solid. Recent experiments by Suck *et al.*[2] show that this is not observed experimentally. Similarly it has been suggested that superheated specimens melt continuously over a soft-phonon mechanism.[4] Gleiter, Perepezko, and Smidoda[1] observe, however, that superheated small specimens apparently melt in a temperature interval reminiscent of what is observed in systems that expand on melting but are constrained by constant-volume conditions.

Conventional theories of the metastable-state transitions are based usually on the hypothesis of homogeneous nucleation which for supercooled specimens is rather successful[5,6] as far as the prediction of a transition temperature is concerned. All other properties (dynamic structure factor, diffusity, etc.), however, cannot be described by such a theory. In particular the observation of Gleiter, Perepezko, and Smidoda[1] of melting in a temperature interval cannot be explained this way. Let us point out that also in systems like quartz and cristobalite, where large superheating has been observed by Ainslie *et al.*,[7] the homogeneous nucleation hypothesis fails because heterogeneous melting is observed. As a matter of fact, the transition is always initiated at the surface or at grain boundaries of the system.

The following interpretation is based on the idea that a system, when it melts, needs free volume in order that the particle aggregate is able to develop liquid-state properties. Similarly a liquid must get rid of the free volume in order to crystallize, and if it is prevented from expelling or annihilating its free volume it vitrifies at sufficiently low temperatures. On a qualitative theoretical level this idea can be incorporated in a model where melting is driven by dislocations, and a theory of the liquid state as a plasma of dislocation loops. Because dislocations are able to move via conservative and nonconservative processes (requiring material transport) and because purely conservative motion leads to immobility of the dislocation system (if more than one glide system is activated), a mobile dislocation loop system is necessarily strongly coupled to point-defect motion. This picture is supported by the observations of Cotterill *et al.*,[8] using computer simulation, that upon melting, point defects are created in large numbers where moving dislocations intersect. In a solid, point defects are generated in vacancy interstitial pairs and dissociation of these pairs provides the point defects for the nonconservative dislocation motion. Owing to the asymmetry of the interparticle-interaction law, the formation energy of vacancies is usually much lower than for interstitials and the mobility of interstitials is usually higher than for vacancies. A consequence of that is that vacancies usually enter the system through an open or free surface, thus circumventing the pair-generation law applying to the bulk. The important role of vacancies for the melting process and the melt itself is supported by the observation that the surface of a specimen is usually the most favorable site for nucleation, and that the concentration of vacancies increases from about (0.01–10)% for typical metals[9] during the melting transition. The role of vacancies for the melting transition and the melt has been studied extensively by Górecki.[10]

Suppose now that a solid specimen of volume $\Omega$ is provided with a surface coating at a temperature $T_{\text{SC}}$. Then the number of unpaired vacancies in the system is $N_V(T_{\text{SC}})$. Under the condition that the surface coating fits smoothly to the specimen, is impenetrable to vacancies, and does not yield, the possible configurations of dislocation loops are subject to the constraint of conservation of matter. This constraint may be put into the form

$$\sum_{\sigma} \frac{1}{\Omega_0} \int_{C^\sigma} \vec{b}^{\,\sigma}\cdot\vec{r}^{\,\sigma}\times d\vec{r}^{\,\sigma}-(N_V-N_I)=-N_V(T_{\text{SC}})\ . \tag{1}$$

Here $\{C^\sigma,\vec{b}^{\,\sigma}\}$ represents an ensemble of dislocation loops, where $C^\sigma$ and $\vec{b}^{\,\sigma}$ are the dislocation line segment and Burgers vector of type $\sigma$, respectively. $N_V$ and $N_I$ represent the total number of vacancies and interstitials, and $\Omega_0=(4\pi/3)r_0^3$ represents the volume per particle. Equation (1) is the general law to which the generation of point defects is subject and includes the case that, e.g., interstitials are condensed in dislocation loops. It is obvious from Eq. (1) that $N_V(T_{\text{SC}})\Omega_0$ is a quantity defining the canonical ensemble corresponding to a given amount of free volume delivered to the system at $T_{\text{SC}}$.

How good a thermodynamic variable is $N_V(T_{\text{SC}})\Omega_0$? It is obvious that this is a conserved quantity under the boundary conditions imposed, in contrast to $N_V(T_{\text{SC}})$, because the number of vacancies in a strongly disordered crystal or a liquid is not well defined, but must be replaced by the free-volume[10,11] concept. There is, however, no reason to not consider the free volume defined by

$$V_f=N_V(T_{\text{SC}})\Omega_0(T) \tag{2}$$

as a thermodynamic variable as long as the surface coating does not yield, i.e., it prevents material from being deposited coherently into the lattice with the bounding misfit dislocation expelled through the surface. This implies that the surface-coated systems under ideal conditions are correctly specified by the three thermodynamic variables $T$, $\Omega$ (or $p$), and $V_f$. Obviously under these conditions superheating and supercooling of surface-coated specimens do not imply that these systems are necessarily in a metastable state but that they may be thermodynamically stable under the given boundary conditions. It is this point of view on which the following theory is based.

In Sec. II the qualitative properties of the model are explained. The starting point of the theory is that the mobility properties of a dislocation loop depend on the density of point defects and their respective mobilities. The evaluation of the partition function is then done such that the configurations of the dislocation loop are integrated out first. This procedure generates an induced interaction between the point defects. The solid-liquid transition of the specimen can now be studied on the background of the gas-liquid transition within the vacancy system. The justification of that method is done in Sec. III but its qualitative features are already discussed in Sec. II, because the theoretical derivation and justification of the induced-interaction law is rather involved. In Sec. IV a critical discussion of the results and shortcomings of the theory is given. Mathematical details are worked out in two appendixes.

## II. QUALITATIVE PROPERTIES OF THE MODEL

In order that a dislocation loop may display its possible conformations with a reasonable speed, material transport is required[12] and this implies that the partition function must contain also the contributions of the point-defect configurations. Assume for the sake of simplicity that the possible configurations of a dislocation loop are formed over random-walk processes on a reference lattice, ignoring the constraint given by Eq. (1). Owing to the globular structure of the mean configuration (an average over all possible configurations), a radius of gyration $R_g(T)$ may be defined and also a corresponding volume of the order of $\Omega_d(T) \simeq (4\pi/3)R_g^3(T)$. The number of vacancies and interstitials in $\Omega_d$ is obtained as

$$N_{pd}=\int_{\Omega_d} d^3r\,[n_V(\vec{r})+n_I(\vec{r})]\ , \tag{3}$$

where $n_V(\vec{r})$ and $n_I(\vec{r})$ are vacancy and interstitial densities. Given the number $N_{pd}$ in $\Omega_d$ (the volume where the dislocation displays its configurations), obviously only loops of lengths $s$, not exceeding a certain length $s^*$, are able to activate all their degrees of freedom. For those loops where $s > s^*$ holds, there are not enough point defects available to keep them mobile. If $q$ is the number of possibilities available for a random walk at each successive step ($q_m \simeq 5$ on a three-dimensional lattice), then the ansatz

$$q(s,\vec{r}) \simeq q(\vec{r})e^{-s/s^*} ,$$

$$q(r) \simeq \begin{cases} q_m , & r \leq R_g \\ q_m e^{-\kappa|\vec{r}-R_g\vec{r}_0|} , & r > R_g \end{cases} \tag{4}$$

$$\vec{r}_0 \equiv \vec{r}/r ,$$

conforms qualitatively to the constraint imposed. The length $\kappa^{-1}$ measures the thickness of the interface boundary between the liquid droplet of volume $\Omega_d$ and the solid material of volume $\Omega - \Omega_d'$. A possible scaling relation for $s^*$ is

$$\frac{\int_{\Omega_d} d^3r\,[n_V(\vec{r})\Omega_{0,V} + n_I(\vec{r})\Omega_{0,I}]}{n_b \Delta_0 l_0 s^*} = Z^*(T,\Omega) . \tag{5}$$

Here it has been assumed that the effective length of a "step" in the random-walk process generating the dislocation loop is $l_0$ and its cross section (forming the core of the dislocation) $\Delta_0$. The definition of these quantities allows one to treat $s$ and $s^*$ as dimensionless quantities. For $\Delta_0 \lesssim l_0^2$ the length $l_0$ defines the lattice unit of the reference lattice. $\Omega_{0,V}(T,\Omega)$ and $\Omega_{0,I}(T,\Omega)$ represent the specific volume of a vacancy and interstitial, respectively. The number of linearly independent Burgers vectors that the branched loops are made up of is given by $n_b$ (see Sec. III). The number $Z^*(T,\Omega)$ decreases for $T$ increasing due to higher mobility of the point defects and increasing efficiency of conservative motion of dislocations to overcome barriers due to interaction and packing effects of dislocations. Because such processes occur via thermally activated motion we assume

$$Z^*(T,\Omega) \sim e^{\Delta(\Omega)/kT} . \tag{6}$$

The next problem is to determine the point-defect concentrations $n_V(\vec{r})$ and $n_I(\vec{r})$. The interaction between the point defects consists of two parts. First, there is the hard-core repulsion between point defects of the same kind and in addition a rather weak long-range interaction[13,14] decaying like $1/r^5$ with distance $r$. This interaction decreases with increasing temperature due to anharmonic effects of the lattice vibrations. Second, there is an induced interaction between point defects which arises from their interaction with the dislocations. It will be obtained (in Sec. III) by integrating out the configurations of the dislocation loop in the partition function. In addition, one obtains a renormalization of their chemical potential, as a function of their relative distance to the center of gravity of the dislocation loop. The effective interaction between point defects of the same kind turns out to be *attractive* and for the others repulsive. Furthermore, the effective coupling constant increases with increasing temperature.

Suppose that $N_V(T) \simeq N_V(T_{\text{SC}}) \gg N_I(T)$ holds. Then at a certain temperature $T_{m_1} > T_m$ (the thermodynamic melting temperature) a gas-liquid—type transition (see Sec. III) within the vacancy system will be nucleated at a certain point in the interior of the specimen, say, at an internal stress center or at a grain boundary. By this mechanism a liquid droplet is nucleated in the specimen extending over a domain $\Omega_d$ with the vacancy density satisfying

$$n_V(\vec{r} \in \Omega_d) \gg n_V(\vec{r} \notin \Omega_d) . \tag{7}$$

This implies that the region outside of the nucleation center is deprived of vacancies [see Figs. 1(a) and 1(b)]. Because the transition temperature is dependent on the vacancy density, a slightly higher temperature than $T_{m_1}$ is required to attract further vacancies into the liquid droplet and to have it grow. It is obvious that if once a liquid nucleus has been formed at a certain position then all other possible nucleation centers are discriminated against the activated one, because the density of vacancies at their positions is now steadily decreasing, as a consequence of getting absorbed by the first nucleation center. Once the liquid domain has absorbed most of the vacancies, the vacancy interstitial pair generation must provide the lubrication to transform the rest of the sample into liquid. Using the numbers quoted earlier for vacancy densities in solid and liquid metals,[9] one concludes that only a fraction of $\lesssim 10^{-4}$ of the sample will be transformed into liquid using the available $N_V(T_{\text{SC}})$ vacancies.

