NANOPHYSIQUE
INTRODUCTION PHYSIQUE AUX NANOSCIENCES

3. AMAS OU AGREGATS ATOMIQUES

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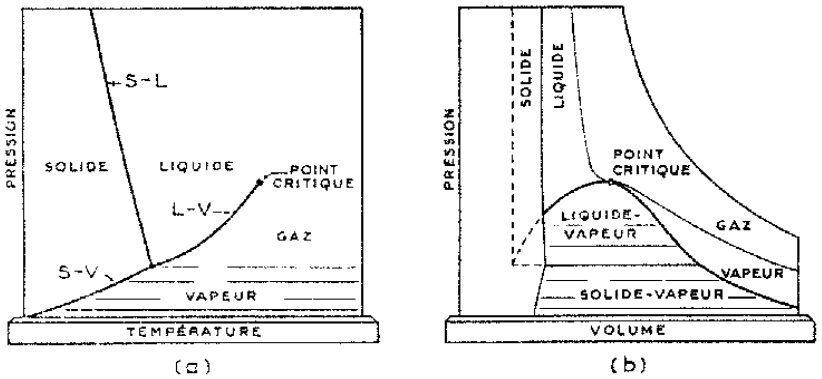
2021-2022

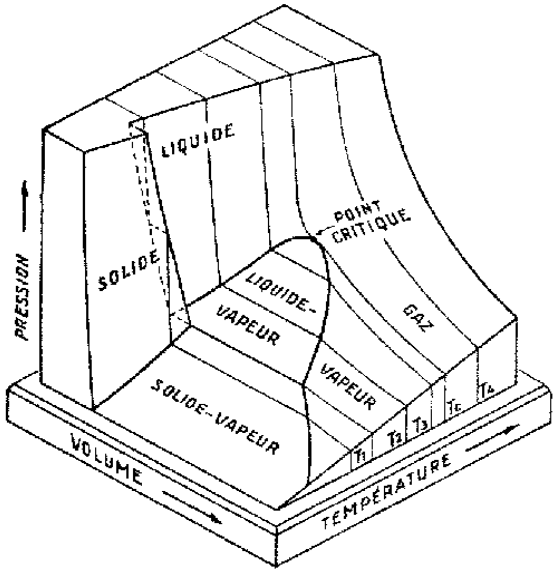
AMAS OU AGREGATS ATOMIQUES

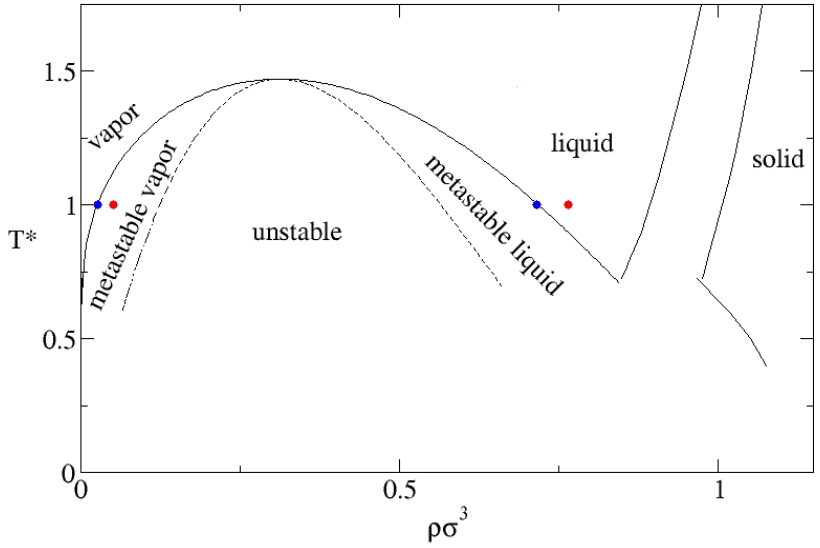
- L'auto-assemblage: Nucleation
  - Modele de l'amas: “capillary model”.
  - Thermodynamics
  - Becker-Doring model
  - Zeldovich equation
  - Taux de nucléation
- Nanoparticules cristalline
  - Structure cristalline
  - Indices de Miller
  - Tension de surface
  - Forme des Cristaux
  - Transistions de phase
- Proprietes electronique des agregats

