

# Morfologia, crescimento e hábito das partículas

# Nucleação

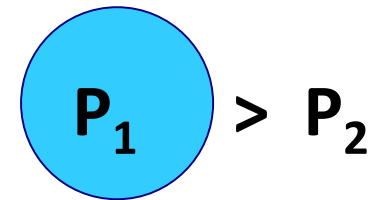
- Formar uma nova fase no interior de outra requer a criação de uma interface...
- ...que contribui para aumentar a energia livre do sistema.
- Não se forma uma nova interface no interior de outra, quando as condições do sistema são exatamente as que permitem equilíbrio entre as duas fases.

# A equação de Young-Laplace

- Diferença de pressão entre as duas fases separadas por uma superfície com raios de curvatura  $R_1$  e  $R_2$ :

$$\Delta p = \gamma (1/R_1 + 1/R_2)$$

- no caso de calota esférica:  $\Delta p = \gamma (2/R)$ ,
- a pressão é maior do lado do centro de curvatura:



# Consequências de Young-Laplace

- a *pressão de vapor de um líquido muda*, se a sua superfície for curva (equação de Kelvin).
- taxas de *nucleação* de vapor são *nulas*, no interior de um líquido na sua *temperatura de equilíbrio L-V*.
- as taxas de *nucleação* de líquido são *nulas*, no interior de um vapor na sua *temperatura de equilíbrio L-V*.
- a *solubilidade um sólido aumenta*, se a sua superfície for curva (o potencial químico aumenta).
- taxas de *nucleação* de cristais são *nulas*, no interior de uma solução na sua *temperatura de equilíbrio L-S*.

# Formação de bolha

- No interior de líquido a temperatura de equilíbrio L-V, a formação de núcleos não ocorre porque significa **formar vapor em pressão mais alta que a do líquido**.
- Só se inicia ou nucleia a formação de bolhas em temperatura mais elevada que a de equilíbrio.
  - A formação de vapor exige **super-aquecimento**.

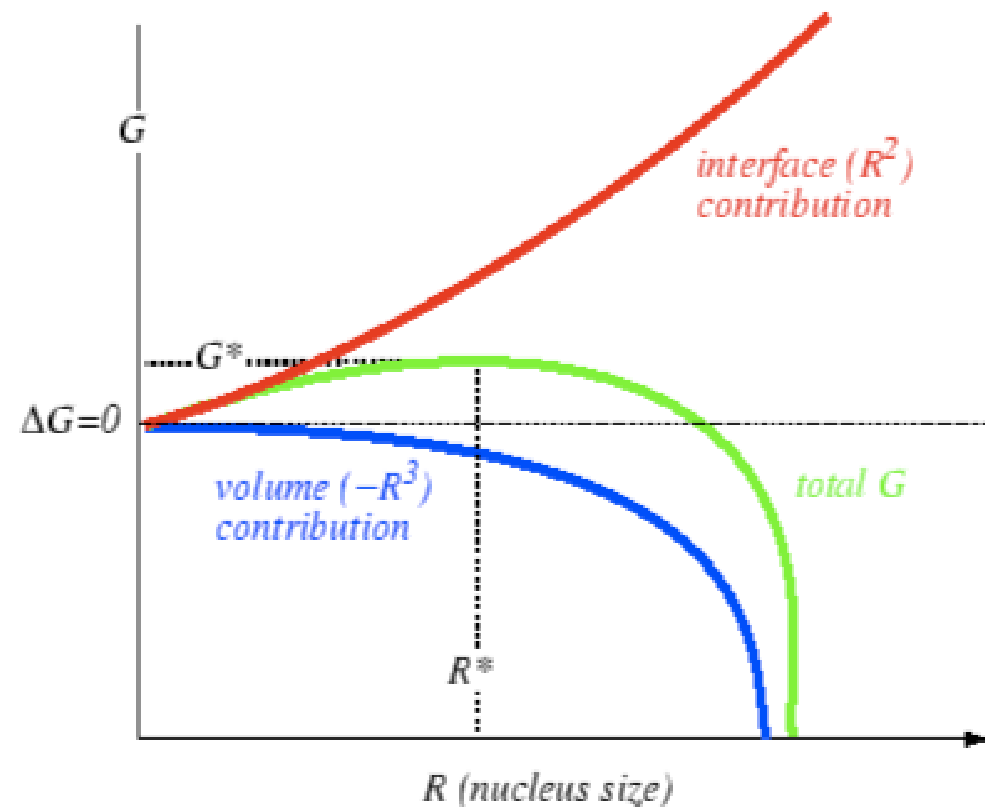
# Borbulhadores

- Criam interfaces L-V de raio grande, reduzindo a necessidade de superaquecimento para a formação de bolhas.
  - Produzem ebulição mais suave e uniforme.
  - Sólidos porosos, tubos com gás sob pressão positiva.

# Nucleação Homogênea

$$\Delta G_{\text{nucleo}} = 4\pi\gamma^{\alpha\beta}R^2 - 4\pi/3 [\Delta G_{\text{nucleo}}]V_{\alpha,m} R^3$$

- O tempo exigido para a nucleação homogênea é o tempo necessário para que ocorra uma flutuação de composição crítica que produza um núcleo de tamanho crítico.
- Esse tempo aumenta exponencialmente com a altura da barreira.



