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Determination of the Contact Angle Based on the Casimir Effect

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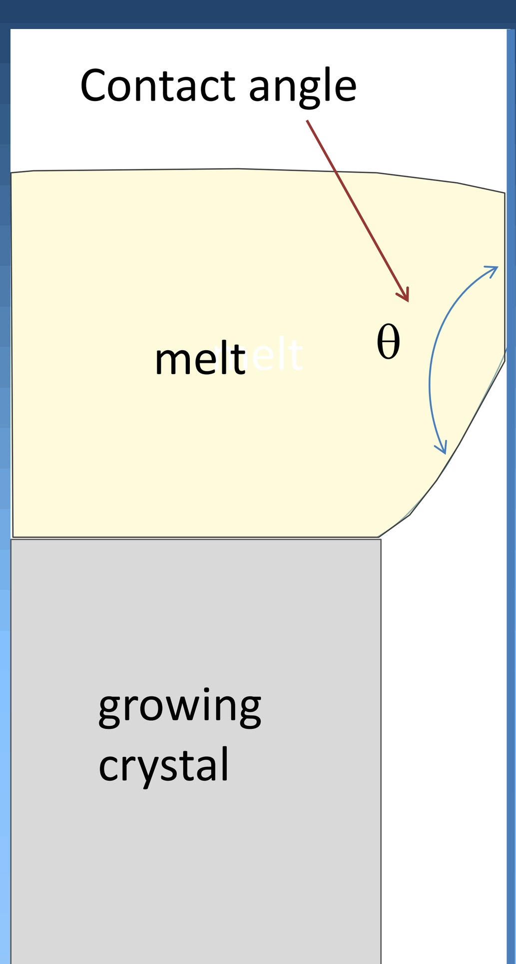
research motivation

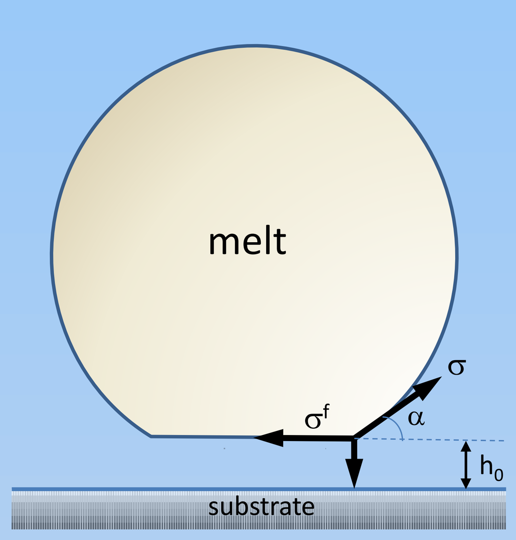
- we propose to investigate a slope correction to the Casimir force that governs the contact angle value. For our microgravity project on detached Bridgman crystal growth, this is the angle that is formed between the Germanium melt and the crucible (BN or quartz).
- better understanding of the microscopic picture near the contact lines 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 the range of the Casimir forces. Therefore, a macroscopic theory of menisci for such small distances is questionable.

introduction



On a macroscopic scale, a nonreactive liquid partially covering a homogeneous solid surface will intersect the solid at an angle called the contact angle. For molten metals and semiconductors, the contact angle is materially dependent upon both the solid and liquid and typical values fall in the range 80-170^0, depending on the crucible material. On a microscopic scale, there does not exist a precise and sharp contact angle but rather the liquid and solid surfaces merge smoothly and continuously. Consider the example of the so called detached Bridgman crystal growth process. In this technique, a small gap is formed between the growing crystal and the crucible. At the crystal/melt interface, a meniscus ring is formed. Its width can be in the range of a few micrometers, approaching a microscopic scale. It then becomes questionable to describe the shape of this meniscus by the contact angle. A more advanced treatment of the interface is needed and here we propose such a refined model. The interaction of the liquid surface with the solid can be calculated by considering two forces: a short-range repulsive force and a longer range (up to a few micrometers) Casimir or van der Waals force.