A simple but realistic example: Liquid-vapor transition



(c)



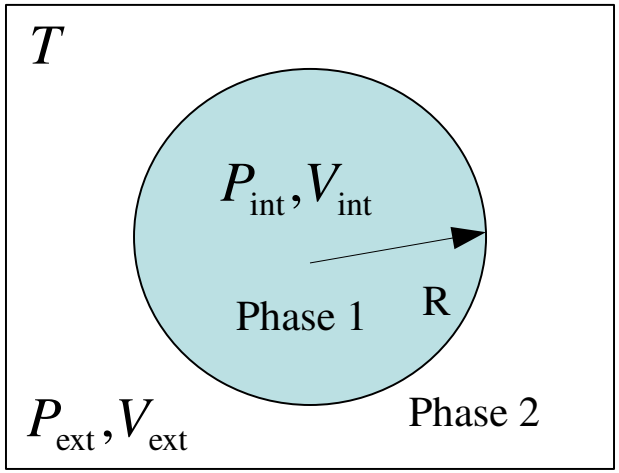


Modele de l'Amas : “Capillary model”

L'energie libre (ensemble généralisé)

$$\Omega = V(R)\omega_1 + S(R)\gamma_{12} + (V - V(R))\omega_2$$

ω est l'energie volumique par unite de volume, γ est l'energie surface



Minimisez par rapport à R:

$$0 = \frac{\partial \Omega}{\partial R} \rightarrow S(R)\omega_1 + S'(R)\gamma_{12} = S(R)\omega_2$$

Si $\omega_i = \omega(\rho_i)$ on droit minimiser par rapport aux densities:

$$0 = \frac{\partial \Omega}{\partial \rho_i} \rightarrow \frac{\partial \omega(\rho_i)}{\partial \rho_i} = 0$$

Rappelez-vous que $\omega(\rho) = f(\rho) - \mu\rho \rightarrow \omega'(\rho) = f'(\rho) - \mu$

Donc, $f'(\rho_i) = \mu \rightarrow \omega(\rho_i) = f(\rho_i) - f'(\rho_i)\rho_i = -P(\rho_i)$

$$0 = \frac{\partial \Omega}{\partial R} \rightarrow -P(\rho_1) + \frac{S'(R)}{S(R)}\gamma_{12} = -P(\rho_2)$$

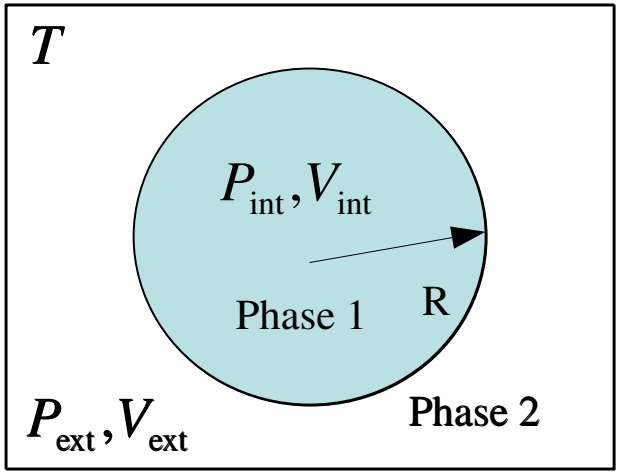
Equation de Laplace: $$P_{int} = P_{ext} + \frac{2g}{R}$$

Modele de l'Amas : “Capillary model”

L'energie libre (ensemble canonique)

$$F = V(R) f_1 + S(R) \gamma_{12} + (V - V(R)) f_2$$

f est l'energie volumique par unite de volume,
est c'est N qui est constante: $\rho_1 V(R) + \rho_2 (V - V(R)) = N$



Minimiser par rapport à R:

$$0 = \frac{\partial F}{\partial R} = S(R) f_1 + S'(R) \gamma_{12} - S(R) f_2 + (V - V(R)) f'_2 \frac{\partial \rho_2}{\partial R}$$

$$S(R) f_1 + S'(R) \gamma_{12} = S(R) f_2 + S(R) f'_2 (\rho_1 - \rho_2)$$

$$S(R)(f_1 - f'_2 \rho_1) + S'(R) \gamma_{12} = S(R)(f_2 - f'_2 \rho_2)$$

Minimize par rapport à la premiere densitie: $0 = V(R) f'_1 + (V - V(R)) f'_2 \frac{\partial \rho_2}{\partial \rho_1} = V(R)(f'_1 - f'_2)$