Since the vacancy interstitial pair formation gets energetically more favorable if the interstitials are condensed into dislocation loops, it is reasonable to assume that once a liquid droplet has been formed, representing a mobile dislocation loop, loop configurations with $N_V > N_V(T_{\text{SC}})$ get activated. It is easy to show, however, that as long as the dislocation loop is confined to the droplet or partially surrounds it in a coil-like configuration, its internal-stress-energy change $\Delta U$ must satisfy the inequality

$$\frac{\lambda'}{2}\Omega_0^2[N_V-N_V(T_{\mathrm{SC}})]^2/\Omega \lesssim \Delta U \lesssim \frac{\lambda'}{2}\Omega_0^2[N_V-N_V(T_{\mathrm{SC}})]^2/\Omega_d \, , \tag{8}$$

where $\lambda'$ is proportional to the Lamé constant $\mu$ and weakly depends on the dislocation configuration. Equation (8) is a consequence of the fact that the long-range dilatational stress fields for fixed $N_V-N_V(T_{\mathrm{SC}})$ cannot be screened out. If an ordinary system melts subject to a constant-volume constraint the influx of $\Delta N_V$ vacancies will lead to an increase of the internal energy $U$ as follows:

$$\Delta U \simeq \tfrac{1}{2}\lambda\Omega_0^2(\Delta N_V)^2/\Omega \, . \tag{9}$$

Because such a system melts over a temperature interval, comparison of Eqs. (8) and (9) shows that the generation of additional vacancies in the surface-coated system does not allow the system to melt at a fixed temperature. Both mechanisms considered, to have a liquid droplet grow in a surface-coated system will lead, therefore, to melting in a temperature interval $[T_{m_1}, T_{m_2}]$; see Fig. 2.

The temperature $T_{m_2}$ marks, under ideal conditions, the end point of the two-phase coexistence region. Experimentally it presumably marks the temperature where liquid touches the surface coating at some place and fuses a hole into it. A schematical plot of the phase diagram of the system is given in

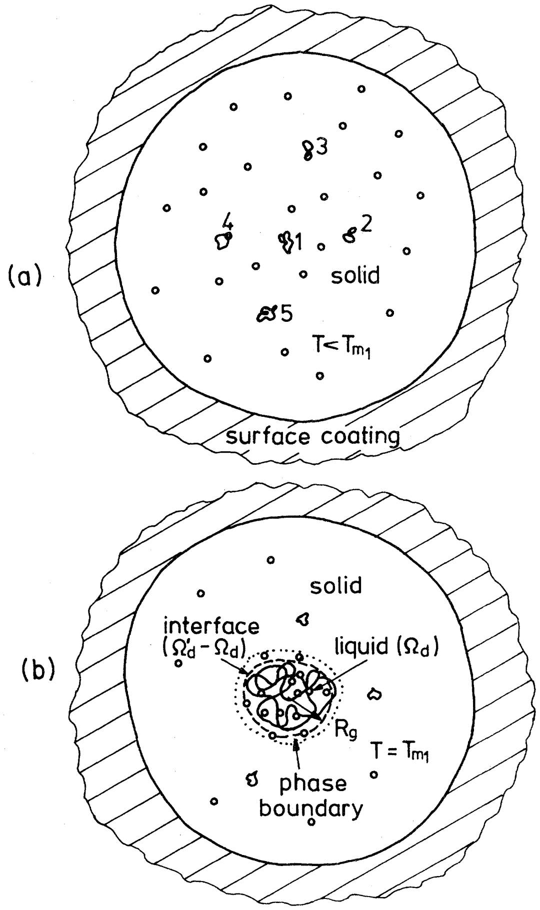

FIG. 1. (a) Schematic plot of specimen, with surface coating drawn hatched. Five possible nucleation centers are schematically depicted, from which number 1 is supposed to be energetically distinguished. The small circles symbolize vacancies. (b) At $T_{m_1}$ nucleation center, 1 gets active and forms a liquid droplet of radius $r_l^*$. Taking up latent heat it grows to a final radius $R_g > r_l^*$ until the system at $T_{m_1}$ is in equilibrium. For $T > T_{m_1}$ the liquid domain grows.

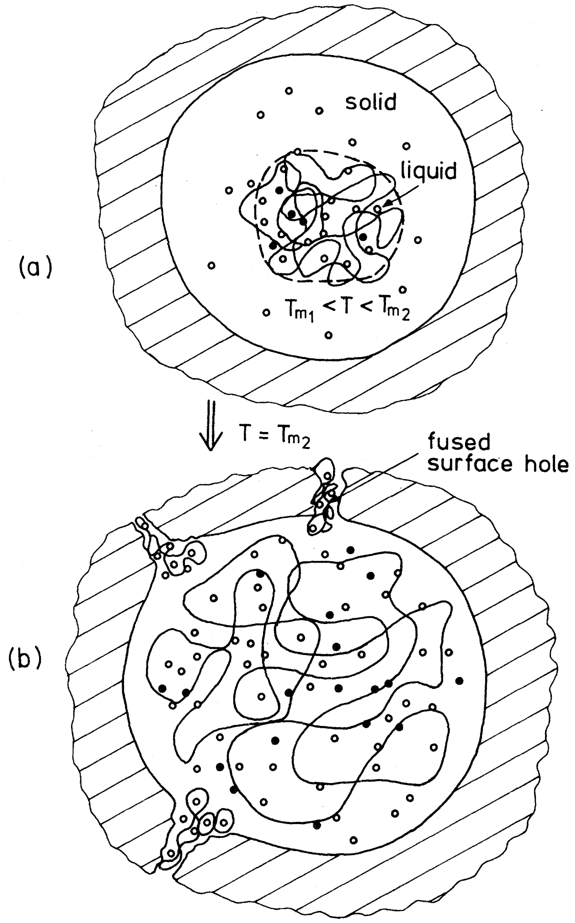

FIG. 2. (a) Solid dots represent interstitials which appear at $T \geq T_{m_1}$ allow the number of vacancies in the solid and liquid region to grow. Condensation of interstitials into dislocation loops as assumed in the text is not drawn. (b) End point of two-phase coexistence region at $T_{m_2}$. Here the liquid domain reaches the boundary and fuses holes into it allowing a flux of free volume to enter the system.

Fig. 3. The dashed-dotted curve starting at $T_{\rm SC}^{(1)}$ and traversing the two-phase coexistence region in the temperature interval $[T_{m_1},T_{m_2}]$ corresponds to the thermodynamic trajectory of the system just discussed. The heat-absorption curve corresponding to the melting process discussed above is schematically plotted in Fig. 4. Accordingly this theory provides a qualitative interpretation of the interval melting observed by Gleiter, Perepezko, and Smidoda.[1]

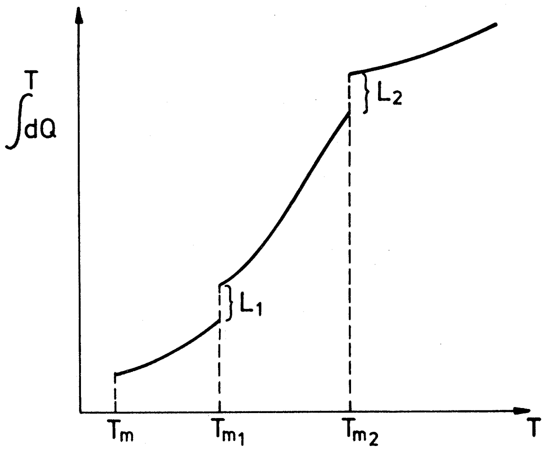

FIG. 4. Schematic plot of heat absorption $\int^T dQ$ of the process illustrated in Figs. 1 and 2. $L_1$ is the latent heat needed to have the liquid droplet grow in Fig. 1(b) from $r_l^*$ to $r_l$. The heat absorbed in the coexistence region, extending from $T_{m_1}$ to $T_{m_2}$, is required to have the liquid droplet grow to larger size until at $T_{m_2}$ it touches the boundary. $L_2$ is required to transform the rest of the sample into liquid through a flux of free volume entering through the fused surface coating [see Fig. 2(b)].

In a similar manner the model allows the discussion of the crystallization of surface-coated liquid droplets. Here it is assumed that the free volume $V_f(T_{\rm SC})$ exceeds the free volume of the system with open boundaries at $T_m < T_{\rm SC}$. Consequently, the formation of a solid nucleus should occur at $T_{f_1} < T_m$ in order to stay consistent with the melting model discussed earlier. Because on lowering the temperature the effective interaction between vacancies (mediated by the dislocation loops which are shrinking) gets weaker, the formation of a solid nucleus is a consequence of the liquid-gas transition in the vacancy system. Suppose that the solid nucleus grows at the surface, forming eventually a crust, then free volume from the solid regions is expelled into the liquid. Consequently the initial solid nucleus grows on lowering the temperature, but the liquid still remains stable for $T < T_{f_1}$ due to the increased density of vacancies or free volume there. It is, however, also possible to assume that once a nucleus is formed at the surface it will not form a smooth crust but one which is perforated with holes and channels, where it accommodates the free volume $\delta V_F$ released during the growth of the solid phase. Because the initial solid nucleus must have a lower free energy per particle than a solid perforated by holes and channels, due to the difference in surface energy, it is not necessarily unstable against growth at $T_{f_1}$. Accordingly, both mechanisms considered to have a solid crust grow on the surface will lead to crystallization in a temperature interval $(T_{f_1},T_{f_2})$. The temperature $T_{f_2}$ marks the point where the sample is transformed into solid material. The situation described is represented in Fig. 3 by means of the dashed-dotted curve starting at $T_{\rm SC}^{(2)}$. It is also possible that for $T > T_{f_2}$ a glass transition occurs in the bulk of the sample.

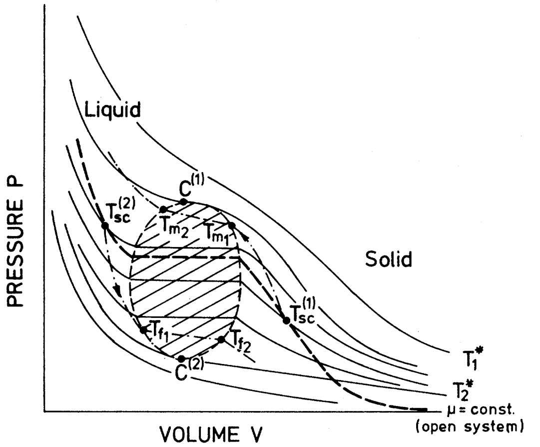

FIG. 3. Schematic plot of the $p$-$V$ diagram of the vacancy system. The hatched domain represents the coexistence region. The thick dashed line represents the trajectory of the system in thermodynamic equilibrium. The dashed-dotted curves correspond to superheating and supercooling trajectories of surface-coated systems, respectively, where scales will depend on the volume $\Omega$ of the sample. Solid curves represent isotherms.