contact angle theory



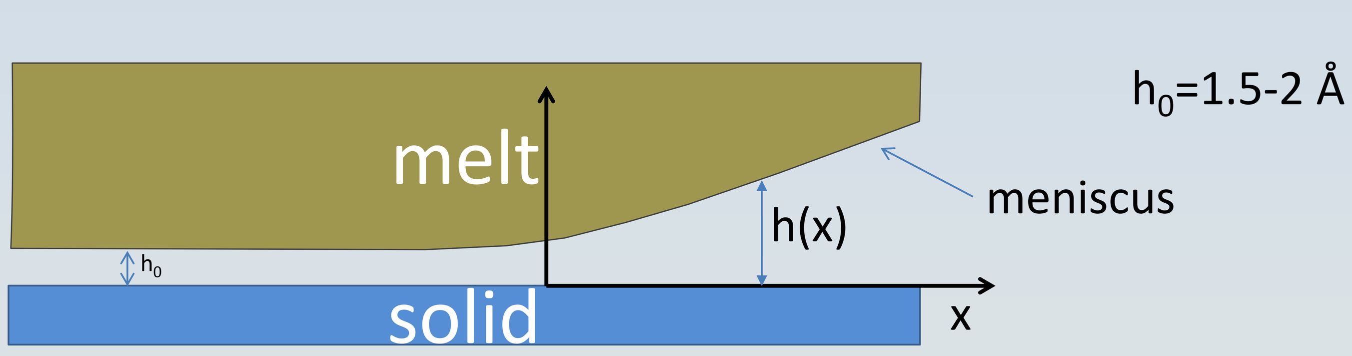
The basic model of the contact angle is due to Derjaguin and Frumkin (1938) [2]. It relies on the concept of the disjoining pressure (Derjaguin, 1936). Below, we will outline this theory. The Fig.(1) depicts the drop of fluid on the surface for a semi-wetting case. When the gap between the drop and the solid is large, the disjoining pressure is zero, and the horizontal surface tension is . At the drop positioned on the solid as depicted in Fig.1, the horizontal surface tension is scosa. The difference is due to the potential energy difference, which can be expressed through the disjoint pressure P as

$$\sigma-\sigma^f=-\int_{h_0}^{\infty}\Pi(h)\,dh \quad\Rightarrow\quad \cos\alpha=1+\frac{1}{\sigma}\int_{h_0}^{\infty}\Pi(h)\,dh$$

microscopic meniscus shape

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

$$\frac{\sigma h''}{\left(1+h'^2\right)^{3/2}}=-\Pi(h)$$



References

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role of zero-point energy

The "physical vacuum" consists primarily of quantum fluctuations of electromagnetic fields. The average energy density of these fluctuations is enormous, and usually it is referred to as the zero-point energy, signifying its existence at zero temperature. One of the effects of these fluctuations is the so called van der Waals or Casimir attraction between the macroscopic bodies. The theory of this effect between the two flat bodies has been developed by Lifshitz in 1956 and an elegant formalism based on photon Green functions has been given by Dzyaloshinskii, Lifshitz, and Pitaevskii. This theory provides the value for the disjoining pressure. The disjoining pressure is the force normal to the unit surface element, derived from the Maxwell electromagnetic stress tensor. Below is displayed a set of equations to be solved:

$$\overleftrightarrow{\mathbf{T}}(\mathbf{r},\mathbf{r})=\lim_{r\to r'}\left[\overleftrightarrow{\theta}(\mathbf{r},\mathbf{r}')-\frac{1}{2}\overleftrightarrow{\mathbf{I}}Tr\overleftrightarrow{\theta}(\mathbf{r},\mathbf{r}')\right]$$