Puis, c'est la même qu'avant sauf $\rho_2 = \frac{N - \rho_1 V(R)}{(V - V(R))} = \frac{N}{V} + (\frac{N}{V} - \rho_1) \frac{V(R)}{V} + \ldots$

Donc, la deux calcul (dans l'ensemble canonique est dans l'ensemble généralisé) sont équivalent dans la limit $V \to \infty$

En fait et en general, les ensembles sont equivalent dans ce cas.

Modele de l'Amas : “Capillary model”

Équivalence d'ensemble (d'apres Oxtoby et Evans, J. Chem. Phys. 89, 7521 (1988)):

$$\Omega = -PV + \gamma S \qquad F = -PV + \gamma S + \mu N = \Omega + \mu N$$

Donc, pour la difference:

$$\Omega_1 - \Omega_2 = -(P_1 - P_2) + \gamma S$$

$$F_1 - F_2 = -(P_1 - P_2)V + \gamma S + (\mu_1 - \mu_2)N$$

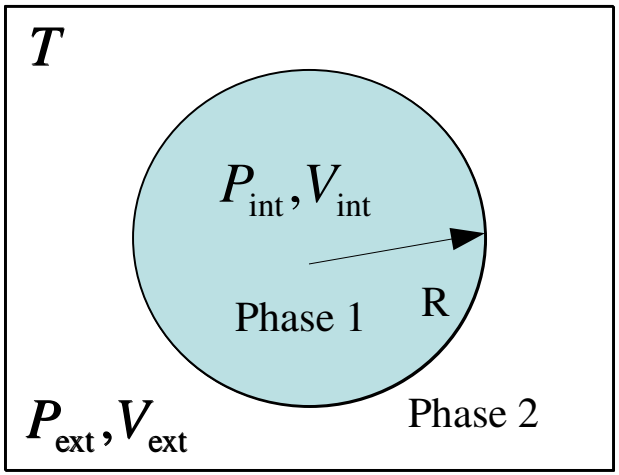
$$\Delta\Omega = \Delta F \Leftrightarrow \mu_1 = \mu_2 \Leftrightarrow \text{thermodynamic limit}$$

Modele de l'Amas : “Capillary model”

Par ailleurs, un methode plus simple
dans l'ensemble canonique:

$$dF = -SdT - PdV + \gamma\, dA$$

$$dF = -SdT - P_{\text{int}}\, dV_{\text{int}} - P_{\text{ext}}\, dV_{\text{ext}} + \gamma\, dA$$



$$V_{\text{int}} = \frac{4\pi}{3} R^3 \qquad dV_{\text{int}} = 4\pi R^2\, dR$$

$$V_{\text{ext}} = V - V_{\text{int}} \qquad dV_{\text{ext}} = -dV_{\text{int}}$$

$$A = 4\pi R^2 \qquad dA = 8\pi R\, dR$$

$$0 = dF = \left(-P_{\text{int}} + P_{\text{ext}}\right) 4\pi R^2\, dR + \gamma\, 8\pi R$$

Equation de Laplace:

$$P_{\text{int}} = P_{\text{ext}} + \frac{2\gamma}{R}$$

Energie libre

Energie libre de Helmholtz (ensemble canonique):

$$F(\rho;T,V)=f(\rho;T)V$$

Gaz parfait:

