Growth angle – a microscopic view

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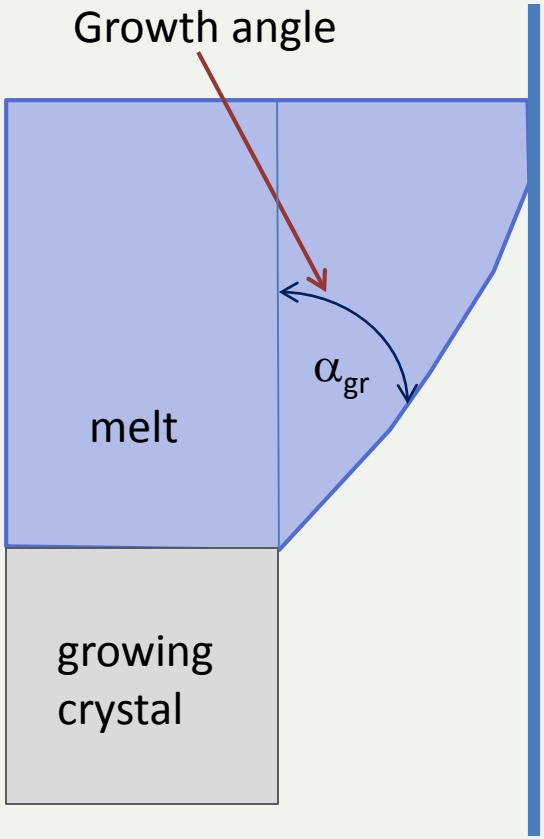
research motivation

- we propose a microscopic model of the triple phase line (TPL) that defines the growth angle. For our microgravity project on detached Bridgman crystal growth, this is the angle that is formed between the Germanium melt and the growing crystal .

- better understanding of the microscopic picture near the TPL is necessary to develop more accurate models of detached Bridgman solidification and other growth technologies.

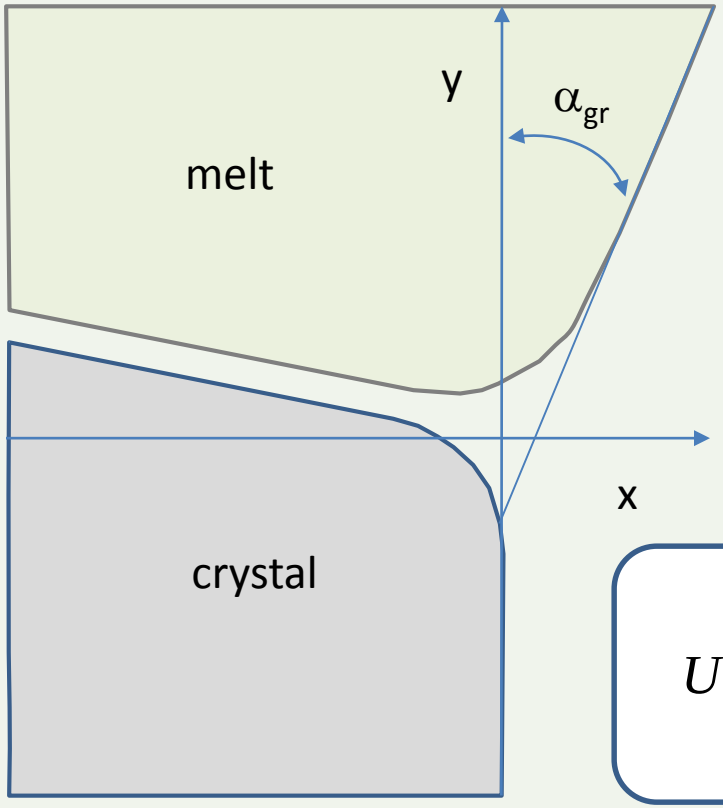
- microscopic theoretical approach to the meniscus shape is required for detached Bridgman growth as the gap width between the growing crystal and the crucible wall is typically in the range of several micrometers. This is within reach of the long range van der Waals forces. Therefore, a macroscopic theory of menisci for such small distances is questionable.