[http://pruffle.mit.edu/3.00/Lecture\\_32\\_web/node4.html](http://pruffle.mit.edu/3.00/Lecture_32_web/node4.html)

[http://pruffle.mit.edu/~ccarter/3.21/Lecture\\_24/](http://pruffle.mit.edu/~ccarter/3.21/Lecture_24/)

# Nucleação de uma nova fase sólida

- *A new mechanism for nuclei formation in suspension crystallizers: the role of interparticle forces. R-Y Qian and G. D. Botsaris, Chem. Eng. Sci. 52(1997)3429.*
- $A+A=A_2$ ;  $A_2+A=A_3$ ; ... ;  $A_{g-1}+A=A_g$ .
- A distribuição de clusters moleculares no estado estacionário pode ser calculada usando argumentos termodinâmicos:

$$n_g = n_1 \exp(-\Delta G_g / kT) \quad \text{para } g = 2, 3, \dots, g_c$$

$$\text{onde } \Delta G_g = (4\pi)^{1/3} \sigma (3gV_m)^{2/3} - kT[\ln(1+S)]g$$

- $\Delta G_g$  é a energia de formação do g-mero,  $n_g$  e  $n_1$  são as concentrações de g-mero e de monômero.
- $k$  é a constante de Boltzmann,  $T$  a temperatura,  $V_m$  o volume molecular,  $\sigma$  a tensão interfacial do cristal,  $S$  é a supersaturação e  $g_c$  é o número de monômeros em um cluster crítico.



# Taxa de nucleação

- $B^0 = K_1 \exp[-(g_c/2) \ln (1+ S)]$ 
  - $K_1 \approx 10^{25} \text{ cm}^{-3} \text{ s}^{-1}$
- Outras referências:
- M. Giuliatti et al.,  
[http://www.scielo.br/scielo.php?pid=s0104-66322001000400007&script=sci\\_arttext](http://www.scielo.br/scielo.php?pid=s0104-66322001000400007&script=sci_arttext)
- <http://www.collectionscanada.gc.ca/obj/s4/f2/dsk2/ftp01/MQ29792.pdf> (Tese de Mestrado, McGill)

# Nucleação heterogênea

- Predomina, na prática.
- Nucleadores heterogêneos permitem a acomodação de moléculas em arranjos semelhantes aos dos próprios cristais.
- Muitas substâncias nucleiam a cristalização de águas supersaturadas.
  - Mecanismo:  
ordenamento da água adsorvida na superfície do sólido.

# Nucleação de chuva

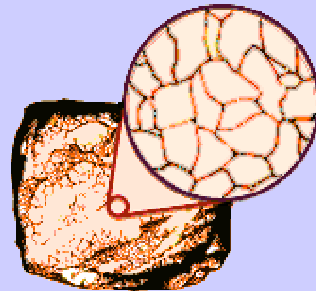
- Em temperaturas baixas, para formar gelo: o nucleador é o iodeto de prata.
  - Maçãs de Santa Catarina
- Em temperaturas altas, usa-se salmoura ou simplesmente água borrifada na atmosfera úmida.
  - O sistema Cantareira, SP

# Crescimento de cristais

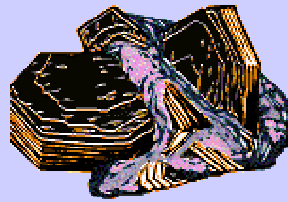
- Qual face predomina em um cristal?
- R.: A de menor tensão interfacial no meio de formação.
- Consequência: é possível obter um mesmo sólido em muitas formas geométricas diferentes, dependendo do meio em que cresceram.
- *Hábitos* mudam, por recristalização.

# Pirita em carvão: crescimento em ambiente confinado

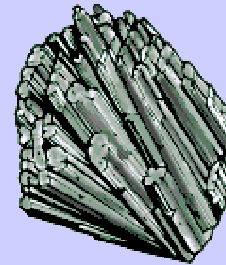




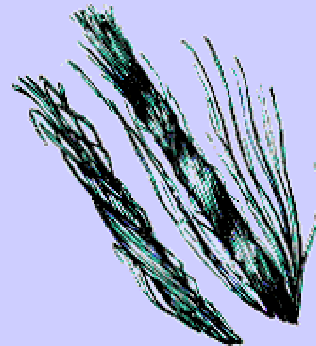
granular, as in marble



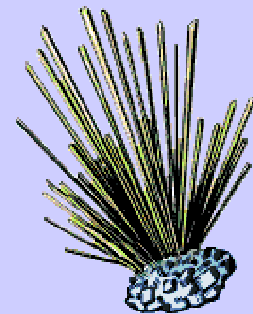
lamellar, foliated,  
micaceous, as in mica



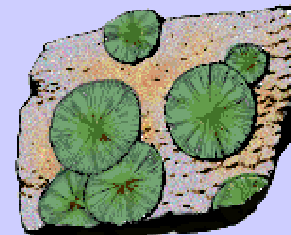
bladed, as in actinolite



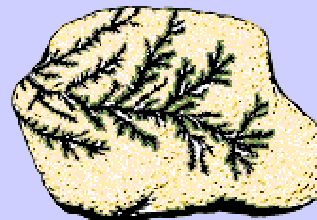
fibrous, as in asbestos



acicular (needlelike),  
radiating, as in millerite



radiating and globular,  
as in wavellite



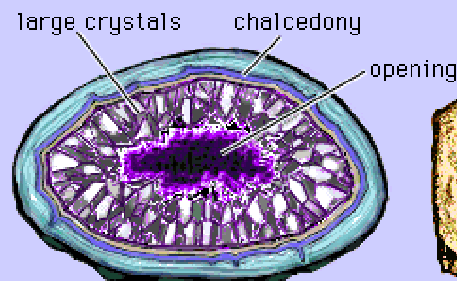
dendritic, as in pyrolusite



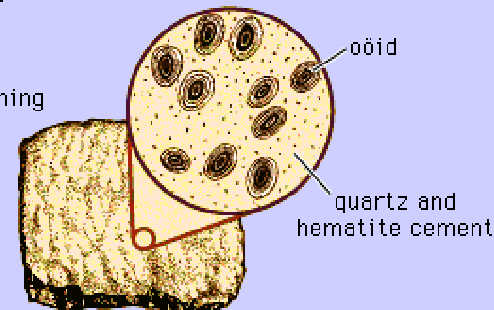
mammillated,  
botryoidal, as in hematite