$$\beta f(\rho;T)\equiv\beta f_{id}(\rho;T)=\rho\ln\rho-\rho$$

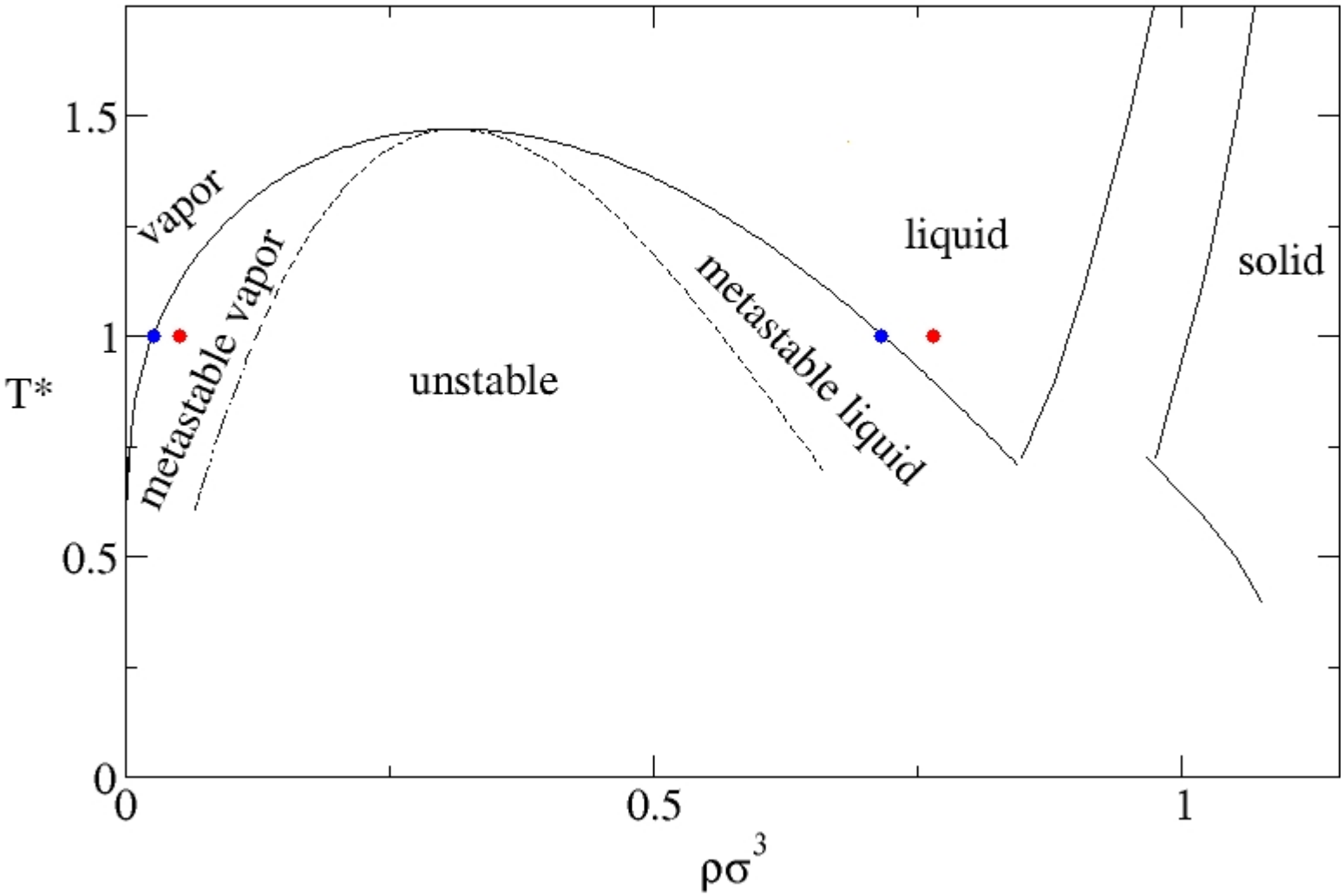
Gaz hard-sphere avec diametre d (Carnahan-Starling approximation):

$$\beta f_{hs}(\rho;T)=\beta f_{id}(\rho;T)+\rho\eta\frac{4-3\eta}{(1-2\eta)^2},\quad \eta=\frac{4\pi}{3}(d/2)^3\rho=\frac{\pi}{6}\rho d^3$$

Champ moyenne (van der Waals):