Experimentally now, crystallization of supercooled samples occurs at sharply defined temperatures and is not observed to be smeared over an interval. A possible explanation for this is that the formation of the solid phase does not proceed via a nucleation mechanism at the surface coating but perhaps in a way as visualized by Schneider *et al.*[3] Within the present model this is possible as follows. On lowering the temperature, free volume is successively annihilated by generating dislocation-loop configurations with $N_V < N_V(T_{\rm SC})$. Because their internal energy again must satisfy Eq. (8), whereas their configurational entropy gets reduced due to annihilated free volume, an *instability* for $T < T_m$ arises only if the internal-energy gain due to collapsed vacancies is in excess of that free-energy loss. It is reasonable to assume that in the case where the free volume is present in the form of finely dispersed vacancies this is not the case. Furthermore, the collapse of vacancies to form a solid nucleus requires an activation barrier to be overcome. It is therefore possible that the free volume is successively converted into dislocation loops, which are expelled to the surface, if this activation barrier always remains small with respect to the thermal energy. In this fashion a continuous transition at $T_2^*$ may result (see Fig. 3). Owing to the large difference in volume between solid and liquid state, surface yield may lead to a mechanical instability of the system for $T > T_2^*$ over a sharp transition.

## III. THEORETICAL TREATMENT OF THE MODEL

We calculate the partition function of the problem starting from the solid phase, assume an impenetrable boundary of the system, and therefore take $N_V(T_{\rm SC})$ fixed. Then we ignore presently the contribution of small thermally produced dislocation rings to the statistical sums, because such rings are only able to grow once they have reached a critical size where the long-range Biot-Savart interaction between different parts of the loop is screened out.[12,15] If a loop has reached a critical size where it is able to grow, it constitutes a small liquid droplet. This process takes place over an activation barrier. The liquid droplet is presumably located at a favorable site, where there is already a dislocation loop grown in or at a grain boundary. Owing to the reasons given in Sec. II it is sufficient to consider just one nucleation center.

In the simplest case a branched loop will be present having an equal distribution of Burgers vectors $\vec{b}^{\sigma}$ for the easiest glide planes. For the sake of simplicity, we assume that for the calculation of the partition function the branched loop can be approximated as a product of $n_b$ unbranched and open-ended loops. The Biot-Savart interaction between loop segments will be neglected for *individual* configurations, since the loops only give a significant contribution once $s^* \gg 1$ holds (activated nucleation center) and in that case these interactions are mainly screened out.[12,15] The constraint given by Eq. (1) will be neglected for $s^* \gg 1$ and $N_I = 0$, $N_V = N_V(T_{\rm SC})$. For $N_V - N_V(T_{\rm SC}) \neq 0$ the unscreened dilatational interactions estimated by Eq. (8) and the associated reduction of the number of loop configurations will be taken into account approximately. The interaction between dislocation loops and point defects, within the path-integral formulation of the dislocation theory,[12] is obtained in Appendix A using formulas given in Refs. 13 and 14 for internal-stress—point-defect interactions. From Appendix A, Eqs. (A1) and (A2), one obtains

$$V^{dp}(\{\vec{b}^{\sigma}\},\{\vec{\tau}_i^{\alpha}\}) = \frac{3\Omega_0\mu}{2\pi} \sum_{\{\vec{\tau}_i^{\alpha}\}} \epsilon_i^{\alpha} \sum_{\sigma} \int_{C^{\sigma}} \frac{\vec{b}^{\sigma}\cdot[\vec{n}(\vec{R})\times\dot{\vec{r}}^{\sigma}]ds^{\sigma}}{|\vec{r}^{\sigma}(s^{\sigma})-\vec{\tau}_i^{\alpha}|^2} , \tag{10}$$

where

$$\epsilon_i^{\pm 1} = \begin{cases} +1 & \text{for an interstitial} \\ -1 & \text{for a vacancy} \end{cases} ,$$

and $\vec{R} \equiv \vec{r}^{\sigma}(s^{\sigma}) - \vec{\tau}_i^{\alpha}$, and the set $\{\vec{\tau}_i^{\alpha}\}$ represents the positions of the defects, $\mu$ is a Lamé coefficient, and $\dot{\vec{r}}^{\sigma} \equiv d\vec{r}^{\sigma}/ds$. The possible configurations of a loop extending from $\vec{r}\,'$ to $\vec{r}$ and being of length $s^{\sigma}$ can be obtained via the Green's function[12] (up to a proportionality factor)

$$G(\vec{r},s^{\sigma};\vec{r}\,',0;\{\vec{\tau}_i^{\alpha}\}) = \int_{\vec{r}\,',s^{\sigma}=0}^{\vec{r},s^{\sigma}} d[r(s^{\sigma})]\exp\left[-\int_0^{s^{\sigma}} ds \left[\frac{m_{\sigma}}{2}(\dot{\vec{r}}^{\sigma})^2 + \frac{1}{kT}V_{\rm rep}^{dp}(\vec{r},\{\vec{\tau}_i^{\alpha}\}) \right.\right.$$

$$\left.\left. + \frac{1}{kT}\sum_{\{\vec{\tau}_i^{\alpha}\}} v_{\sigma}^{dp}(\vec{r}^{\sigma}(s),\vec{b}^{\sigma},\{\vec{\tau}_i^{\alpha}\}) + \frac{s}{s^*} + \gamma_{\sigma}\right]\right] , \tag{11}$$

where $v_{\sigma}^{dp}$ is defined via Eq. (10) as follows:

$$V^{dp}(\{\vec{b}^{\sigma}\},\{\vec{\tau}_i^{\alpha}\}) \equiv \sum_{\sigma} \int_{C^{\sigma}} ds^{\sigma} v_{\sigma}^{dp}(\vec{r}^{\sigma}(s^{\sigma}),\vec{b}^{\sigma},\{\vec{\tau}_i^{\alpha}\}) ,$$

and from Eq. (4)

$$\begin{aligned}&\gamma_\sigma(|\vec{r}(s)-\vec{r}\,'|)=\gamma_\sigma^0-\ln[q(|\vec{r}(s)-\vec{r}\,'|)/q_m]\,,\\&\gamma_\sigma^0\equiv(\gamma_\sigma^i-kT\ln q_m)kT\,.\end{aligned}\tag{12}$$

Here $\gamma_\sigma^i$ is the internal energy of the dislocation per step unit $l_0$. It can be considered as a renormalized core energy of the dislocation. $V_{\text{rep}}^{dp}$ represents the hard-core repulsion between the point defects and the dislocation for $\vec{r}^{\,\sigma}\in\{\vec{\tau}_i^{\underline{\sigma}}\}$. This term must be included because otherwise the degrees of freedom of the system are overcounted. The evaluation of Eq. (11) via the differential equation satisfied by the Green's function is done in Appendix B. There one obtains approximately [see Eq. (B12′)]

$$\begin{aligned}G_\sigma(\vec{r},\vec{r}\,',\{\vec{\tau}_i^{\underline{\sigma}}\})&\equiv\sum_{s^\sigma=1}^{\infty}G(\vec{r},s^\sigma;\vec{r}\,',0;\{\vec{\tau}_i^{\underline{\sigma}}\})\\&\simeq\frac{m_\sigma e^{-\kappa_{rp}R}}{2\pi^{3/2}R}\int_{-\infty}^{\infty}dy\,e^{-y^2}\sum_{\epsilon=\pm1}\Theta(\epsilon\gamma'_\sigma)\exp(-\epsilon\{2m_\sigma[iy/(s^*/2)^{1/2}+\gamma'_\sigma]\}^{1/2}R)\,.\end{aligned}\tag{13}$$

Here the following abbreviations have been introduced: $R=|\vec{r}-\vec{r}\,'|$, $\gamma'_\sigma\equiv\gamma_\sigma^0+\delta\gamma_\sigma$, and

$$\begin{aligned}\delta\gamma_\sigma(\{\vec{\tau}_i^{\underline{\sigma}}\in\Omega'_d\})\equiv&-\frac{\alpha^2}{2m_\sigma}\frac{\pi}{\Omega'_d}\frac{8}{3r_0}(b^\sigma)^2\sum_{\{\vec{\tau}_i^{\underline{\sigma}}\}}g_0(\vec{\tau}_i^{\sigma}/R'_d)\\&-\frac{3}{2}\frac{\alpha^2}{m_\sigma}\frac{\pi}{\Omega'_d}(b^\sigma)^2\sum_{\{\vec{\tau}_i^{\underline{\sigma}}\neq\vec{\tau}_{i'}^{\underline{\sigma}}\}}\frac{\epsilon_i^{\underline{\sigma}}\epsilon_{i'}^{\underline{\sigma}'}\cos^2(b^\sigma,\vec{n}_{\vec{\tau}_i^{\underline{\sigma}}-\vec{\tau}_{i'}^{\underline{\sigma}'}})}{|\vec{\tau}_i^{\underline{\sigma}}-\vec{\tau}_{i'}^{\underline{\sigma}'}|}g_{\text{rep}}(\{\vec{\tau}_i^{\underline{\sigma}}\})\\&\times g_1\left[\frac{\vec{\tau}_i^{\underline{\sigma}}}{R'_d},\frac{\vec{\tau}_{i'}^{\underline{\sigma}'}}{R'_d}\right]\exp(-\kappa_r|\vec{\tau}_i^{\underline{\sigma}}-\vec{\tau}_{i'}^{\underline{\sigma}'}|)\,,\end{aligned}\tag{14}$$

where $\alpha^2=(3\mu\Omega_0/2\pi kT)^2$ represents the intrinsic coupling constant, $\vec{n}_{\vec{\tau}}\equiv\vec{\tau}/\tau$, $R'_d=[(3/4\pi)\Omega'_d]^{1/3}$, and $g_0$ and $g_1$ are geometrical factors satisfying $g_0(0)=g_1(0,0)=1$, and $g_0(1)\simeq0$, $g_1(1,1)\simeq0$. $\Omega'_d$ is of the order of $\Omega_d$ and Eqs. (13) and (14) apply to all defects which are located within $\Omega'_d$. The first term of Eq. (14) represents the modification of the chemical potential of the point defects and the second term their mutual interaction. It is seen that due to the induced interaction the point-defect system develops the properties of a Coulomb plasma with long-range interactions. Before we discuss the significance of the exponential factors in Eqs. (13) and (14), some remarks with respect to the derivation of these equations shall be made.

Equation (14) has been derived by calculating the eigenvalue spectrum of the differential operator determining the Green's function given by Eq. (11), as a function of the second and third term of the argument of the exponential, in perturbation theory up to second order in $\alpha$. For the sake of simplicity Eq. (12), which is derived from Eq. (4), has been taken into account approximately by using instead of the exact bound-state wave functions for the construction of the Green's function plane waves which are confined to $\Omega'_d$. According to Eq. (4) the volume $\Omega'_d$ will be of the order of $\Omega_d$ or slightly larger depending on $\kappa$. The volume $\Omega_d$ is obtained subject to the condition that $\gamma'_\sigma<0$ holds, because this implies liquid properties and is certainly a necessary condition that a dislocation loop is mobile. $\Omega_d$ must then be determined self-consistently over the radius of gyration of the dislocation loop in the volume $\Omega'_d$.