colloform, stalactitic,  
as in cave deposits

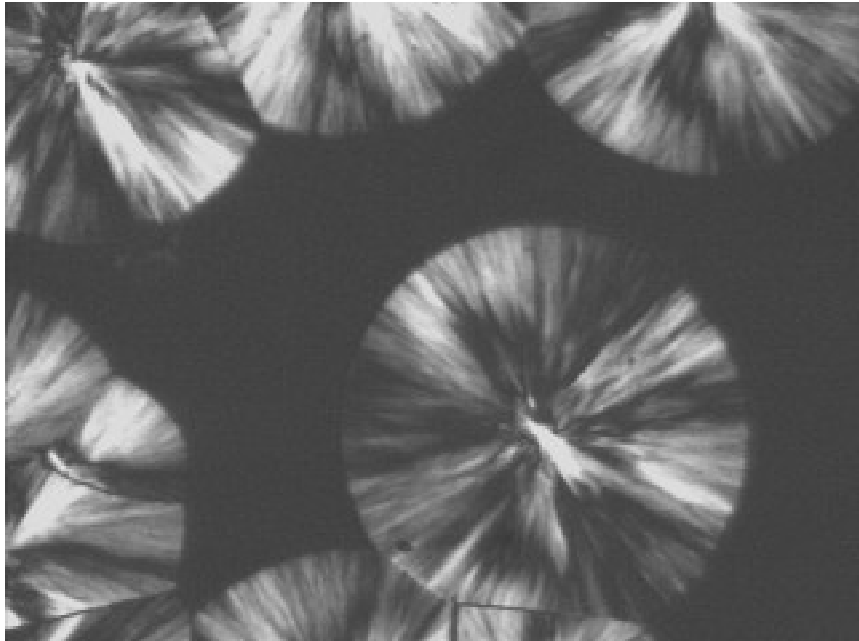


geode

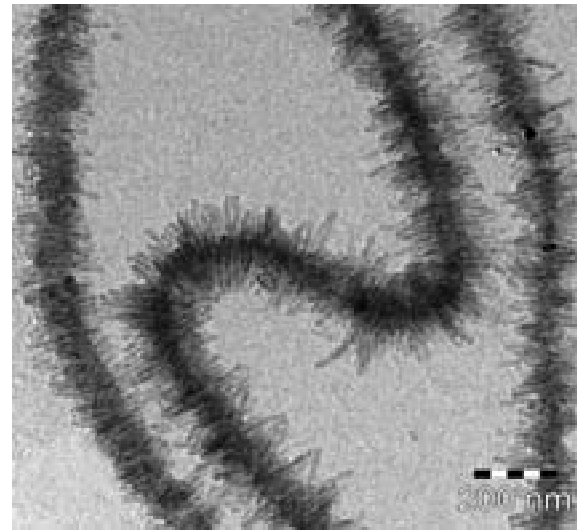


oolitic, as in oolitic limestone

# Esferulitose "shish kebab"

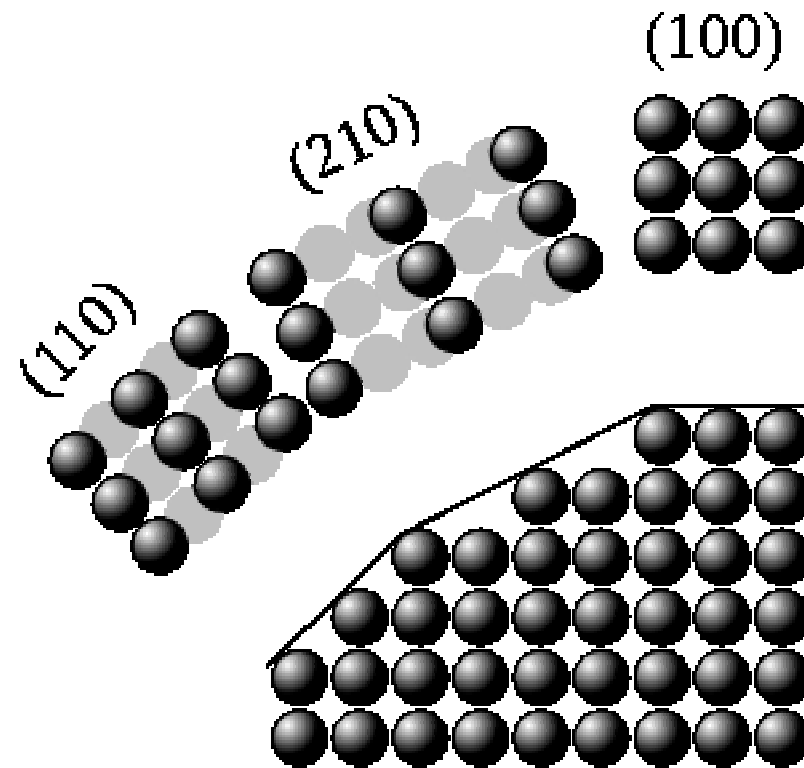


[www.ictp.cnr.it/raimo%20sample.html](http://www.ictp.cnr.it/raimo%20sample.html)