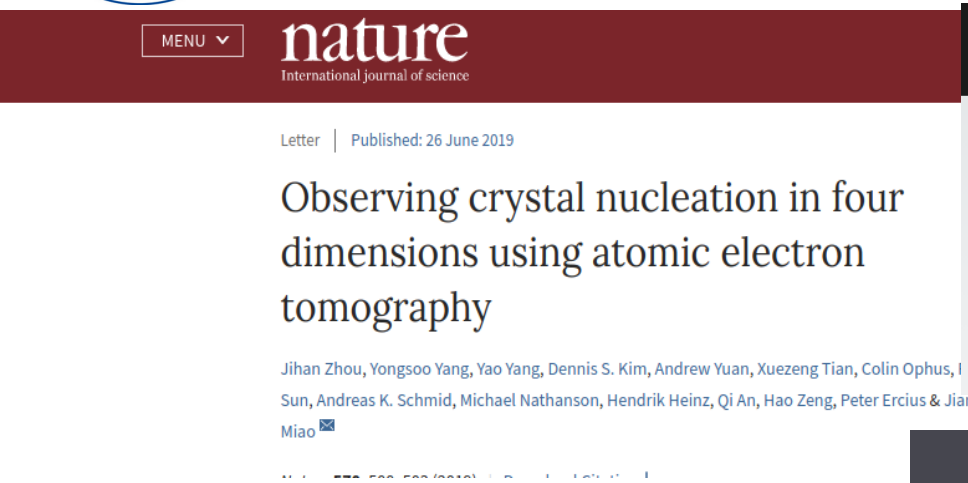
$$\beta f(\rho;T)=\beta f_{hs}(\rho;T)-\frac{1}{2}a\rho^2 \qquad a=\beta\int v_{\text{att}}(\boldsymbol{r})\,d\boldsymbol{r}$$

Les transitions de phase



Coexistence de deux phase: $p_1 = p_2,$ $, f_1 = f_2$

Crystallization is a hot topic …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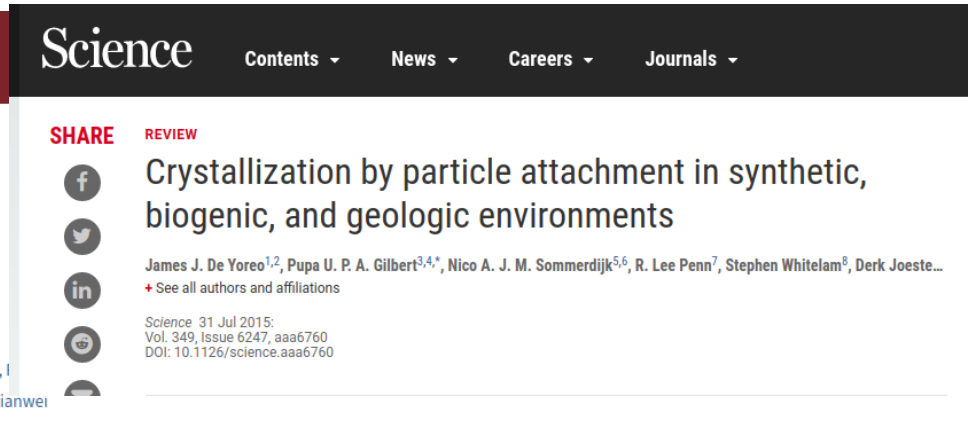
Letter | Published: 26 June 2019

Observing crystal nucleation in four dimensions using atomic electron tomography

Jihan Zhou, Yongsoo Yang, Yao Yang, Dennis S. Kim, Andrew Yuan, Xuezeng Tian, Colin Ophus, … Sun, Andreas K. Schmid, Michael Nathanson, Hendrik Heinz, Qi An, Hao Zeng, Peter Ercius & Jianwei Miao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Crystallization by particle attachment in synthetic, biogenic, and geologic environments

James J. De Yoreo[1,2], Pupa U. P. A. Gilbert[3,4,*], Nico A. J. M. Sommerdijk[5,6], R. Lee Penn[7], Stephen Whitelam[8], Derk Joeste…

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Science 31 Jul 2015:
Vol. 349, Issue 6247, aaa6760
DOI: 10.1126/science.aaa6760