introduction



The growth angle that is formed between the side of the growing crystal and the melt meniscus is an important parameter in detached Bridgman crystal growth method, where it defines the very existence of the crystal-crucible wall gap, and in Czochralski and float zone methods, where it defines the size and stability of the crystals. The growth angle is a non-equilibrium parameter, defined for the crystal growth process only. For the melt-crystal interface translating towards the crystal (melting), there is no specific angle between the melt and the sidewall of the solid. In this case, a corner at the triple phase line becomes rounded, and the angle between the sidewall and the incipience of meniscus can take a number of values, depending on the position of the triple line. In this work, a microscopic picture of the growth angle is discussed in the framework of the van der Waals continuum mechanical approach. Specifically, a model that describes the microscopic meniscus shape for the case of the fluid interacting through the long range van der Waals or Casimir dispersive forces with the solid surface, terminated with the corner of an arbitrary angle, is formulated. This growth angle model is applied to Si and Ge and compared with the macroscopic approach of Herring. The proposed microscopic approach will address also the case of a rounded, non-sharp, corner, where, instead of a growth angle, a contact angle concept is applicable. As the corner radius goes to zero, the growth angle should describe the meniscus angle. However, as the radius of the round corner goes to zero, the macroscopic Young theory of contact angles does not recover this limit. This interesting issue will be considered within the proposed microscopic model.

growth angle model



The proposed microscopic model of the growth angle is based on minimization of free energy that is taken as a sum of pair interactions between the molecules with the hard cores and soft Lennard-Jones long-range potentials. It can be termed as van der Waals model. The energy is defined as a sum of the interaction potentials between the two bodies, in our case, growing crystal and melt. The densities of the molecules are taken as constants within the corresponding volumes.

$$U_{12} = \rho_1 \rho_2 \int_{V_1} \int_{V_2} d^3 r_1 d^3 r_2 \left(\frac{B_{12}}{|\mathbf{r}_1 - \mathbf{r}_2|^{12}} - \frac{C_{12}}{|\mathbf{r}_1 - \mathbf{r}_2|^{6}} \right)$$

microscopic meniscus shape

Equating the two forces: the disjoining pressure and the capillary force due to the curvature of the melt surface, we obtain the Laplace equation for the microscopic meniscus shape *h*(x) of the melt:

$$\sigma\left(\frac{h'}{\sqrt{1+h'^2}}\right)' = \frac{\delta U_{12}}{\delta h(x)}$$

Here σ is the melt surface tension. The shape of the solid phase can be considered as a given function *H*(x). Then the variational derivative can be evaluated as:

$$\frac{\delta U_{12}}{\delta h(x)} = \pi C_{12}\rho_1\rho_2\int_{-\infty}^{\infty}\frac{dx_0}{4\Delta_x^4}\left(1+\frac{\Delta_H^3+\frac{3}{2}\Delta_H\Delta_x^2}{\left(\Delta_H^2+\Delta_x^2\right)^{3/2}}\right)-$$

$$-\pi B_{12}\rho_1\rho_2\int_{-\infty}^{\infty}\frac{dx_0}{10\Delta_x^{10}}\left(1+\frac{\Delta_H^9+\frac{9}{2}\Delta_H^7\Delta_x^2+\frac{63}{8}\Delta_H^5\Delta_x^4+\frac{105}{16}\Delta_H^3\Delta_x^6+\frac{315}{128}\Delta_H\Delta_x^8}{\left(\Delta_H^2+\Delta_x^2\right)^{9/2}}\right)$$

$$\Delta_x = x-x_0, \quad \Delta_H = H(x_0)-h(x)$$

microscopic crystal phase shape

The growing crystal shape is considered as obeying the same minimization energy principle. It leads to the following equations:

$$\sigma_s\left(\frac{H'}{\sqrt{1+H'^2}}\right)' = \frac{\delta U_{12}}{\delta H(x)}$$

$$\frac{\delta U_{12}}{\delta H(x)} = -\frac{\delta U_{12}}{\delta h(x)}$$

$$H' = -\frac{\sigma}{\sigma_s}\frac{h'}{\sqrt{1+h'^2\left(1-\sigma/\sigma_s\right)^2}}$$