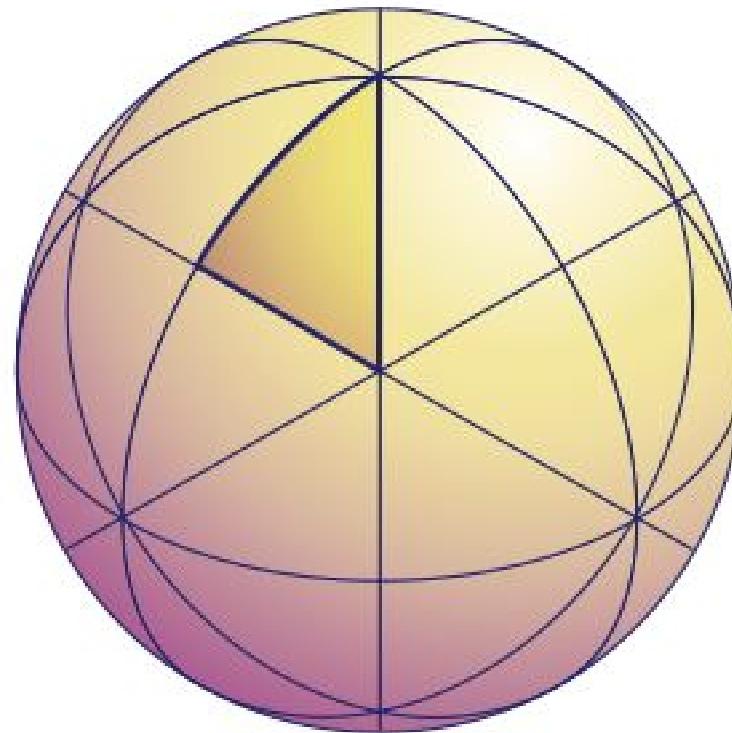
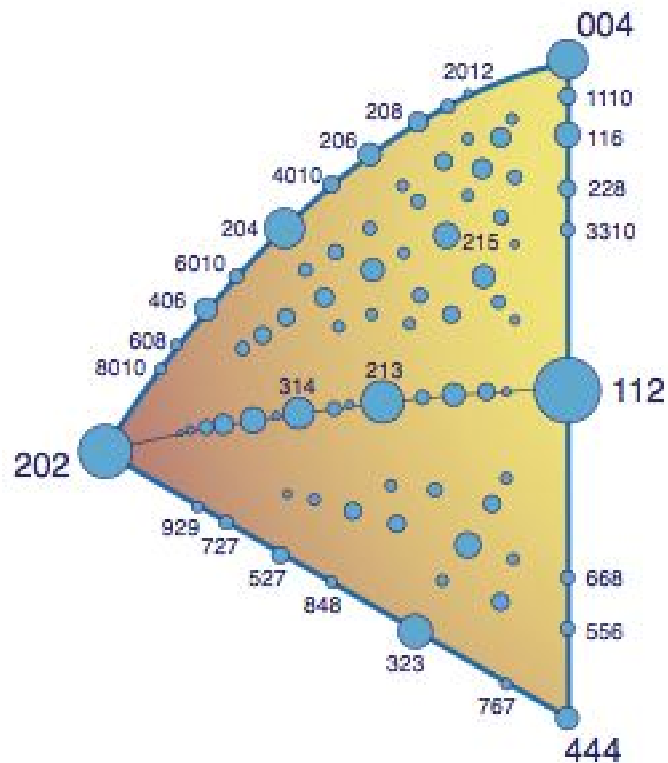
<http://www3.interscience.wiley.com/journal/122581893/issue>

# Formando esferas com planos



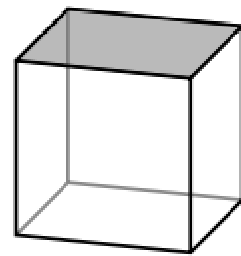


# Planos com índices de Miller elevados

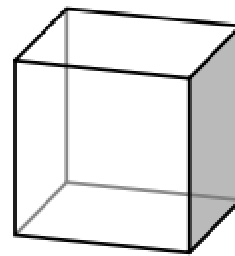


[http://www.lps.u-psud.fr/Collectif/gr\\_15/Soft\\_Crystals.htm](http://www.lps.u-psud.fr/Collectif/gr_15/Soft_Crystals.htm)