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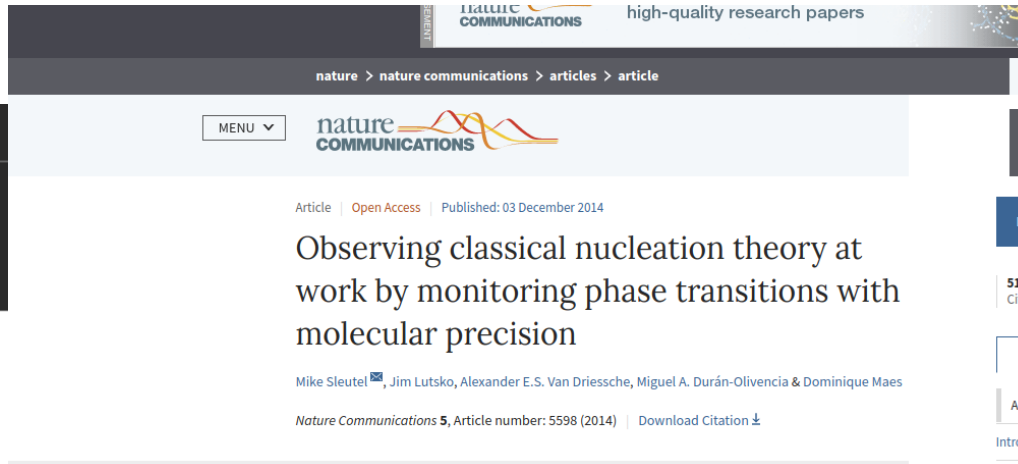
Science 06 Jan 2012:
Vol. 335, Issue 6064, pp. 11
DOI: 10.1126/science.335.6064.11-f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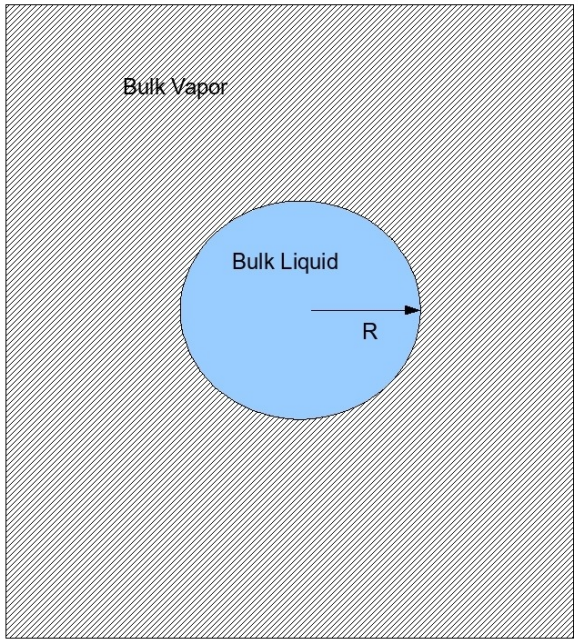
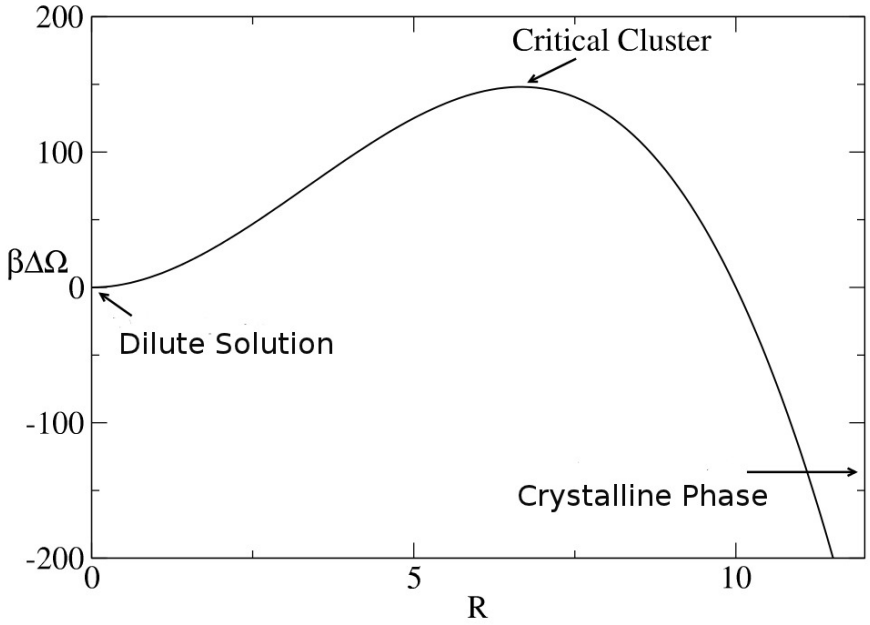
Observing classical nucleation theory at work by monitoring phase transitions with molecular precision