Equal surface energies model: $\sigma = \sigma_s$, $H'(x) = -h'(x)$
The non-dimensional Laplace equation for the meniscus shape is:

$$\frac{h''}{\left(1+h'^2\right)^{3/2}} = 3A\int_{-\infty}^{\infty}\frac{dx_0}{\Delta^4}\left(1-\frac{S^3+\frac{3}{2}S\Delta^2}{\left(S^2+\Delta^2\right)^{3/2}}\right) - 9A\int_{-\infty}^{\infty}\frac{dx_0}{\Delta^{10}}\left(1-\frac{S^9+\frac{9}{2}S^7\Delta^2+\frac{63}{8}S^5\Delta^4+\frac{105}{16}S^3\Delta^6+\frac{315}{128}S\Delta^8}{\left(S^2+\Delta^2\right)^{9/2}}\right)$$

$$A = \frac{\pi C_{12}\rho_1\rho_2}{12\sigma h_0^2} \qquad 15h_0^6C_{12} = 2B_{12} \qquad \Delta = x - x_0, \quad S = h(x_0) + h(x)$$

growth angle for equal surface energies

An approximate Laplace equation for the meniscus for $\sigma = \sigma_s$ case is:

$$\frac{h''}{\left(1+h'^2\right)^{3/2}} = A\left(\frac{1}{4h^3} - \frac{1}{256h^9}\right)$$

The growth angle then can be obtained analytically and is:

$$\sin\left(\frac{\alpha_{gr}}{2}\right) = 1 - \frac{3}{8}A$$

Our general model can be used to relate the contact angle to the parameter A. For the contact angle, we have

$$\cos\theta_C = \frac{3}{4}A - 1$$

Dependence of the contact angle on the growth angle for this particular case is

$$\cos\theta_C = 1 - 2\sin\left(\alpha_{gr}/2\right)$$

Interestingly, the macroscopic Herring formula can be also used for our equal energies case, and yields just exactly the same result.

model testing

The Young and Herring formulas for:

1. contact angle $\cos\theta_C = \sigma_s/\sigma - \sigma_{int}/\sigma,$
2. growth angle $2\cos\alpha_{gr} = \sigma/\sigma_s + \sigma_s/\sigma - \sigma_{int}^2/\sigma\sigma_s$
3. interface tilt angle $2\sin\beta = \sigma_{\text{int}}/\sigma_s + \sigma_s/\sigma_{\text{int}} - \sigma^2/\sigma_{\text{int}}\sigma_s$

Consider our symmetric model, $\sigma = \sigma_s$, for which the tilt angle β is the same as the growth angle. On the other hand, from Young and Herring formulas we obtain $\beta = \alpha_{gr}/2$, twice smaller than predicted by our model. Surface energy data for Si and Ge give consistently $\sigma_{\text{int}}/\sigma \simeq 0.5$. Formulas (1,2) then yield $\sigma_s/\sigma \simeq 1.4$. Assuming that the contact angle and the surface tension are given, we obtain for Si the following values:

$$\sigma = 880\frac{mJ}{m^2},\ \sigma_s = 1280\frac{mJ}{m^2},\ \sigma_{\text{int}} = 440\frac{mJ}{m^2},\ \alpha_{gr} = 10^0,\ \theta_C = 17.5^0,\ \beta = 69^0.$$

For Ge we obtain this set of values:

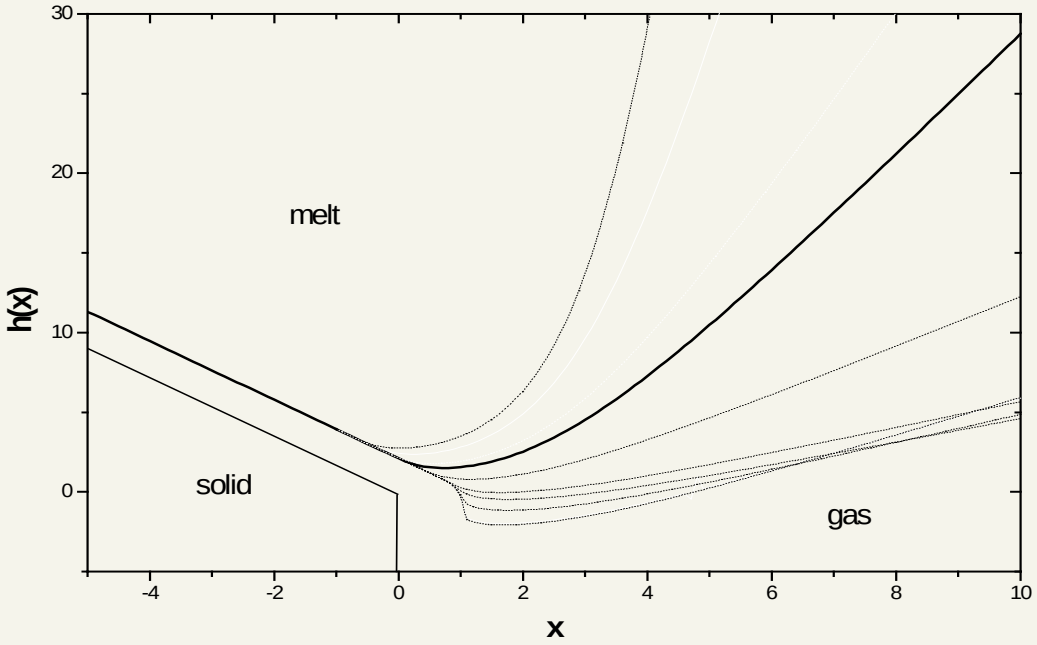
$$\sigma = 591\frac{mJ}{m^2},\ \sigma_s = 830\frac{mJ}{m^2},\ \sigma_{\text{int}} = 300\frac{mJ}{m^2},\ \alpha_{gr} = 14.3^0,\ \theta_C = 25.3^0,\ \beta = 60^0.$$

Comments:

1. The value for crystalline Ge appears too low.
2. The microscopic model does not relate the three interface energies with the TPL angles.

meniscus shapes for sharp corner

For a solid with the microscopically sharp corner and a tilted interface, the meniscus shape depends on its incipience region. Far left from the corner, the meniscus corresponds to the flat surface case, and the contact angle is its asymptotic angle. The same occurs when the melt is covering the corner area and extends well below it. In the intermediate region, the asymptote angle diminishes as we move from the left to the right, reaches minimum, and then increases to the contact angle value. However, if a corner is smooth with small curvature, then this minimum effect is not present.



conclusion

A microscopic continuum mechanical model of the growth angle is proposed. It is based on the van der Waals type framework that is used for surface force phenomena. The obtained augmented Laplace type integro-differential equations are, in general, difficult to analyze. Here we focused primarily on the particular case of equal melt and crystal surface energies. We derived an approximate equation for the meniscus shape, and obtained an analytical relationship between the contact and the growth angle. Interestingly, the same result can be obtained using the macroscopic model of Herring. The case of a macroscopically sharp corner is also considered. For this case, the macroscopic angle is not defined and it can be any angle between the contact angles of both flat surfaces. The microscopic model yields the smooth shape for the meniscus that also is not unique, but depends on the initial position of the meniscus.

References

1. Israelachvili J. N. , Intermolecular and surface forces", Academic Press, New York, 2000.
2. Derjaguin B. V. , *Theory of Stability of Colloids and Thin Liquid Films*, Plenum Press, New York, 1989.
3. Bukovets V. V, "Growth and wetting angles as the control parameters of crystal shape in Czochralski method", *Journal of Crystal Growth* 193 (1998) 720-727.
4. Voronkov V. V., *Sov. Phys. Crystallogr*. 23(2) (1978) 137.
5. Satunkin G. A., "Determination of growth angles, wetting angles, interfacial tensions and capillary constant values of melts", *Journal of Crystal Growth* 255 (2003) 170–189.
6. Satunkin G. A., "Modelling the dynamics and control design for Czochralski, Liquid Encapsulated Czochralski and Floating Zone processes", *Progress in Crystal Growth and Characterization of Materials* 56 (2010) 1-121.
7. Herring C., *Phys. Rev*. 82 (1) (1951) 87.
8. Antonov V.A., V.V. Selin, "The growth angle and particular case of stabilization of the shape of the crystallized small drops of the melt", Journal of Crystal Growth 241 (2002) 507–511.
9 Tegetmeier A. , A. Cröll, M. Schweizer, P.Dold, K.W. Benz, "Surface tension and growth angle – two important parameters of the floating zone process", The Fourth Asian Thermophysical Conference, Tokyo, Sept. 1995.