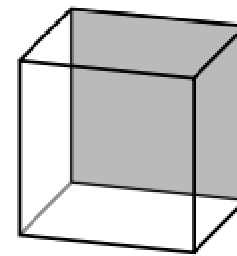
# Índices de Miller no sistemacúbico



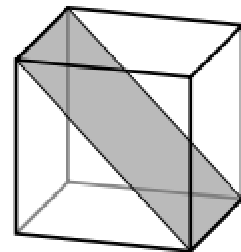
$(001)$



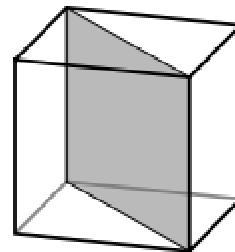
$(100)$



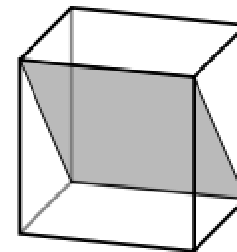
$(010)$



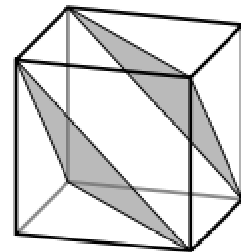
$(101)$



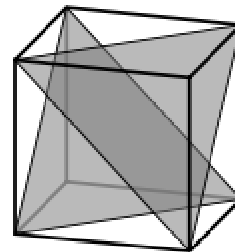
$(110)$



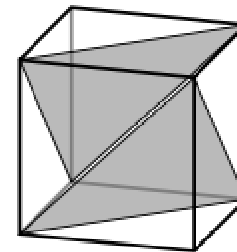
$(011)$



$(111)$

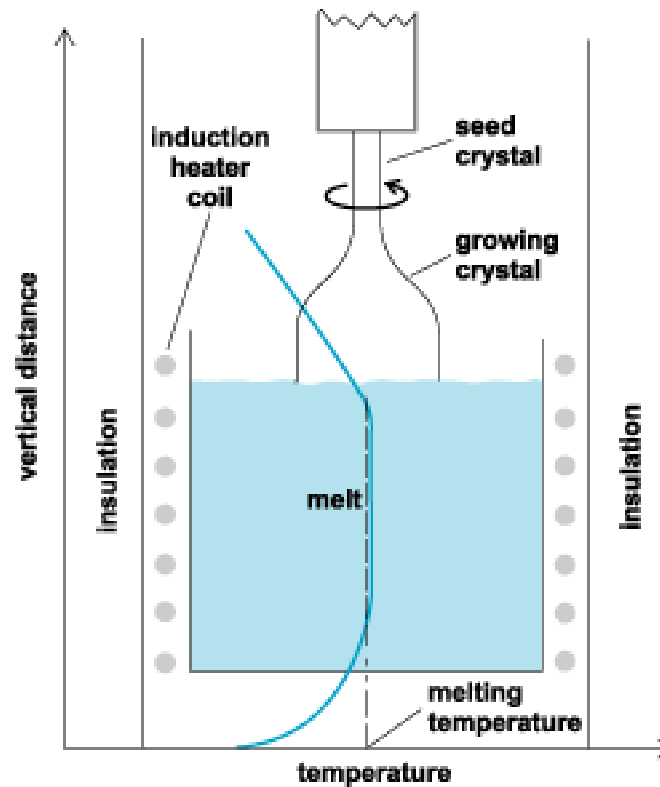


$(1\bar{1}1)$



$(\bar{1}11)$

# Crescimento de monocristais de silício: método de Czochralski



<http://content.answers.com/main/content/img/McGrawHill/Encyclopedia/images/CE171500FG0020.gif>

# Efeitos do hábito

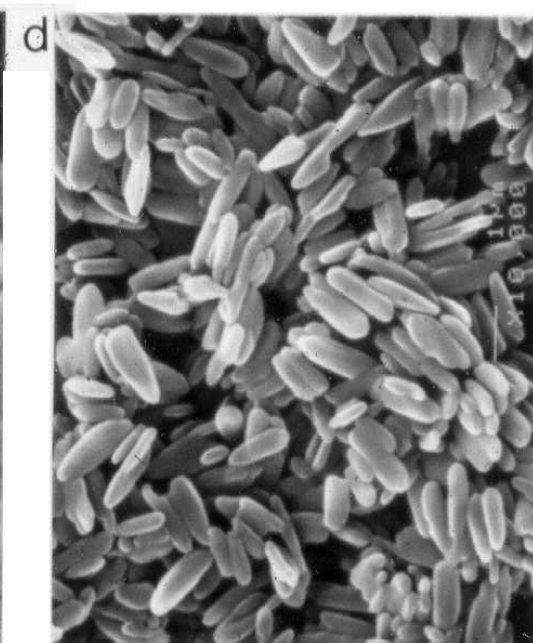
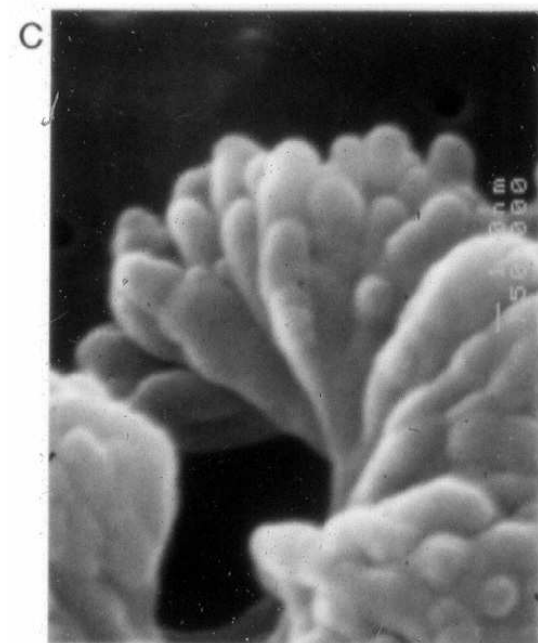
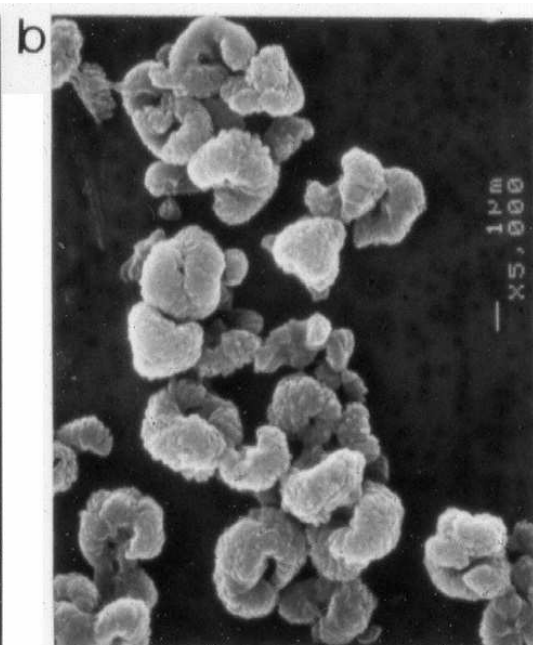
- Capacidade de adsorção
  - Hidroxiapatita
- Velocidade de solubilização
  - Importante em farmacotécnica, construção civil...