Mike Sleutel, Jim Lutsko, Alexander E.S. Van Driessche, Miguel A. Durán-Olivencia & Dominique Maes

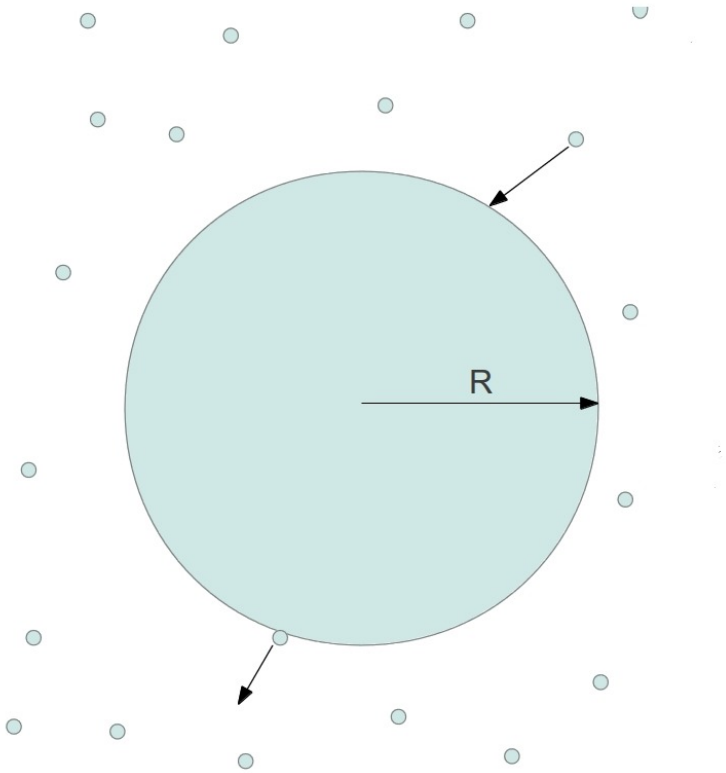
Nature Communications **5**, Article number: 5598 (2014) | Download Citation

