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MULTILAYER MODEL OF SOLID-LIQUID INTERFACE: METASTABILITY LIMITS AND NON-EQUILIBRIUM CHARACTERISTICS

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Abstract. A multilayer mean-field model of a solid-liquid interface (SLI) is studied. The interface stability diagram is constructed on the basis of both discrete and the continuous approach taking into account the multistability phenomenon. An analytical expression is derived for the demarcation line, which separates two different SLI propagation modes: a barrier-controlled growth and an activationless one. The dynamics of the SLI propagation at high supercooling conditions is considered, the SLI runaway phenomenon accompanied by the SLI kinetical roughening is predicted.

1. INTRODUCTION

The interplay between the ensemble of metastable configurations, which takes place in a complex system driven far from equilibrium, deserves at present much attention. One of the notorious examples of such an interplay represents the solid-liquid interface (SLI), which is characterized by a high degree of multistability, controlled by the degree of supercooling [1,2].

Below we analyse a multi-level S-L interface model. The diagram of the interface stability is obtained on the basis of both discrete and continuum approximations. The analytical expression for the SLI stability boundary is found. The propagation of a steady SLI profile (in the form of a switch-wave) is discussed. The SLI kinetical roughening phenomenon is predicted for the conditions far from the equilibrium.

2. MODEL

We start with the free energy F for the multilayer model [3] and consider a simple-cubic solid-on-solid lattice model at finite temperature T. The system is divided into layers which are identical lattices of N sites; each lattice site is occupied by either of a "solid-like" atom (SA) or a "liquid-like" atom (LA). The free energy per one degree of freedom $f= F/N k_B T$ (with N tending to infinity and k_B being Boltzmann constant) is given by the expression

$$f = 0.5\sum[-\beta\sigma_n + 0.5\alpha(1-\sigma_n^2) + (\sigma_n - \sigma_{n+1})\ln(\sigma_n - \sigma_{n+1})], \qquad (1)$$

with $\alpha = \Delta\varepsilon/k_B T$ being the Jackson-like parameter [2], while $\beta = \Delta\mu/k_B T$ reflects the measure of supercooling; here $\Delta\mu$ is the chemical potential difference between the solid (S) and the liquid (L) phase, and $\Delta\varepsilon$ denotes the energy scale of the problem [3]. We present Eq. (1) in terms of the symmetrical "order parameter" σ_n $(-1 \le \sigma_n \le 1)$, which is related to the fraction of the "solid-like" atoms in the n-th layer, c_n, as $\sigma_n=2c_n-1$. The logarithmic term in (1) represents a configurational entropy of arranging SA's in $(n+1)$ – th layer on the 'solid-like" sites in n – th layer. For more details regarding the model used see e.g. [2,3].

The equilibrium structure of the SLI is to be determined from the condition $\partial f/\partial\sigma_n=0$, which reduces to

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$$\beta + \alpha\sigma_n = \ln \frac{\sigma_n - \sigma_{n+1}}{\sigma_{n-1} - \sigma_n}. \quad (2)$$

The conventional boundary conditions $\sigma_n \to \pm 1$ as $-n \to \pm\infty$ [2] should be imposed far away from the SLI. Note that true equilibrium corresponds only to the case $\beta=0$; for $\beta \neq 0$ a set of metastable positions of the SLI becomes possible.

3. METASTABILITY LIMITS

Temkin [3] solved Eq. (2) numerically and obtained a "phase" diagram. He found that the $\alpha - \beta$ plane is divided into two regions (see Fig. 1.): in the region A joining with the α-axis, Eq.(2) posesses two solutions, one of which maximizes f and the other minimizes f; outside the region A (region B) there is no solution to Eq. (2) [2,3].

3.1 Envelope curve

We have studied the system free energy as a function of the order parameter values at n=0 and n=1, (i.e. σ_0 and σ_1), which parametrically determine the location of both solutions to Eq. (2) in the α-β plane. Our analysis reveals that "trajectories" of the minimum and maximum solutions coincide at the demarcation line (DL), which, therefore represents their envelope curve (EC) $\beta=\beta_c(\alpha)$. Inside the region A ($|\beta| \leq \beta_c(\alpha)$) a series of local minima is possible (multistability) due to the atomistic discreteness of the SLI structure. Outside the region A the existence of static structures is not possible. It is found that the region A is symmetric with respect to the α-axis. From a numerical analysis we find that the width of the region A increases with α.