**Review** - *Nature Reviews Drug Discovery* **3**, 42-57 (January 2004) |  
doi:10.1038/nrd1280

## **Crystal structures of drugs: advances in determination, prediction and engineering**

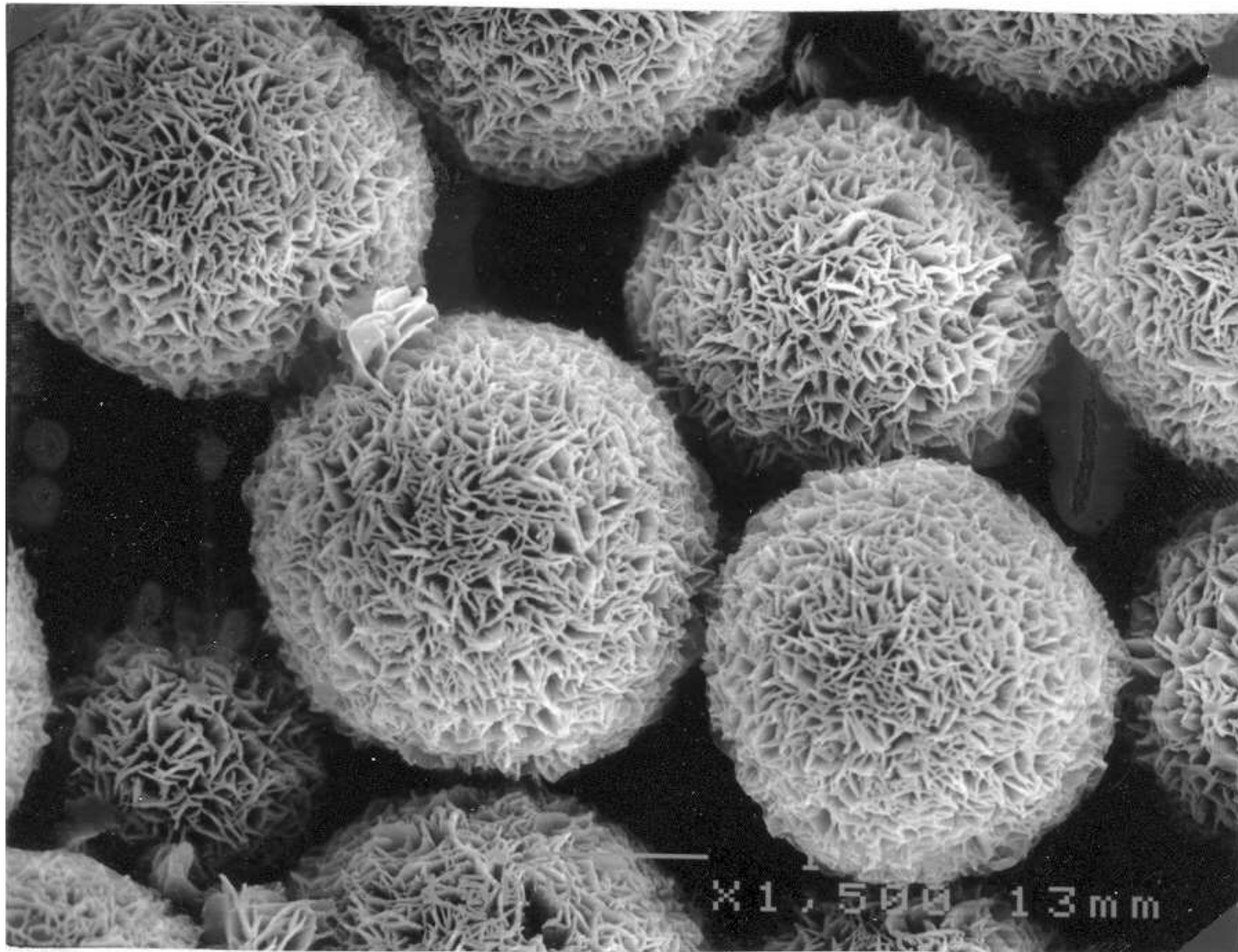
**Sharmistha Datta & David J. W. Grant**

**Most marketed pharmaceuticals consist of molecular crystals. The arrangement of the molecules in a crystal determines its physical properties and, in certain cases, its chemical properties, and so greatly influences the processing and formulation of solid pharmaceuticals, as well as key drug properties such as dissolution rate and stability. A thorough understanding of the relationships between physical structures and the properties of pharmaceutical solids is therefore important in selecting the most suitable form of an active pharmaceutical ingredient for development into a drug product. In this article, we review the different crystal forms of pharmaceuticals, the challenges that they present and recent advances in crystal structure determination. We then discuss computational approaches for predicting crystal properties. Finally, we review the analysis of crystal structures in furthering **crystal engineering to design novel pharmaceutical compounds with desired physical and mechanical properties.****



NAPROXEN

## Ba - NAPROXENATE





## The Effect of Additives on Glycine Crystal Growth Kinetics

Li Li, David Lechuga-Ballesteros, Beth A. Szkudlarek and Naír Rodríguez-Hornedo

College of Pharmacy, The University of Michigan, Ann Arbor, Michigan 48109

### Abstract

The effect of  $\alpha$ -amino acids ("tailor-made" additives) on the morphology and nucleation of glycine crystals was studied in batch experiments, and the **effect of L-leucine on glycine crystal growth kinetics** was investigated in flow cell experiments at constant supersaturation. From dissolution and growth experiments in a flow cell system, L-leucine was found to adsorb onto the (0 -1 0) face of glycine crystals and to inhibit the growth of that face, modifying the crystal habit. At high L-leucine concentrations (>8 mg/ml), the growth rate of the (010), (011), and (01-1 ) faces was faster than that in the absence of additive. This may be the result of the effect L-leucine has on the crystal/solution interfacial tension and on the aggregation of glycine in solution. **Oriented nucleation and growth of glycine crystals on the (0 -1 0) face were observed.** This may be a consequence of multilayer L-leucine adsorption onto the (0 -1 0) face, which provides a template for nucleation and growth of glycine twinned crystals about the (0 -1 0) basal plane.

[Journal of Colloid and Interface Science](#)

[Volume 168, Issue 1](#), November 1994, Pages 8-14



# Efeitos de concentração

- Em baixa concentração de leucina ( $<8$  mg/mL), adsorção de leucina impede o crescimento da face (0 -1 0) de cristais de glicina.
- Morfologia muda de bipiramidal (na ausência de leucina) para piramidal.
- Em concentrações de leucina mais altas, a dimerização de glicina em solução aumenta e promove o crescimento das faces (0 1 0), (0 1 1) e (0 1 -1).
- Adsorção de múltiplas camadas de leucina em (0 -1 0) produz um *template* para a nucleação orientada e crescimento de cristais geminados de glicina.