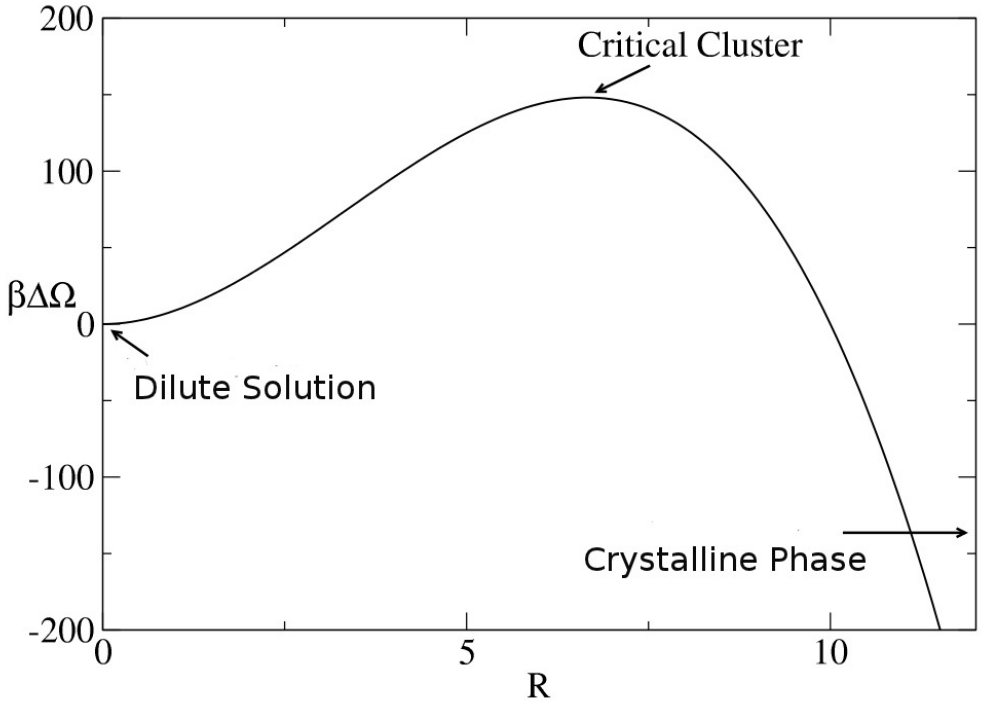
Les transitions de phase : le processus





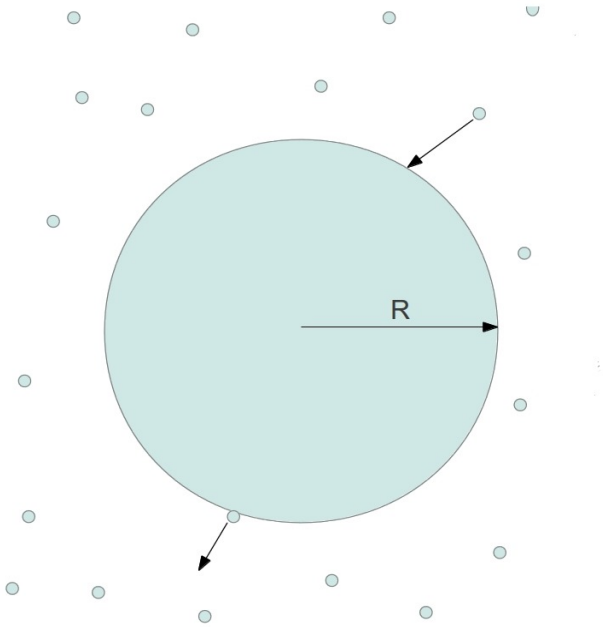
Classical Nucleation Theory (CNT) : Thermodynamics

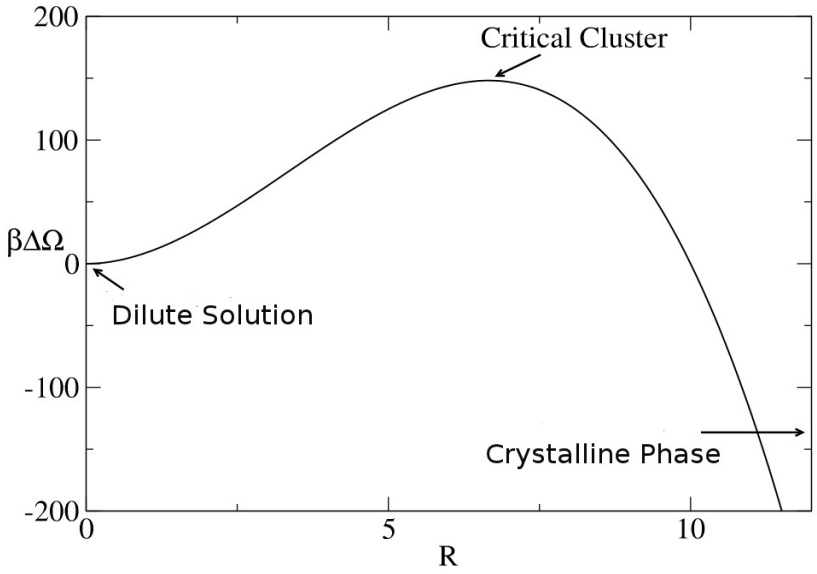




$$\Omega = V(R)\omega_2 + S(R)\gamma + (V - V(R))\omega_1$$
$$= V(R)\Delta\omega + S(R)\gamma + V\omega_1$$
$$\Delta\Omega = V(R)\Delta\omega + S(R)\gamma$$

Classical Nucleation Theory (CNT) : Dynamics





Monomer attachment/detachment (Becker-Doring c. 1930):

$$\frac{dc_n}{dt} = \left(f_{n-1} c_{n-1} c_1 - g_n c_n\right) - \left(f_n c_n c_1 - g_{n+1} c_{n+1}\right)$$

f_n, g_n sont les taux de fixation et de détachement des monomères