$$\overleftrightarrow{\theta}(\mathbf{r},\mathbf{r}')=-2k_BT\sum_{n=0}^{\infty}a_n\left[\frac{\varsigma_n^2}{c^2}\overleftrightarrow{G}^S(\mathbf{r},\mathbf{r}',\varsigma_n)+\nabla\times\overleftrightarrow{G}^S(\mathbf{r},\mathbf{r}',\varsigma_n)\times\overleftarrow{\nabla}'\right],\quad a_0=\frac{1}{2},\quad a_{n>0}=1$$

$$\nabla\times\nabla\times\overleftrightarrow{G}(\mathbf{r},\mathbf{r}'',\varsigma_n)+\frac{\varsigma_n^2}{c^2}\tilde{\varepsilon}(\mathbf{r},i\varsigma_n)\overleftrightarrow{G}(\mathbf{r},\mathbf{r}'',\varsigma_n)=\overleftrightarrow{\mathbf{I}}\delta(\mathbf{r}-\mathbf{r}'')$$

angular dependence of disjoining pressure

The disjoining pressure is the normal to the unit surface force coming from the Maxwell stress tensor T

$$\Pi=T_{nn}=\hat{\mathbf{n}}\cdot\overleftrightarrow{\mathbf{T}}\cdot\hat{\mathbf{n}}=\left[h'^2T_{xx}+T_{yy}-h'\left(T_{yx}+T_{xy}\right)\right]\left(1+h'^2\right)^{-1}$$

For flat collinear surfaces, $T_{xx}=T_{xy}=T_{yx}=0$. Such an approximation leads to the formula

$$\Pi(h,h')=T_{yy}(h)/\left(1+h'^2\right)\qquad T_{yy}=-\frac{A_H}{6\pi h^3}$$

Here A_H is the Hamaker constant. This formula yields the following equation for the contact angle

$$\frac{1}{\cos\alpha_{corr}}=1-\frac{1}{\sigma}\int_{h_0}^{H}T_{yy}(h)\,dh$$

This formula yields a slightly smaller angle than the contact angle a proposed by Derjaguin :