# Metodologia

- Cinética de crescimento de cristais, em supersaturação controlada (em fluxo e em batelada). Observação do crescimento de cristais em microscópio invertido.
- Incorporação de leucina feita em experimentos de dissolução feitos com leucina tritiada.

DOI: 10.1306/212F8D69-2B24-11D7-8648000102C1865D

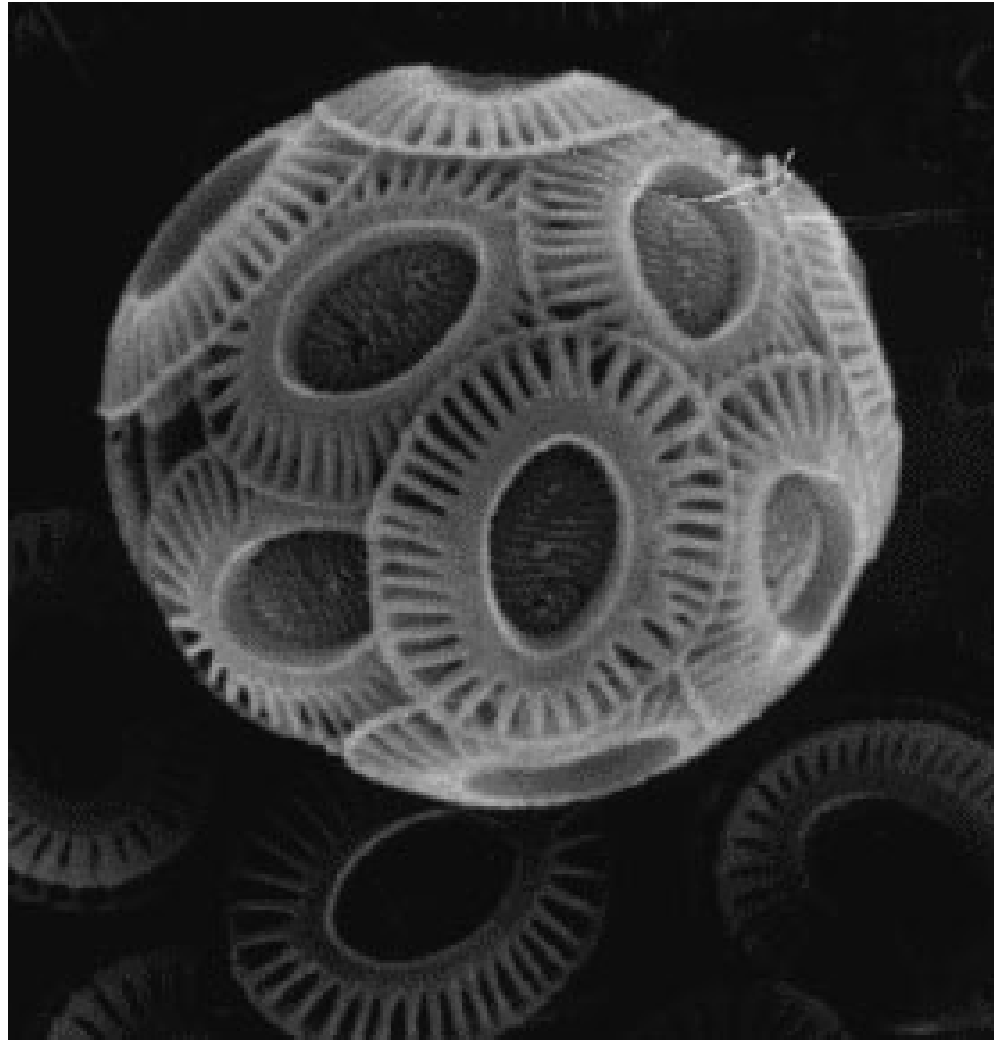
## **Gypsum Nucleation and Crystal Morphology in Analog Saline Terrestrial Environments**

R. D. Cody, A. M. Cody

Journal of Sedimentary Research, Volume 58 (1988)

Gypsum crystals were grown in **experimental conditions analogous to saline terrestrial environments** within bentonite clay gels by diffusion control at three different temperatures, four brine salinities, and four tannic acid (a model terrestrial humic substance) concentrations. **The resulting crystals correspond to natural gypsum formed in terrestrial environments.** **Prismatic gypsum** typically grew at both high and low temperatures in the absence of the organic additive. With increasing organic acid concentrations, **the prismatic crystals progressively became flattened perpendicular to [001]**, and two temperature-dependent trends developed. At low temperatures, a **hemi-bipyramidal** habit dominated by 111 faces developed, whereas **the lenticular 103 dominated** habit formed at higher temperatures. With progressively greater concentrations of organic material (100) penetration twinning developed, secondary complex nucleation occurred near the twin interfaces, and finally, **rosette and rosette-like aggregates formed**. Higher temperatures generally favored better-formed and larger rosettes. The presence of 5% and 15% **NaCl greatly decreased nucleation density and resulted in larger single crystals and crystal aggregates**. The (100) penetration twins appear to be diagnostic of gypsum growth in natural terrestrial sediments at a pH greater than 7.5.