If $V_{\text{rep}}^{dp}$ in Eq. (11) is ignored, then the factor $g_{\text{rep}}(\{\vec{\tau}_i^{\underline{\sigma}}\})$ and the exponential factor in Eq. (14) must be replaced by 1. In this case, rather long-range interactions are induced by the dislocation loops and an instability of the point-defect system to condense into clusters of defects of equal type is obvious. This will lead to a breakdown of perturbation theory as explained in Appendix B. Taking $V_{\text{rep}}^{dp}$ into account produces the factor $g_{\text{rep}}(\{\vec{\tau}_i^{\underline{\sigma}}\})$ which vanishes whenever the defects try to form clusters because the dislocation gets expelled from such regions. The physical significance of $V_{\text{rep}}^{dp}$ has to be understood as follows. In order to count the degrees of freedom of the system correctly those configurations where a point defect gets absorbed by the dislocation loop belong to a sector in phase space with one defect less, etc. On the other hand, we have just introduced the point defects in order to allow the dislocation to move nonconservatively. Absorption and emission of point defects is therefore an intrinsic property of the model, and is taken into account over $s^*$ which guarantees that the dislocation can display all its possible configurations. Because Eqs. (13) and (14) are obtained (without the exponential decay factors) by holding all point-defect positions fixed and integrating over the configurations of the dislocation this important constraint is violated. Taking the constraint into account will have two consequences. First, the interaction between two point defects will not sample all configurations of the dislocation loop due to the finite lifetime of the defects and thus will diminish in the mean. Second, if a point defect moves or is absorbed at one place and emitted at some other place, e.g., in the process of a climbing motion of the dislocation, then its interaction with another point defect, which moves and suffers a similiar recycling, will get a stochastic character due to retardation for defects which are rather far apart. Because the induced interaction between two defects which are rather far apart gets pretty small it must result from a cancellation process over many dislocation configurations, which can only be reached over many intermediate point-defect configurations. One expects that over the time two defects have well-defined positions, only a small number of paths entering Eq. (11) will contribute. In Eq. (14) this effect is taken into account by means of the exponential decay factor. Let us point out that even if it is assumed that the scattering centers represented by $V^{dp}_{\text{rep}}$ in Eq. (11) attribute a stochastic character to the wave functions of the related eigenvalue problem, from which Eq. (11) is calculated, this seems not to be sufficient to produce the exponential decay factor of Eq. (14). The exponential factor in front of Eq. (13), can however, be obtained this way. From this discussion it follows that it is reasonable to assume that $\kappa_{rp}$ and $\kappa_r$ in Eqs. (13) and (14) will be proportional to the point-defect densities. Their dependence on the mobility of the point defects via retardation will be such that they increase with increasing mobility.

The partition function of a closed loop with Burgers vector $\vec{b}^{\sigma}$ is obtained from Eq. (13) by means of the limiting procedure

$$Z_\sigma(\{\vec{\tau}_i^{\sigma}\})=\frac{1}{\Omega_0}\int d^3r\, G_\sigma(\vec{0},\vec{r},\{\vec{\tau}_i^{\sigma}\}) \,, \tag{15}$$

where the integral is performed over the volume $\Omega_0$ of a unit cell.[12] This expression guarantees that the loop is closed. Integration of Eq. (15) yields

$$Z_\sigma(\{\tau_i^{\sigma}\})=\frac{3m_\sigma}{2\pi^{3/2}r_0^3}\int_{-\infty}^{\infty} dy\, e^{-y^2}\sum_{\epsilon=\pm 1}\Theta(\epsilon\gamma'_\sigma)f(-\epsilon\{2m_\sigma[iy/(s^*/2)^{1/2}+\gamma'_\sigma]\}^{1/2}) \,, \tag{16}$$

where

$$f(z)\equiv z^{-2}[1-e^{-zr_0}(1+zr_0)]\geq 0 \,. \tag{17}$$

Integration of Eq. (16) can be done by means of steepest-descent methods. As has been pointed out earlier, the problem which actually should be solved is that of a branched loop. The partition function to that problem will be approximated by a product over $n_b$ dislocation strings. Using a slight generalization of the theory developed so far to the case where $\Delta N_V=N_V-N_V(T_{\text{SC}})$ vacancies are created or annihilated, one obtains

$$\begin{aligned}Z_{\Delta N}(\{\vec{\tau}_i^{\sigma}\})&\simeq\exp\left[-\frac{\lambda'}{2}\Omega_0^2(\Delta N_V)^2(\Omega'_d)^{-1}/kT\right]\prod_{\sigma=1}^{n_b}\int_{s_{\Delta N_V}}^{\infty} ds\,\exp(-s\gamma'_\sigma-s^2/2s^*_{\Delta N_V})\\&=\exp\left[-\frac{\lambda'}{2}\Omega_0^2(\Delta N_V)^2(\Omega'_d)^{-1}/kT\right]\prod_{\sigma=1}^{n_b}\left[\frac{\pi s^*_{\Delta N_V}}{2}\right]^{1/2}\exp(\gamma'^2_\sigma s^*_{\Delta N_V}/2)\\&\qquad\times[1-\phi((s_{\Delta N_V}+s^*_{\Delta N_V}\gamma'_\sigma)/(2s^*_{\Delta N_V})^{1/2})] \,.\end{aligned} \tag{18}$$

Equation (18) applies to the case that the dislocation loops are confined to $\Omega'_d$ and its surroundings as explained below Eq. (8), and

$$s_{\Delta N_V}\simeq 2\,|\,\Delta N_V\,|\,\Omega_0/(n_b l_0 b^{\sigma} R'_d) \tag{19}$$

takes approximately into account the constraint given by Eq. (1). Furthermore, $s^*_{\Delta N_V}$ is calculated over Eq. (5). $\phi(Z)$ represents the probability integral.[16] The main property of this expression used to support the following arguments is that it is increasing monotoneously with $\gamma'_\sigma$ decreasing. This follows immediately from the well-known properties of the probability integral. The total partition function of the problem outlined in Sec. II can now be represented in the form (suppressing kinetic terms)

$$Q(\Omega,T,V_f)=\sum_{N_V \gtrless N_V(T_{\mathrm{SC}})} e^{-\mu_V \Delta N_V/kT}\frac{1}{N_V!}\left[\delta_{N_V,N_V(T_{\mathrm{SC}})}Z_0'(\Omega,T,V_f) + \sum_{\{\vec{\tau}_i^{\alpha}\}_{N_V}} e^{-V_{\mathrm{dir}}^{pp}(\{\vec{\tau}_i^{-}\})/kT} Z_{\Delta N_V}(\{\vec{\tau}_i^{-}\})\right], \tag{20}$$

where

$$Z_0'(\Omega,T,V_f)=\sum_{\{\vec{\tau}_i^{-}\}_{N_V(T_{\mathrm{SC}})}} \exp[-V_{\mathrm{dir}}^{pp}(\{\vec{\tau}_i^{-}\})/kT] \tag{21}$$

represents the canonical partition function of the vacancy gas (without activated nucleation center) and $V_{\mathrm{dir}}^{pp}(\{\vec{\tau}_i^{-}\})$ takes account of the direct interaction between the vacancies. The second term of Eq. (20) takes care of a single nucleation center where it is assumed that the excitations of the nucleation center (liquid droplet) are such that interstitials due to energetical reasons are condensed in dislocation loops. The problem is now defined by Eqs. (18)–(21), (5), and (6). Owing to the fact that a number of quantities like $\Omega_d$, $n_V(r)$, and $s_{\Delta N_V}^*$ must be obtained self-consistently, the statistical mechanics of the present problem is rather complex. The qualitative features of the problem can, however, be easily understood. It should be observed that each term of Eq. (20) must be multiplied in principle with the partition function due to the phonon excitations defined on the defect lattice supplemented by a dilute gas of small fluctuating dislocation loops to be discussed at the end of Sec. IV.

At very low temperatures it follows from Eqs. (5) and (6) that $s^*(T)\sim e^{-\Delta/kT}$ holds. Accordingly, for $T\rightarrow 0$, $Z_{\Delta N_V}\rightarrow 0$ will be obtained as follows from Eq. (18) and the fact that for $T\rightarrow 0$, $|\delta\gamma_\sigma|(s^*)^{1/2}\rightarrow 0$ holds. In Eq. (20) then only the $Z_0'$ term survives. It should be noted that despite $\delta\gamma_\sigma\sim -1/T^2$, no condensation phenomena of the vacancies takes place, because the main saddle point of $Q(\Omega,T,V_f)$ is given by the $Z_0'$ term. The saddle point of the second term of Eq. (20) is realized for the condensed phase of the vacancies ($\gamma_\sigma'<0$) for $T\rightarrow 0$, and therefore describes a metastable state within the present model. In fact, it describes a smooth extension of the liquid-droplet state illustrated in Fig. 1(b) to $T<T_{m_1}$, and for $T$ approaching $T_{m_1}$ from below it serves as an activated nucleation center of the liquid phase.

Consider now what happens when the system approaches $T_{m_1}$ from below. Because $s^*(T)$ increases with increasing temperature according to Eqs. (5) and (6), the second term of Eq. (20) will grow in magnitude. However, because $\delta\gamma_\sigma\sim -1/T^2$ the intrinsic coupling constant of the induced point-defect interaction decreases. This implies that the saddle point of this term describes a two-phase coexistence state, which consists of the condensed phase of vacancies, which represents the liquid droplet, and a gas phase, which represents the solid domain. Assume that at $T_{m_1}$ the saddle point of the first and second term of Eq. (19) are of equal magnitude and for $T>T_{m_1}$ the saddle point of the second term dominates. Then at $T_{m_1}$ a first-order phase transition occurs into a two-phase state consisting of the liquid droplet surrounded by solid material. It is important to note that this is a first-order transition absorbing heat and that the growth of the initial nucleus of radius $r_l^*$ to its final radius $R_g(T)$ as illustrated in Fig. 1(b) is accomplished with that heat. If it is assumed that $\Delta\sim kT_{m_1}$, then further growth of $s^*$ for $T>T_{m_1}$ is only guaranteed if the free volume, given by

$$\int_{\Omega_d} d^3r\, n_V(r)\Omega_{0,V}$$

in the range of the dislocation, is increasing. On the other hand, the term $\delta\gamma_\sigma\sim -1/T^2$ will counteract this tendency partly because with diminishing coupling constant it will succeed in driving a liquid-gas transition. This situation is modified when the additional terms in Eq. (19) with $\Delta N_V>0$ are taken into account. The additional vacancies generated will increase $s_{\Delta N_V}^*$, and will also increase the density of the vacancy gas, which will suppress the liquid-gas transition mentioned above. It is reasonable to assume therefore that this process will come to a halt once the liquid domain extends over the whole sample. If the corresponding temperature is identified with $T_{m_2}$ then the analytical model constructed in this section agrees with the qualitative model outlined in Sec. II and leads to the state depicted in Fig. 2(b).