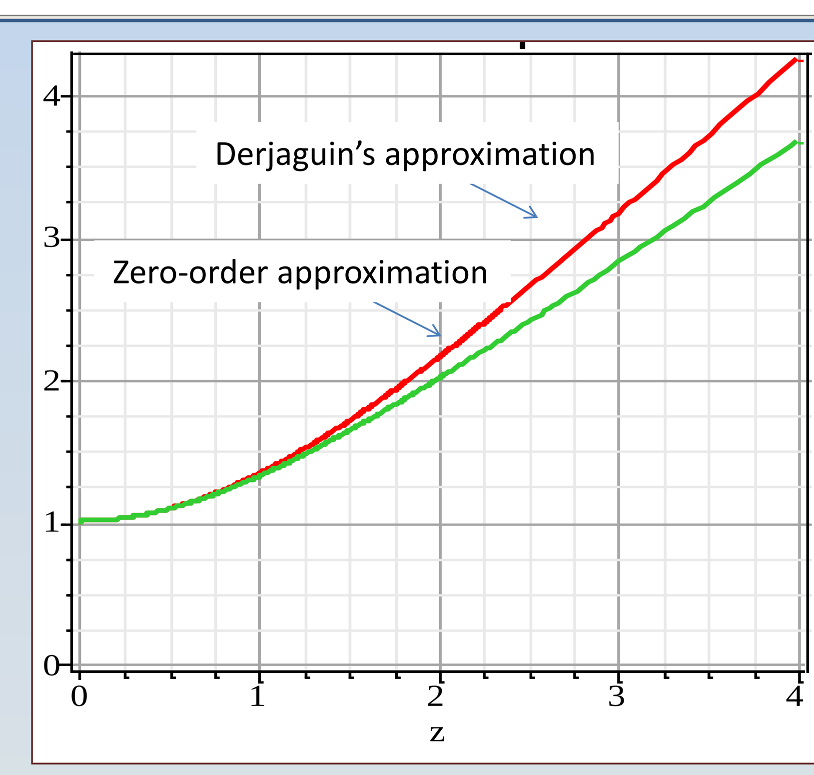
$$\cos\alpha_{corr}=1/(2-\cos\alpha)$$

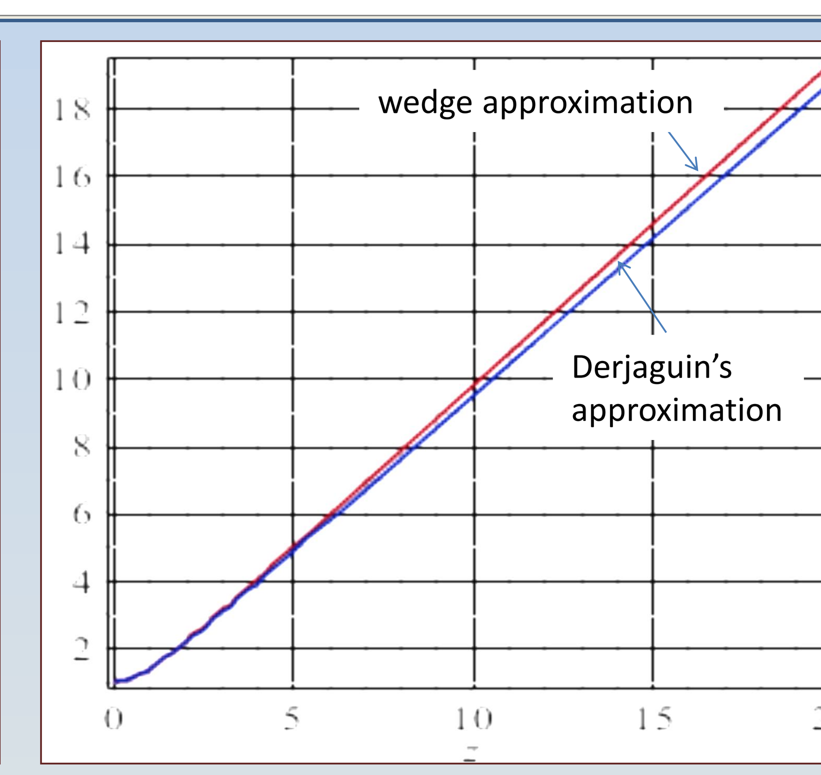
A second model. A Casimir force for the wedge geometry could provides its required angular dependence [5]:

$$\Pi(z,\alpha)=-\frac{A_H}{6\pi h(z)^4}\frac{\sin\alpha^4}{\pi^4}\left(\frac{\pi^2}{\alpha^2}+11\right)\left(\frac{\pi^2}{\alpha^2}-1\right)$$

This formula is valid for two perfect conductors and defines the Casimir force (retardation limit). No similar formula exists for the van der Waals force (non-retardation limit, small gaps), which would be more appropriate. The other disadvantage is that the higher order derivatives of the surface shape are neglected. The numerical solution of the meniscus shape for this approximation follows closely the Derjaguin's solution, and only for large angles, > 45^0, is shows a small difference.

Below, we display two menisci derived for the same Hamaker constant. The distance is scaled by the microscopic gap between the melt and solid. For consistency, the wedge approximation was compared with Derjaguin's formula with a Casimir force factor of 4: $T_{yy}=-\frac{A_H}{6\pi h(z)^4}$





conclusion

The slope correction for the contact angle is small for small angles. For larger angles, the slope correction has to be taken into account. Therefore, the macroscopic concept of balancing forces as applied to the interface intersections is not accurate, and a microscopic picture should be implemented. The available models of Casimir force that can be implemented for the discussed issue, are not well justified. An accurate numerical evaluation of the van der Waals force is needed at this point to reach more conclusive results. The presented idea can further be extended to include effects of electrostatic fields, or other forces. In the forthcoming paper, a more elaborate evaluation of the shape effect on the Casimir pressure will be presented. The discussed here idea can also be used to study capillary surface waves, close to the contact line, induced by fluctuating electromagnetic fields.