3.2 Continual approximation

The alternative way of finding the DL is to employ the Poisson summation method (PSM). By taking the limit $N \to \infty$, which permits a continual approach [4] it is useful to replace the finite-difference Eq. (2) by the ordinary-differential one with respect to the variables $\sigma(z)$ and $z=na$:

$$-\frac{\delta f}{\delta\sigma} = \beta + \alpha\sigma - a\frac{d^2\sigma}{dz^2} \Big/ \frac{d\sigma}{dz} = 0. \quad (3)$$

Eq. (3) permits an analytical solution for the SLI profile in the case $\beta=0$ [4]

$$\sigma(z) = -\tanh\frac{z - z_0}{\Delta z}, \quad (4)$$

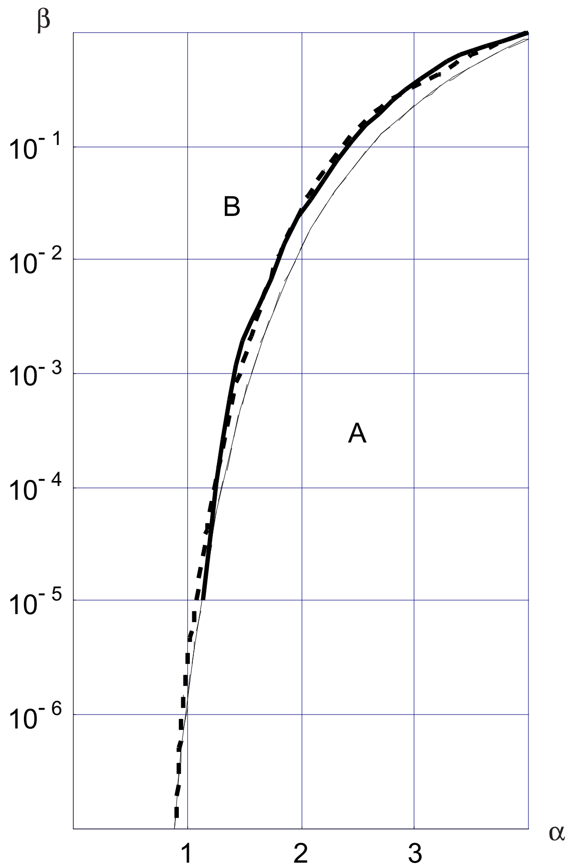

Fig. 1: State diagram. A: barrier-controlled growth regime, B: activationless one. Temkin's result [3] (thick solid) envelope curve of numerical solutions to Eq. (2) (thick broken), and analytical solutions based on the Poisson summation (thin) are plotted.

where z_0 denotes the SLI position and $\Delta z=2a/\alpha$ is the SLI width. In the opposite case $\beta \neq 0$ it is possible to derive the SLI-position-dependent free-energy, minimization of which with respect to the most favorable SLI coordinate z_0 gives a closed-form expression $\beta_c(\alpha)$ [5]. In the limit $\alpha \to 0$ the latter reduces to

$$\beta_c(\alpha) \approx 16\, \pi^2/\alpha\, \exp(-2\pi^2/\alpha).$$

The SLI stability diagram in the α-β plane is shown in Fig.1, in which besides original Temkin DL [4], the envelope curve $\beta_c(\alpha)$ as well as the stability threshold obtained with the help of the PSM are presented. The comparison reveals rather good coincidence between original DL and that given by the envelope solution. The semi-analytical PSM results provide sufficiently correct description of the DL in a small-β region, but obviously fail with the increase of β. It is worth noting here that the height of the free-energy barrier $\Delta f=f_+-f_-$ between adjacent local minima decreases with β in accordance with the *power law* $\Delta f \sim (1-|\beta|/\beta_c)^{3/2}$. Recently similar power exponents were reported for physically different systems including lattice-trapped crack [6] or the current-driven Abrikosov vortices in superconductors [7]. This result may be treated as a manifestation of the universal feature of the depinning threshold in complex non-equilibrium systems posessing a high degree of metastability.

4. DYNAMICS OF SOLID-LIQUID INTERFACE

In the case of a *finite* supercooling, $\beta \neq 0$ the SLI is basically metastable since it is forced to reach an energetically most favorable configuration. Thus, the SLI has a tendency to move. It is obvious that within the region A ($|\beta| \leq \beta_c(\alpha)$) the SLI dynamics is controlled by the barrier height Δf between adjacent minima. Indeed, waiting time τ, necessary for the SLI to move forward/backward by one lattice site *a,* may be simply estimated as $\tau=\tau_0 \exp(\Delta f/kT)$, where τ_0^{-1} is the characteristic phonon frequency. Therefore, the average speed for the barrier-controlled SLI propagation is exponentially small: $v_{th} \approx a/\tau_0 \exp(-\Delta f/kT)$, which reflects the thermally activated nature of the process. At the S-L interface depinning threshold ($|\beta| = \beta_c(\alpha)$) the SLI dynamics changes drastically. Since no metastable states are possible in the region B ($|\beta| \geq \beta_c(\alpha)$), the SLI, moves in the barrierless regime.