It should be pointed out that the effective coupling constant of the point-defect system depends in a rather complicated way on $s_{\Delta N_V}^*$ and the intrinsic coupling constant of the term $\delta\gamma_\sigma$ given by Eq. (14). It is the effective coupling constant on which the discussion of Sec. II is based. Furthermore, it follows from Eq. (5) that for $\Omega_d \to \Omega$, $s^*_{\Delta N_V} \sim N_V$, and from Eq. (18) that the free energy of the canonical ensemble labeled by $\Delta N_V$ has the usual extensivity property. Notice that when $\lambda'$ is sufficiently small, the growth of the initial nucleus of radius $r_l^*$ may only stop once the whole specimen is liquified. In that case no interval melting is observed. As will be discussed in more detail in Sec. IV, the operation of a Bardeen-Herring source[17] may imply that the argument of the prefactor in Eq. (18) has to be substituted by the first term of Eq. (8). Also in that case the initial droplet will spread over the whole specimen. Because $\lambda'$ will be proportional to the Lamé constant $\mu$ but will also depend on the configurations of the dislocation loops in the droplet, an evaluation of the instabilities mentioned above is rather difficult. On account of this discussion it seems possible, however, that depending on $\lambda'$ there will be materials which show melting in a temperature interval when surface coated and others which melt at a sharp temperature.

The present model can also be used to discuss the crystallization phenomena in supercooled droplets. $T_{f_1}$ marks then the temperature where a solid nucleus is created, e.g., at the surface coating of the droplet, and corresponds to $T_{m_2}$. For $T > T_{f_2}$ one may have two-phase coexistence and annihilation of free volume, taken into account by the $\Delta N_V < 0$ terms in Eq. (20). This process comes to halt at $T_{f_2}$ where the vacancies (or free volume) of the remaining liquid domain suffer a liquid-gas transition and the whole sample solidifies. $T_{f_2}$ corresponds naturally to $T_{m_1}$. The problem under which conditions $T_{f_2} < T_{f_1}$ holds is discussed in Sec. II.

## IV. DISCUSSION AND CONCLUSION

The main idea advocated in this paper is that melting of a solid is not simply a problem of calculating dislocation configurations, where the mobility properties of the system can be ignored completely, but that the latter properties are most significant. Nucleation of the liquid phase at an open boundary of a solid as mostly observed is under these premises favorable not only because the system is there free to expand readily, but because the surface acts also as a source of free volume and reduces activation barriers by means of mirror forces. Nucleation of a liquid droplet in the bulk of a specimen with open surfaces suffers, under these conditions, two handicaps. First, a current of vacancies from the surface to the droplet has to be set up in order to provide the free volume. However, the force driving this current comes only into existence once a nucleus has been formed and this implies a rather large free-energy barrier to be overcome as explained in Ref. 12. Second, mirror forces cannot be exploited. Obviously in such a problem the boundary of the system does not play a secondary role, like providing a free-energy contribution of the order of $\Omega^{2/3}$, and may therefore be ignored in the thermodynamic limit, but is of primary importance in determining the bulk properties.

The main assumption underlying the deductions presented in this paper is that once the specimens are surface coated, the free-volume content $V_f$ of the system plays the role of a thermodynamic variable. Practically, this implies that the experiments are done on a time scale, where vacancy diffusion through the surface coating is small. Theoretically, it implies that creation and annihilation of free volume during superheating and supercooling, respectively, are strongly coupled to the generation of dislocation loops whose dilatational and compressional stress fields cannot be screened out by the system. The simple analytical model presented to describe the statistical mechanics of the problem predicts for a given solid sample that melting is initiated at a temperature $T_{m_1}$ through a discontinuous phase transition leading to a liquid droplet and a solid region. At a temperature $T_{m_2}$ the sample is transformed into liquid. In the temperature interval $[T_{m_1}, T_{m_2}]$ one has two-phase coexistence with the liquid domain growing for $T$ increasing (see Fig. 3). Because the fractional change of vacancies from the solid to the liquid state in typical metals is about $10^{-4}$, there the initial size of a nucleus can be estimated to be of the order of $10^{-4}\Omega$ with $T_{m_1} > T_m$. For increasing sample size $\Omega$, an increasing number of nucleation centers located closely to the surface of the system can be expected. The probability that an initial nucleus will touch the surface and perforate a hole into it will therefore increase and accordingly the extension of the interval $[T_{m_2}, T_{m_1}]$ will decrease. It can also be expected that with increasing $\Omega$, $T_{m_1}$ gets reduced and may approach $T_m$. This is a consequence of the fact that fluctuations in the number of vacancies at a possible nucleation site get larger with increasing $\Omega$.

In a typical experiment usually not just one specimen is studied but a whole collection of them. A statistical average over a distribution of specimens of varying size and therefore different amounts of free volume and nucleation centers should correspond to an average over various heat-absorption curves of the kind depicted in Fig. 4. The average over such curves will produce a smooth curve which is reasonably differentiable, allowing the calculation of the specific heat of the averaged samples and thus may conform to what is observed in the experiments.[1]

The discussion of the crystallization of supercooled samples follows the same line of thought in the interval $[T_{f_1}, T_m]$ with $T_{f_1} < T_m$ (see Fig. 3). The transition here, however, may be relatively sharp if the crystalline nucleus grows into a structure that is perforated with holes and channels and in this way takes care of the free volume.

The nucleation mechanisms have not been discussed so far. For a supercooled system the surface coating may provide possible nucleation centers. The other possibility is that a nucleus is formed over a Bardeen-Herring—type source,[17] which is a well-known mechanism in quenched materials to get rid of vacancies. Such a mechanism, however, will not be operative in a supercooled liquid if the free volume is present in a finely dispersed form. Furthermore, the intimate coupling of the free volume, in the form of vacancies or fractions of vacancies, to the dislocation motion makes it suggestive that the free volume below $T_{\mathrm{SC}}$ is successively and uniformly transferred according to Eq. (1) into the dislocation system. Ignoring for the present the formation of a solid nucleus at the boundary, the end point of such processes may be a continuous transition[3] at $T_2^*$ into a solid phase with a network of dislocations and free volume grown in. In order to check the viability of this idea the properties of the present model have to be studied in its domain of metastability.

With respect to the nucleation mechanisms in the superheated state, the possible operation of a Bardeen-Herring—type source[17] must also be taken into account, in particular for the case $N_V(T_{\mathrm{SC}}) \rightarrow 0$. In the latter case the dislocation loop representing the nucleation center should also provide the free volume which guarantees its mobility. The formation of such a source requires first the excitation of a big number of vacancy interstitial pairs. Then the interstitials are condensed into a dislocation loop forming the liquid droplet of size $\Omega_d$. This droplet acts now as a Bardeen-Herring source[17] if it expels concentric rings of dislocation which climb to the surface by generating a flux of vacancies which is absorbed by the droplet. If the dislocation rings are not expelled through the surface, then the elastic energy is bounded by the left-hand side of Eq. (8) and, according to the theory developed in Sec. III, the initial nucleus may spread at $T_{m_1}$ over the whole specimen. Expelling the rings from the domain $\Omega_d$ implies also that $s_{\Delta N_V} \equiv 0$ is used instead of Eq. (19). Consequently, this seems to be a much more favorable case than the one assumed in Sec. III, where the free volume-generating loop was supposed to be confined to the liquid droplet and its surroundings. The viability of the Bardeen-Herring mechanism as explained here depends on the order of magnitude of the activation barriers to form the initial nucleus and to expel dislocation rings to the surface. Although this problem has so far not been studied in detail it is reasonable to assume that $T_{m_1} > T_m$ holds because the activation barrier in the bulk must be larger than at an open surface. The transition, however, may be rather sharp if the initial liquid droplet is unstable against growth via the Bardeen-Herring mechanism as explained above. In the latter case the results obtained by Gleiter, Perepezko, and Smidoda[1] must be interpreted as an average over an ensemble of samples with individually well-defined transition temperatures.

Finally we consider the possibility that no nucleation mechanism of the dislocation type is operative in the solid-liquid transition. In that case only the first term of Eq. (20) contributes. As has already been pointed out this term in principle should be supplemented by the phonon and small-dislocation-loop partition function. The vacancy problem alone could be studied by means of a lattice-gas model which, due to the long-range interaction $V_{\mathrm{dir}}^{pp}(\{\vec{\tau}_i^{\sigma}\})$, would lead to a van der Waals equation of state.[18] A gas-liquid transition within that system would not lead to a gain in free energy if it is not assumed that such a process liberates additional degrees of freedom. Taking the phonon partition function into account, such a feature would be provided by a softening of the phonon spectrum in the domain of vacancy condensation. Propagation of soft-lattice modes into the bulk can, however, only occur either via a shear instability and the multiplicative processes of dislocations invoked earlier or over the generation of many small dislocation rings. Such a gas of dipolar rings may be looked at as a system of ballistic anharmonic phonons. Its instability against condensation would then lead to a macroscopic shear instability and liquid-type properties of the sample. In cases where no nucleation mechanism works, it can be imagined that the solid-liquid transition occurs over such a process in a continuous fashion at $T_1^*$ (see Fig. 3). On approaching $T_1^*$ from below, liquid-type properties would then be realized sucessively from small to large scales. A similar interpretation of the continuous transition at $T_2^*$ postulated by Schneider *et al.*[3] has been given in Ref. 19. There it has been claimed that in situations where no nucleation mechanism works solid properties will be realized successively from small to large scales on approaching $T_2^*$ from above. In conclusion, we state that the phase diagram of surface-coated systems may be of the type depicted in Fig. 3 whose two-phase regime is bordered by two critical points (which attract those trajectories where no nucleation mechanism is operative) and where melting and freezing may occur in temperature intervals. Figure 3 has been obtained by mapping the problem outlined in Secs. II and III onto a van der Waals equation of state. With the use of the fact that the effective interaction between vacancies vanishes for $T \to 0$ and runs through a maximum at some temperature $T_\Delta$, which scales with $\Delta(\Omega)$ as defined in Eq. (6), it can be shown that a phase diagram with two critical points must arise.[20]

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## APPENDIX A: THE DISLOCATION-INDUCED POINT-DEFECT INTERACTION

The interaction between a spherical inclusion of radius $r_0$ and a stress field $\sigma_{\alpha\beta}(\vec{r})$ is given by[13]

$$W(\vec{r}) = -\frac{4\pi}{3} r_0^3 \delta \sigma_{\alpha\alpha}(\vec{r}) , \qquad \text{(A1)}$$

where $\delta = 3\epsilon(1-\nu)/(1+\nu)$, $\nu$ is the Poisson modulus, and $\epsilon$ is a number which determines the effective radius of the point defect, i.e.,

$$r_{\text{eff}} = r_0(1+\epsilon) .$$

Obviously $\epsilon > 0$ for interstitials and $\epsilon < 0$ for vacancies.