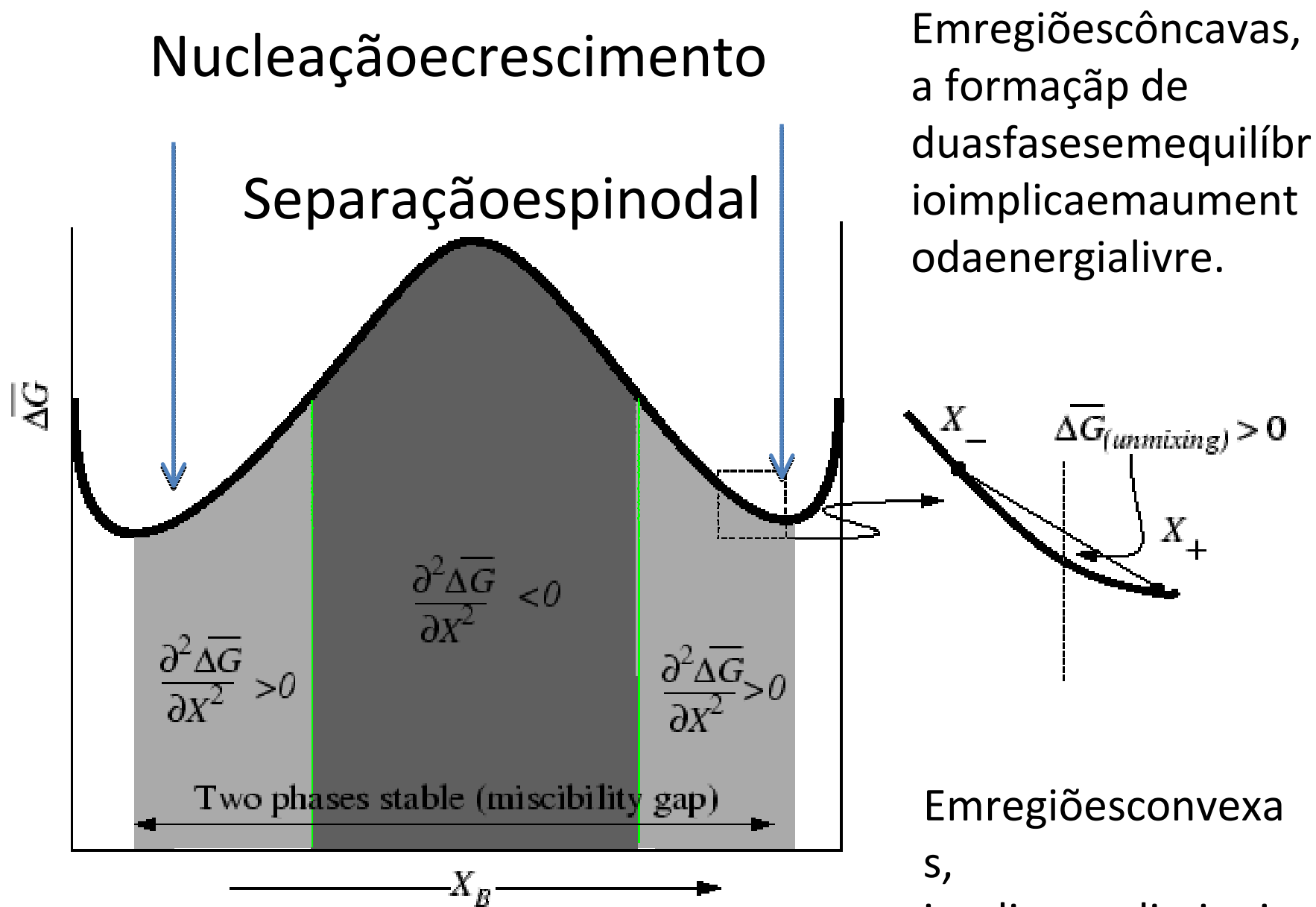
# Coccolito, de *coccolitophora*



<http://homepages.see.leeds.ac.uk/~earssh/research.shtml>

# Decomposiçãoespinal

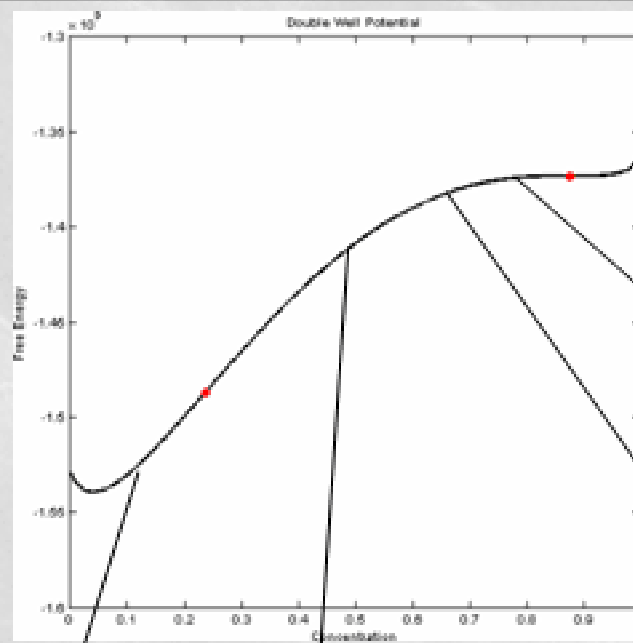
- [http://pruffle.mit.edu/3.00/Lecture\\_32\\_web/node3.html](http://pruffle.mit.edu/3.00/Lecture_32_web/node3.html)



Em regiões côncavas, a formação de duas fases em equilíbrio implica uma diminuição da energia livre.

Em regiões convexas, implica uma diminuição.

# Symplectite Formation: Morphologies



final configuration

moving interface

shortening

- **Spinodal Decomposition in a Model Colloid-Polymer Mixture in Microgravity**
- ***A.E. Bailey et al, Physical Review Letters 99, 205701 (2007) We study phase separation in a deeply quenched colloid-polymer mixture in microgravity on the International Space Station using small-angle light scattering and direct imaging. We observe a clear crossover from early-stage spinodal decomposition to late-stage, interfacial-tension-driven coarsening. Data acquired over 5 orders of magnitude in time show more than 3 orders of magnitude increase in domain size, following nearly the same evolution as that in binary liquid mixtures. The late-stage growth approaches the expected linear growth rate quite slowly.***