When considering the kinetics of the activationless SLI propagation we employ time-dependent Ginzburg-Landau equation (TDGLE), which describes the order parameter σ_n evolution in time and distribution in space

$$\tau^* \frac{\partial \sigma_n}{\partial t} = -\frac{\delta f}{\delta \sigma_n}, \quad (5)$$

where τ^* is the system relaxation time [5]. With the help of Eq. (2) one may present (5) in the form of a partial finite-difference equation

$$2\tau^* \frac{\partial \sigma_n}{\partial t} - \beta - \alpha\sigma_n + \ln\frac{\sigma_n - \sigma_{n+1}}{\sigma_{n-1} - \sigma_n} = 0, \quad (6)$$

to be solved analytically in the continuum limit. Retaining nonlinearity within the logarithmic term and expanding finite difference terms brings

$$2\tau^* \frac{\partial \sigma_n}{\partial t} - \beta - \alpha\sigma_n + \ln\left[1 + a\frac{d^2\sigma}{dz^2} \Big/ \frac{d\sigma}{dz}\right] = 0. \quad (7)$$

The Eq. (7) was analysed previously with the help of the logarithm-linearization scheme [5]. In what follows we prefer to employ the nonlinear ansatz while solving (7). Searching for the solution in the traveling-wave form $\sigma(z,t)=\sigma(z-Vt)\equiv\sigma(\xi)$ one arrives at the first order differential equation with respect to the auxiliary variable $u(\sigma)\equiv d\sigma/d\xi$:

$$1 + au'_\sigma = \exp[\beta + \alpha\sigma + 2V\tau^* u]. \quad (8)$$

The straightforward solution of Eq. (8) by means of the variables separation with due account for the standard switching-wave boundary conditions $u(\sigma=\pm1)=0$ results in a transcendental equation to find the SLI propagation velocity V

$$(\alpha - \nu)\sinh\nu = \exp(\beta)\nu\sinh(\alpha - \nu), \quad (9)$$

where parameter $v= 2V\tau^*/a$ represents the dimensionless velocity of the S-L interface. The analysis of (9) shows that the *finite* solution for V exists only within the parameters range $|\beta| < \alpha$. The shape of the switching-wave can be found by analyzing the expression $u(\sigma)$ in the limit $\sigma\to\pm1$. After performing simple algebra we arrive at the expansion valid for $z\to\pm\infty$:

$$\frac{d\sigma}{dz} \approx -\frac{1-\sigma^2}{\Delta Z_\pm},$$

from which it follows that the switching-wave profile is essentially asymmetric. Indeed, the ratio between the backfront width ΔZ_- and that of the forefront, ΔZ_+: $\Delta Z_-/\Delta Z_+=(\alpha-\beta)/(\alpha+\beta)$ may vary from 0 (at $\beta\to+\alpha$) up to infinity (at $\beta\to-\alpha$). For example, in the high supercooling limit ($\beta\to+\alpha$) the width of the forefront, ΔZ_+ greatly exceeds that of the backfront, tending to infinity as $\beta\to\alpha$.

Such an asymmetry of the moving SL interface reflects the *kinetical roughening* phenomenon, which is a generical feature of the far-from-equilibrium solidification [5]. It is worth noting that the SLI propagation speed tends to infinity ($|V|\to\infty$) as b approaches the SLI *runaway* border (i.e. $\beta\to\pm\alpha$). Analogous results obtained within the logarithm-linearization scheme (see Eq. (7)) were reported in [5]. Such a boundless divergency of the SLI propagation velocity ($|\boldsymbol{V}(\beta)|\to\infty$ as $|\beta|\to\alpha$) is analogous to the high-current-driven normal zone acceleration in locally heated superconductors with a transport current. It is clear, that a more advanced treatment of the problem should be carried out near the SLI runaway threshold to avoid the unphysical divergency of the SLI propagation speed.

5. SUMMARY

We have studied there a multi-layer model of the solid-liquid interface. The results are summarized as follows:

(1) The *demarcation line* is described both analytically and numerically, which separates the barrier-controlled SLI motion and the activationless one.

(2) The steady propagation of the S-L interface is considered on the basis of the time-dependent Ginzburg-Landau equation. The supercooling range is determined in which a finite SLI propagation velocity exists. The SLI *runaway* phenomenon, accompanied by the SLI *kinetical roughening* is predicted for the extremely high supercooling conditions.

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