The trace of the stress-field tensor of a dislocation with Burgers vector $\vec{b}$ can be represented in the form of a contour integral[14]

$$\sigma_{\alpha\alpha}(\vec{r}) = \frac{\mu}{2\pi} \frac{1+\nu}{1-\nu} \oint \frac{1}{R^2} \vec{b} \cdot [\vec{n}_{\vec{R}} \times \dot{\vec{r}}'] ds , \qquad \text{(A2)}$$

where

$$\vec{n}_{\vec{R}} \equiv [\vec{r} - \vec{r}'(s)]/R, \quad R \equiv |\vec{r} - \vec{r}'(s)| ,$$

$$\dot{\vec{r}}' \equiv \frac{d}{ds} \vec{r}'(s) ,$$

and $\mu$ is a Lamé constant. The interaction between a network of dislocations and an ensemble of point defects can now be represented in the form of Eq. (10).

In Ref. 12 it has been shown that the Hamilton operator which is needed to calculate the Green's function of a dislocation loop with Burgers vector $\vec{b}^\sigma$, subject to self-interactions and interactions of the type given by Eq. (10), is obtained in the form

$$H_\sigma = \frac{1}{2m_\sigma} \left[ \frac{1}{i} \vec{\nabla} - \vec{\Omega}_\sigma(\vec{r}) - \kappa \vec{b}^\sigma \times \vec{r} - \frac{1}{i} \vec{\Phi}_\sigma(r, \{\vec{\tau}_i^\sigma\}) \right]^2 , \qquad \text{(A3)}$$

where

$$\vec{\Phi}_\sigma(\vec{r}, \{\vec{\tau}_i^\sigma\}) \equiv \frac{1}{kT} \frac{3\Omega_0}{2\pi} \mu \times \sum_{\{\vec{\tau}_i^\sigma\}} \epsilon_i^\sigma \left[ \vec{b}^\sigma \times \frac{\vec{n}_{\vec{r}-\vec{\tau}_i^\sigma}}{|\vec{r} - \vec{\tau}_i^\sigma|^2} \right] ,$$

$$\operatorname{div} \vec{\Phi}_\sigma = 0 . \qquad \text{(A4)}$$

Here $\vec{\Omega}_\sigma(\vec{r})$ is a stochastic vector potential representing the effect of the long-range Biot-Savart interaction,[12] and $\kappa \vec{b}^\sigma \times \vec{r}$ represents a mass constraint and takes care of Eq. (1).

It follows from Eq. (A3) that the mathematical problem of determining the Green's function in the presence of point defects is equivalent to finding the eigenfunctions of a charged particle moving in a vector potential

$$\vec{A}(\vec{r}) = \vec{\Omega}_\sigma(\vec{r}) + \kappa \vec{b}^\sigma \times \vec{r} + \frac{1}{i} \vec{\Phi}_\sigma(\vec{r}, \{\vec{\tau}_i^\sigma\}) ,$$

to which corresponds the "magnetic field"

$$\vec{H} = \vec{\nabla} \times \vec{A}(\vec{r}) = \vec{\nabla} \times \vec{\Omega}_\sigma(\vec{r}) + 2\kappa \vec{b}^\sigma + \frac{1}{i} \frac{3\mu\Omega_0}{2\pi kT} \sum_{\{\vec{\tau}_i^\sigma\}} \epsilon_i^\sigma \left[ \frac{-\vec{b}^\sigma}{|\vec{r} - \vec{\tau}_i^\sigma|^3} + \frac{3 b_\alpha^\sigma (r_\alpha - \tau_{i,\alpha}^\sigma)^2}{|\vec{r} - \vec{\tau}_i^\sigma|^5} \vec{e}_\alpha \right] . \qquad \text{(A5)}$$

Here $\{\vec{e}_\alpha\}$ represents three orthogonal unit vectors. The last term of Eq. (A5) represents the magnetic field of an ensemble of magnetic dipoles of imaginary dipole strength. Note that $\vec{r} = \vec{\tau}_i^\sigma$ corresponds to the absorption of a point defect by the dislocation, and therefore this case must be excluded in the formulas above, otherwise overcounting of degrees of freedom results. In the following we will take care of this effect by adding to $H_\sigma$ a repulsive potential, i.e.,

$$H_\sigma(\vec{r}, s^\sigma) \to H_\sigma(\vec{r}, s^\sigma) + V_{\text{rep}}^{dp}(\vec{r}, \{\vec{\tau}_i^\sigma\}) . \qquad \text{(A3')}$$

## APPENDIX B: EVALUATION OF THE GREEN'S FUNCTION

The differential equation which is satisfied by the Green's function given by Eq. (11) is

$$[\partial/\partial s^{\sigma}+H_{\sigma}(\vec{r},s^{\sigma})]G(\vec{r},s^{\sigma};\vec{r}\,',0,\vec{\Phi}_{\sigma})=\delta(s^{\sigma})\delta^{3}(\vec{r}-\vec{r}\,') \; . \tag{B1}$$

Using the simplifications explained in the main text, we have

$$H_{\sigma}(\vec{r},s^{\sigma})=\frac{1}{2m_{\sigma}}\left[\frac{1}{i}\vec{\nabla}-\frac{1}{i}\vec{\Phi}_{\sigma}(\vec{r},\{\vec{\tau}_{i}^{g}\})\right]^{2}+V_{\text{rep}}^{dp}(\vec{r},\{\vec{\tau}_{i}^{g}\})+\gamma_{\sigma}(\,|\vec{r}-\vec{r}\,'|\,)+s/s^{*} \; . \tag{B2}$$

Here only the dipolar part of the vector potential has been taken into account, and furthermore, $H_{\sigma}$ has been supplemented by two terms obtained from Eqs. (4) and (12).

The Green's function $G_{\sigma}(\vec{r},\vec{r}\,',\{\vec{\tau}_{i}^{g}\})$ defined by Eq. (13) can be represented in the form

$$G_{\sigma}(\vec{r},\vec{r}\,',\{\vec{\tau}_{i}^{g}\})=\sum_{s^{\sigma}=1}^{\infty}\sum_{k}\psi_{k}(\vec{r})\psi_{k}^{*}(\vec{r}\,')\exp[-(\gamma_{\sigma}^{0}+E_{k})s^{\sigma}-(s^{\sigma})^{2}/2s^{*}] \; . \tag{B3}$$

Here $\psi_{k}(\vec{r})$ and $E_{k}$ are obtained from the eigenvalue problem

$$\left[-\frac{1}{2m_{\sigma}}\Delta+\frac{1}{m_{\sigma}}\vec{\Phi}_{\sigma}\cdot\vec{\nabla}-\frac{1}{2m_{\sigma}}\vec{\Phi}_{\sigma}\cdot\vec{\Phi}_{\sigma}+V_{\text{rep}}^{dp}+\ln\left[\frac{q_{m}}{q(r)}\right]\right]\psi_{k}(\vec{r})=E_{k}\psi_{k}(\vec{r}) \; , \tag{B4}$$

and $\{\psi_{k}\}$ is supposed to form a complete set of orthonormal eigenfunctions, i.e.,

$$\sum_{k}\psi_{k}(\vec{r})\psi_{k}^{*}(\vec{r}\,')=\delta^{3}(\vec{r}-\vec{r}\,') \tag{B5}$$

holds. Furthermore, $\gamma_{\sigma}^{0}\to\gamma_{\sigma}^{0}-i\delta$, $\delta>0$, in the case that $s^{*}\to\infty$. At reasonably high temperatures, summation over $s^{\sigma}$ in Eq. (B3) can be substituted by integration and yields

$$G_{\sigma}(\vec{r},\vec{r}\,',\{\vec{\tau}^{g}\})\simeq\sum_{k}\psi_{k}(\vec{r})\psi_{k}^{*}(\vec{r}\,')(s^{*})^{1/2}\left[\frac{\pi}{2}\right]^{1/2}\exp\left[\frac{(\gamma_{\sigma}^{0}+E_{k})^{2}s^{*}}{2}\right][1-\phi((\gamma_{\sigma}^{0}+E_{k})(s^{*}/2)^{1/2})] \; , \tag{B6}$$

where $\phi(z)$ is the probability integral as defined in Ref. 16.

Evaluation of $E_{k}$ and $\psi_{k}(\vec{r})$ is done using perturbation theory starting from $\vec{\Phi}_{\sigma}\equiv 0$, $V_{\text{rep}}^{dp}\equiv 0$. The perturbation operator is then given by

$$\begin{aligned}V_{\sigma}=&\frac{\alpha}{m_{\sigma}}\sum_{\{\vec{\tau}_{i}^{g}\}}\epsilon_{i}^{g}\left[\vec{b}^{\sigma}\times\frac{\vec{n}_{\vec{r}-\vec{\tau}_{i}^{g}}}{|\vec{r}-\vec{\tau}_{i}^{g}|^{2}}\right]\cdot\vec{\nabla}\\&-\frac{\alpha^{2}}{2m_{\sigma}}\sum_{\{\vec{\tau}_{i}^{g}\},\{\vec{\tau}_{i'}^{g'}\}}\epsilon_{i}^{g}\epsilon_{i'}^{g'}\left[\vec{b}^{\sigma}\times\frac{\vec{n}_{\vec{r}-\vec{\tau}_{i}^{g}}}{|\vec{r}-\vec{\tau}_{i}^{g}|^{2}}\right]\cdot\left[\vec{b}^{\sigma}\times\frac{\vec{n}_{\vec{r}-\vec{\tau}_{i'}^{g'}}}{|\vec{r}-\vec{\tau}_{i'}^{g'}|^{2}}\right]+V_{\text{rep}}^{dp}(\vec{r},\{\vec{\tau}_{i}^{g}\}) \; ,\end{aligned} \tag{B7}$$

where

$$\alpha=\frac{3\mu\Omega_{0}}{2\pi kT} \; .$$

It is well known that $V_{\text{rep}}^{dp}$ which is of a hard-core type cannot be taken into account via simple perturbation theory. We will come back to that point later. Setting $V_{\text{rep}}^{dp}\equiv 0$ presently and applying second-order perturbation theory using $V_{\sigma}$, one obtains

$$\begin{aligned}
E_k=\frac{k^2}{2m_\sigma}&+\frac{i\alpha}{m_\sigma}\sum_{\{\vec{\tau}_i^{\sigma}\}}\epsilon_i^{\sigma}\frac{1}{\Omega_d'}\int d^3r\left[\vec{\mathrm{b}}^{\sigma}\times\frac{\vec{\mathrm{n}}_{\vec{\mathrm{r}}-\vec{\tau}_i^{\sigma}}}{|\vec{\mathrm{r}}-\vec{\tau}_i^{\sigma}|^2}\right]\cdot\vec{\mathrm{k}}\\
&-\frac{\alpha^2}{2m_\sigma}\sum_{\{\vec{\tau}_i^{\sigma}\},\{\vec{\tau}_{i'}^{\sigma'}\}}\epsilon_i^{\sigma}\epsilon_{i'}^{\sigma'}\frac{1}{\Omega_d'}\int d^3\vec{\mathrm{r}}\left[\vec{\mathrm{b}}^{\sigma}\times\frac{\vec{\mathrm{n}}_{\vec{\mathrm{r}}-\vec{\tau}_i^{\sigma}}}{|\vec{\mathrm{r}}-\vec{\tau}_i^{\sigma}|^2}\right]\cdot\left[\vec{\mathrm{b}}^{\sigma}\times\frac{\vec{\mathrm{n}}_{\vec{\mathrm{r}}-\vec{\tau}_{i'}^{\sigma'}}}{|\vec{\mathrm{r}}-\vec{\tau}_{i'}^{\sigma'}|^2}\right]\\
&-\left[\frac{2\alpha^2}{m_\sigma}\right]\mathscr{P}\sum_{k'}\frac{1}{\Omega'^2_d}\frac{1}{k^2-k'^2}\sum_{\{\vec{\tau}_i^{\sigma}\},\{\vec{\tau}_{i'}^{\sigma'}\}}\epsilon_i^{\sigma}\epsilon_{i'}^{\sigma'}\int d^3r\int d^3r'\left[\vec{\mathrm{b}}^{\sigma}\times\frac{\vec{\mathrm{n}}_{\vec{\mathrm{r}}-\vec{\tau}_i^{\sigma}}}{|\vec{\mathrm{r}}-\vec{\tau}_i^{\sigma}|^2}\cdot\vec{\mathrm{k}}\right]\\
&\times\left[\vec{\mathrm{b}}^{\sigma}\times\frac{\vec{\mathrm{n}}_{\vec{\mathrm{r}}'-\vec{\tau}_{i'}^{\sigma'}}}{|\vec{\mathrm{r}}'-\vec{\tau}_{i'}^{\sigma'}|^2}\cdot\vec{\mathrm{k}}'\right]e^{i(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\cdot(\vec{\mathrm{r}}-\vec{\mathrm{r}}')}\,,
\end{aligned}\tag{B8}$$

where $\Omega_d'=(4\pi/3)R_d'^{\,3}$ is the normalization volume, and $\mathscr{P}$ projects the principal value. Owing to the logarithmic term in Eq. (B4), the unperturbed problem will have only bound-state eigenfunctions for $E_k$ less than the energy barrier represented by that term. For the sake of simplicity, we will take care of this energy barrier by using plane waves normalized to the volume $\Omega_d'>\Omega_d$. Integrations in Eq. (B8) are rather tedious and in the following only the result will be given:

$$\begin{aligned}
E_k\simeq k^2/2m&-\frac{4\pi}{3}i\frac{\alpha}{m_\sigma}\frac{1}{\Omega_d'}\sum_{\{\vec{\tau}_i^{\sigma}\}}\epsilon_i^{\sigma}\vec{\mathrm{k}}\times\vec{\mathrm{b}}^{\sigma}\cdot\vec{\tau}_i^{\sigma}-\frac{\alpha^2}{2m_\sigma}\frac{\pi}{\Omega_d'}\frac{8}{3r_0}(b^{\sigma})^2\sum_{\{\vec{\tau}_i^{\sigma}\}}g_0\left[\frac{\vec{\tau}_i^{\sigma}}{R_d'}\right]\\
&-\frac{3\alpha^2}{2m_\sigma}\frac{\pi}{\Omega_d'}(b^{\sigma})^2\sum_{\{\vec{\tau}_i^{\sigma}\neq\vec{\tau}_{i'}^{\sigma'}\}}\epsilon_i^{\sigma}\epsilon_{i'}^{\sigma'}\frac{\cos^2(\vec{\mathrm{b}}^{\sigma},\vec{\mathrm{n}}_{\vec{\tau}_i^{\sigma},\tau_{i'}^{\sigma'}})}{|\vec{\tau}_i^{\sigma}-\vec{\tau}_{i'}^{\sigma'}|}g_1\left[\frac{\vec{\tau}_i^{\sigma}}{R_d'},\frac{\vec{\tau}_{i'}^{\sigma'}}{R_d'}\right]\\
&+\frac{\pi^2\alpha^2}{m_\sigma}\frac{(\vec{\mathrm{b}}^{\sigma}\times\vec{\mathrm{k}})^2}{k}\frac{1}{\Omega_d'}\sum_{\{\vec{\tau}_i^{\sigma},\vec{\tau}_{i'}^{\sigma'}\}}\epsilon_i^{\sigma}\epsilon_{i'}^{\sigma'}\left[J_0(2k\,|\vec{\tau}_i^{\sigma}-\vec{\tau}_{i'}^{\sigma'}|)-\left[\frac{2(\vec{\mathrm{b}}^{\sigma}\times\vec{\mathrm{k}}\cdot\vec{\mathrm{n}}_{\vec{\mathrm{t}}_i^{\sigma}\tau_{i'}^{\sigma'}})^2}{(\vec{\mathrm{b}}^{\sigma}\times\vec{\mathrm{k}})^2}-1\right]J_2(2k\,|\vec{\tau}_i^{\sigma}-\vec{\tau}_{i'}^{\sigma'}|)\right]\\
&\times g_2\left[\frac{\tau_i^{\sigma}}{R_d'},\frac{\tau_{i'}^{\sigma'}}{R_d'}\right]+O(k^3)\,,
\end{aligned}\tag{B9}$$

where

$$\begin{aligned}
g_0\left[\frac{\vec{\tau}}{R_d'}\right]=1-\frac{3r_0}{8}\frac{\tau}{R_d'^{\,2}-\tau^2}&\left\{[1+\cos^2(\vec{\mathrm{b}}^{\sigma},\vec{\tau})]\left[1+\frac{R_d'}{\tau}+\frac{R_d'^{\,2}-\tau^2}{2\tau^2}\ln\frac{R_d'+\tau}{R_d'-\tau}\right]\right.\\
&\left.+\tfrac{1}{2}[1-3\cos^2(\vec{\mathrm{b}}^{\sigma},\vec{\tau})]\left[1+\frac{1}{2}\left[\frac{R_d'}{\tau}+\frac{R_d'^{\,2}}{\tau^2}\right]-\frac{1}{4}\left[\frac{R_d'^{\,2}-\tau^2}{\tau^2}\right]\ln\frac{R_d'+\tau}{R_d'-\tau}\right]\right\},
\end{aligned}\tag{B10}$$

and $J_n(z)$ is the Bessel function of $n$th order. A difficulty in evaluating the integrals in Eq. (B8) is that for finite $\Omega_d'$ these integrals are (owing to the variables $\{\vec{\tau}_i^{\sigma}\}$) position dependent. This position dependence has only been calculated for the second and third term of Eq. (B9) explicitly. For the other factors, one obtains

$$\lim_{R_d'\to\infty}g_{1(2)}\left[\frac{\tau}{R_d'},\frac{\tau'}{R_d'}\right]=1,\quad \tau<\infty\,,\quad \tau'<\infty\,. \tag{B11}$$

Furthermore, Eq. (B9) applies only for such defects which are located within the domain $\Omega_d'$. Induced interactions for point defects outside that domain are much weaker because they get reduced by powers of their distance to the liquid domain $\Omega'_d$. It follows then from Eqs. (B9)–(B11) that for $\Omega'_d \to \infty$ and a finite number of defect centers $E_k = k^2/2m_\sigma$ holds. In this case only phase-shifted wave functions arise. Note that the second and fifth terms of Eq. (B9) are proportional to $k$. The next quantity to be calculated by perturbation theory is the wave function. Because this will lead to rather complicated expressions which we are not able to manipulate further, wave-function corrections will be ignored presently but discussed on a qualitative level later. Within that approximation one obtains for Eq. (B6)

$$G_\sigma(\vec{r},\vec{r}',\{\vec{\tau}^\alpha\}) \simeq \frac{1}{(2\pi)^3} \int d^3k\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} s^{*1/2} \left[\frac{\pi}{2}\right]^{1/2} \exp\left[\frac{s^*}{2}(\gamma_\sigma^0+E_k)^2\right] [1-\phi((\gamma_\sigma^0+E_k)\sqrt{s^*/2})] \,. \tag{B12}$$

Observing that Eq. (B9) implies that $E_{\vec{k}} = E^*_{-\vec{k}}$ holds, one notes that $G_\sigma(\vec{r},\vec{r}',\{\vec{\tau}^\alpha\})$ is real. The integration of Eq. (B12), however, is rather difficult due to the angular dependence of the second and fifth terms of $E_k$. Because the second term of Eq. (B9) represents the leading correction in the expansion parameter $\alpha$, it is important to notice that this term contributes only for nonuniform point-defect distributions, that is, where

$$\sum_{\{\vec{\tau}_i^\alpha\}} \epsilon_i^\alpha \vec{\tau}_i^\alpha = 0 \tag{B13}$$

does not hold. Because this condition is a constraint on the center of gravity of the point defects, for which it is reasonable to assume that it lies in the center of the specimen, it will be assumed to be fulfilled in the following. If Eq. (B13) does not hold, then $G_\sigma(\vec{r},\vec{r}'\{\vec{\tau}^\alpha\})$ will develop anisotropic properties to leading order in $\alpha$ as can be seen by eliminating the second term of $E_k$ in Eq. (B12), by means of shifting the origin of the $k$ integration. Obviously this leads to an unnecessary complication of the problem and therefore Eq. (B13) will be assumed to hold in the following.

Consider next the fourth and fifth terms of Eq. (B9). For those cases where the number of vacancies and interstitials is equal, these terms are proportional to the density of these defects. However, if these terms are calculated for a distribution of vacancies only, then the fourth term is proportional to $(\Omega'_d)^{2/3}$ and the fifth term proportional to $k\Omega'_d$. Observe that the Bessel functions do not decay exponentially. It is obvious that under these circumstances the validity of the perturbation theory breaks down, because with $\Omega'_d \to \infty$ the unperturbed first term of Eq. (B10) becomes negligible. A possible reason for the problem lies in the use of plane waves to derive Eq. (B9). The correct starting point to derive Eq. (B9) should be to use the eigenfunctions of the Hamilton operator (in the domain $\Omega'_d$)

$$H_\sigma^0 = -\frac{1}{2m_\sigma}\Delta + V_{\text{rep}}^{dp}(\vec{r},\{\vec{\tau}_i^\alpha\}) \,, \tag{B14}$$

which takes the hard-core repulsive potential of Eq. (B7) into account. For a finite density of point defects the classical problem corresponding to Eq. (B14) will lead to stochasticity, since all constants of motion with the exception of the energy will be destroyed. This implies that for the quantal system the eigensolutions to Eq. (B14) should get random functions.[21,22] Although for conservative systems a strong rearrangement of eigenvalue level spacings occurs the density of eigensolutions changes insignificantly.[21]

Assume that a mapping between the plane waves and a possible set of eigenfunctions of Eq. (B14) exists in the form

$$e^{i\vec{k}\cdot\vec{r}}/\sqrt{\Omega'_d} \to \psi_k(\vec{r}) \,, \tag{B15a}$$

$$e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}/\Omega'_d \to \psi_k(\vec{r})\psi_k^*(\vec{r}') \equiv \rho_k(\vec{r},\vec{r}')/\Omega'_d \,. \tag{B15b}$$

It can be expected that the scattering phase shifts suffered by the plane waves get randomized over a distance $\kappa_{rp}^{-1}$, which will be a function of the density of defects. Under this condition it is reasonable to assume that for a uniform distribution of point defects

$$\frac{1}{\Omega'_d} \int_{\Omega'_d} d^3(\vec{r}-\vec{r}')\rho_k(\vec{r},\vec{r}') \simeq \exp[i\vec{k}\cdot(\vec{r}-\vec{r}') - \kappa_{rp}\,|\,\vec{r}-\vec{r}'\,|\,] \tag{B16}$$

holds. If Eq. (B15b) is substituted into Eq. (B8) it follows that the fifth term of Eq. (B9) will contain an exponential decay factor of the form $\exp(-\kappa_r\,|\,\vec{\tau}_i^\alpha - \tau_{i'}^{\alpha'}\,|\,)$ in its double sum. This implies that it will be of the order of $(\Omega'_d)^0$. The third term of Eq. (B8), however, still gives trouble, for here enters the diagonal term of Eq. (B15b) which satisfies $\rho_k(\vec{r},\vec{r}) \geq 0$. Although the integrant of that term varies in sign over the domain of integration, the stochastic character of $\rho_k(\vec{r},\vec{r})$ will get smoothed out over the domains of integration where the integrant is of positive or negative sign, respectively. We expect from this that the fourth term of Eq. (B9) is the leading term. However, due to the fact that the diagonal term $\rho_k(\vec{r},\vec{r})$ must satisfy the constraint

$$\rho_k(\vec{r},\vec{r})=0 \quad \text{for } \vec{r}=\vec{\tau}_i^{\underline{\sigma}}\in\{\vec{\tau}_i^{\underline{\sigma}}\}\ , \tag{B17}$$

this term cannot lead to a collapse of the defect system. A consequence of Eq. (B17) is that within the double sum of the fourth term of Eq. (B9) a function $g_{\text{rep}}(\{\vec{\tau}_i^{\underline{\sigma}}\})$ appears which will vanish whenever the defects try to form clusters. The problem that this term is proportional to $(\Omega_d')^{2/3}$ for finite density of point defects therefore cannot be eliminated this way. The origin of that problem must consequently be looked for somewhere else, for instance, in retardation effects. As explained in the main text it is reasonable to assume that the retardation effects provide an additional exponential or algebraic decay law for the interaction terms in Eq. (B9). Because we are not able to calculate this decay law from first principles, we also cannot say if the retardation effect leads to a stronger decay as the stochasticity effect discussed earlier or not. For the sake of simplicity we will use for $E_k$ the following expression:

$$\begin{aligned}E_k\simeq{}&k^2/2m_\sigma-\frac{\alpha^2}{2m_\sigma}\frac{\pi}{\Omega_d'}\frac{8}{3r_0}(b^\sigma)^2\sum_{\{\vec{\tau}_i^{\underline{\sigma}}\}}g_0\left[\frac{\vec{\tau}_i^{\underline{\sigma}}}{R_d'}\right]\\&-\frac{3}{2}\frac{\alpha^2}{m_\sigma}\frac{\pi}{\Omega_d'}(b^\sigma)^2\sum_{\{\vec{\tau}_i^{\underline{\sigma}}\neq\vec{\tau}_{i'}^{\underline{\sigma}'}\}}\epsilon_i^{\underline{\sigma}}\epsilon_{i'}^{\underline{\sigma}'}\frac{\cos^2(\vec{b}^\sigma,\vec{n}_{\tau_i^{\underline{\sigma}}-\tau_{i'}^{\underline{\sigma}'}})}{|\vec{\tau}_i^{\underline{\sigma}}-\vec{\tau}_{i'}^{\underline{\sigma}'}|}g_{\text{rep}}(\{\vec{\tau}_i^{\underline{\sigma}}\})e^{-\kappa_r|\vec{\tau}_i^{\underline{\sigma}}-\vec{\tau}_{i'}^{\underline{\sigma}'}|}g_1\left[\frac{\vec{\tau}_i^{\underline{\sigma}}}{R_d'},\frac{\vec{\tau}_{i'}^{\underline{\sigma}'}}{R_d'}\right]\\\equiv{}&k^2/2m_\sigma+\delta\gamma_\sigma(\{\vec{\tau}_i^{\underline{\sigma}}\})\ .\end{aligned}\tag{B9$'$}$$

The angular integration in Eq. (B12) can now be performed and yields

$$\begin{aligned}G_\sigma(\vec{r},\vec{r}\,',\{\vec{\tau}_i^{\underline{\sigma}}\})\simeq{}&\frac{1}{(2\pi)^3}\frac{-2\pi i}{|\vec{r}-\vec{r}\,'|}(s^*)^{1/2}\left[\frac{\pi}{2}\right]^{1/2}e^{-\kappa_{rp}|\vec{r}-\vec{r}\,'|}\\&\times\int_{-\infty}^{\infty}dk\,ke^{ik|\vec{r}-\vec{r}\,'|}\exp\left[\frac{(\gamma_\sigma'+k^2/2m_\sigma)^2s^*}{2}\right][1-\phi((\gamma_\sigma'+k^2/2m_\sigma)(s^*/2)^{1/2})]\ ,\end{aligned}$$

where $\gamma_\sigma'\equiv\gamma_\sigma^0+\delta\gamma_0$ has been introduced. Here for the sake of consistency the substitution given by Eq. (B15b) has been made in Eq. (B12). For nonuniform distributions of the defects, $\kappa_{rp}$ will be position dependent and a function of the defect density. With the use of the following representation of the probability integral[16]

$$\phi(xy)=1-\frac{2x}{\pi}e^{-x^2y^2}\int_0^\infty\frac{e^{-t^2y^2}dt}{t^2+x^2},\quad \text{Re}\,y^2>0\ ,$$

and the residue theorem, one obtains

$$G_\sigma(\vec{r},\vec{r}\,',\{\vec{\tau}^{\underline{\sigma}}\})\simeq\frac{m_\sigma e^{-\kappa_{rp}R}}{2\pi^{3/2}R}\int_{-\infty}^{\infty}dy\,e^{-y^2}\sum_{\epsilon=\pm1}\Theta(\epsilon\gamma_\sigma')\exp(-\epsilon\{2m_\sigma[iy/(s^*/2)^{1/2}+\gamma_\sigma']\}^{1/2}R)\ , \tag{B12$'$}$$

where

$$R\equiv|\vec{r}-\vec{r}\,'|,\quad \Theta(x)=\begin{cases}1, & x\geq0\\0, & x<0\ .\end{cases}$$

For the case $(s^*)^{1/2}\gg1$ and $\gamma_\sigma'>0$, one obtains

$$G_\sigma(\vec{r},\vec{r}\,',\{\vec{\tau}_i^{\underline{\sigma}}\})\simeq\frac{m_\sigma}{2\pi R}\exp[-(\sqrt{2m_\sigma\gamma_\sigma'}+\kappa_{rp})R]\ . \tag{B18}$$

This is just the Green's function of a "free" particle with a modified decay constant. In the limit $(s^*)^{1/2}\gg1$ and $\gamma_\sigma'<0$, one obtains approximately, expanding the argument of the exponential in Eq. (B12),

$$\begin{aligned}G_\sigma(\vec{r},\vec{r}\,',\{\vec{\tau}_i^{\,\sigma}\}) \simeq \frac{m_\sigma}{2\pi R}\frac{e^{-\kappa_{rp}R}}{\sqrt{2}} \sum_{\kappa=\pm 1} & \left\{ \exp(-i\kappa\sqrt{2m\,|\gamma'_\sigma|}\,R) \Bigg/ \left[ 2\left[1-i\kappa\frac{\sqrt{2m_\sigma\,|\gamma'_\sigma|}}{4s^*\gamma'^{\,2}_\sigma}R\right]^{1/2}\right]\right\} \\ & \times \exp\left\{ m_\sigma R^2 \Bigg/ \left[ 4s^*\,|\gamma'_\sigma|\,\left[1-\frac{i\kappa\sqrt{2m_\sigma\,|\gamma'_\sigma|}}{4s^*\gamma'^{\,2}_\sigma}R\right]\right]\right\} \\ & \times \left[ 1-\phi\left\{ -(m_\sigma/s^*\,|\gamma'_\sigma|\,)^{1/2}R \Bigg/ \left[2\left[1-\frac{i\kappa\sqrt{2m_\sigma\,|\gamma'_\sigma|}}{4s^*\gamma'^{\,2}_\sigma}R\right]^{1/2}\right]\right\}\right] . \end{aligned} \tag{B19}$$

Equation (B19) allows the discussion of various special cases. The essential point, however, is that $G_\sigma(\vec{r},\vec{r}\,',\{\vec{\tau}_i^{\,\sigma}\})$ is an oscillating function of $|\vec{r}-\vec{r}\,'|$ for $|\vec{r}-\vec{r}\,'|/s^* \ll 1$. All other cases are less interesting.

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[1] H. Gleiter, J. H. Perepezko, and K. Smidoda (unpublished).

[2] J. B. Suck, J. H. Perepezko, I. E. Anderson, and C. A. Angell, Phys. Rev. Lett. 47, 424 (1981), and work cited therein.

[3] T. Schneider, R. Brout, H. Thomas, and J. Feder, Phys. Rev. Lett. 25, 1432 (1970).

[4] M. Born, J. Chem. Phys. 7, 591 (1939).

[5] D. Turnbull and R. E. Cech, J. Appl. Phys. 21, 804 (1950); D. Turnbull, *ibid.* 21, 1022 (1950); J. Chem. Phys. 20, 411 (1952).

[6] H. B. Singh and A. Holz, Solid State Commun. (in press).

[7] N. G. Ainslie, J. D. Mackenzie, and D. Turnbull, J. Am. Ceram. Soc. 65, 1718 (1961).

[8] R. J. M. Cotterill, W. D. Kristensen, and E. J. Jensen, Philos. Mag. 30, 245 (1974).

[9] A. Seeger, J. Phys. F 3, 248 (1973).

[10] T. Górecki, Scr. Metall. 11, 1051 (1977).

[11] H. Gleiter and H. Hahn, Acta Metall. 29, 601 (1981).

[12] A. Holz, Physica 111A, 217 (1982).

[13] R. Bullough and R. C. Newman, Rep. Prog. Phys. 33, 101 (1970).

[14] M. O. Peach and J. S. Koehler, Phys. Rev. 80, 436 (1950).

[15] A. Holz, Physica 97A, 75 (1979).

[16] I. S. Gradshteyn and I. M. Ryzhik, in *Table of Integrals, Series and Products,* edited by A. Jeffrey (Academic, New York, 1965), p. 930.

[17] J. Bardeen and C. Herring, *Imperfections in Nearly Perfect Crystals* (Wiley, New York, 1925), p. 261.

[18] N. G. van Kampen, Phys. Rev. 135A, 362 (1964).

[19] H. B. Singh and A. Holz, Physica A (in press).

[20] A. Holz and H. Gleiter, Phys. Lett. A (in press).

[21] G. M. Zaslavsky, Phys. Rep. 80, 157 (1981).

[22] S. W. McDonald and A. N. Kaufman, Phys. Rev. Lett. 42, 1189 (1979).