

Lecture 3

D. Frenkel, Boulder, July 7, 2006

Computing free-energy landscapes

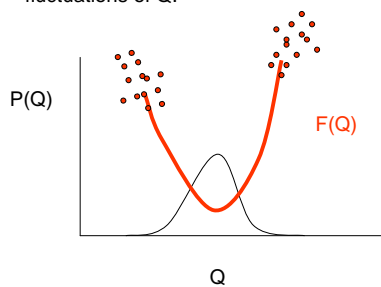
Suppose we have an "order parameter" $Q(r^N)$.
The probability that $Q(r^N)$ has a value Q is given by

$$P(Q_0) = \frac{\int \exp(-\beta U(r^N)) \delta(Q(r^N) - Q_0)}{\int \exp(-\beta U(r^N))}$$

From this probability we can derive the variation of the free energy with Q :

$$F(Q) = -kT \ln(P(Q)) + \text{constant}$$

This indicates a route to determine $F(Q)$: just make a histogram of the spontaneous fluctuations of Q .



Problem: $F(Q)$ is very noisy, except near its minimum.

Solution: perform a biased MC simulation and determine $P_w(Q)$

$$P_w(Q_0) = \frac{\int \exp[-\beta(U(r^N) + w(Q(r^N)))] \delta(Q(r^N) - Q_0)}{\int \exp[-\beta(U(r^N) + w(Q(r^N)))]}$$

But this we can rewrite as

$$P_w(Q_0) = \exp(-\beta w(Q_0)) \frac{\int \exp[-\beta U(r^N)] \delta(Q(r^N) - Q_0)}{\int \exp[-\beta(U(r^N) + w(Q(r^N)))]}$$

Clearly,

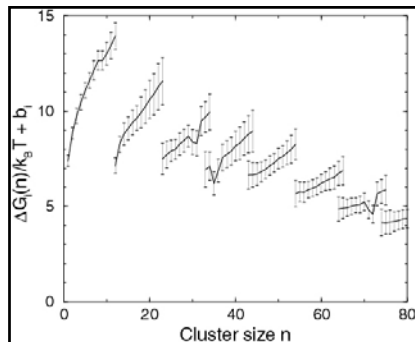
$$P_w(Q_0) = c \exp(-\beta w(Q_0)) P(Q_0)$$

or

$$-kT \ln(P(Q_0)) = -kT \ln(P_w(Q_0)) + w(Q_0) - kT \ln c$$

$$F(Q_0) = -kT \ln(P_w(Q_0)) + w(Q_0) - kT \ln c$$

We can choose the bias $w(Q)$ such that any desired range of Q -values is sampled. And we can correct for the bias.

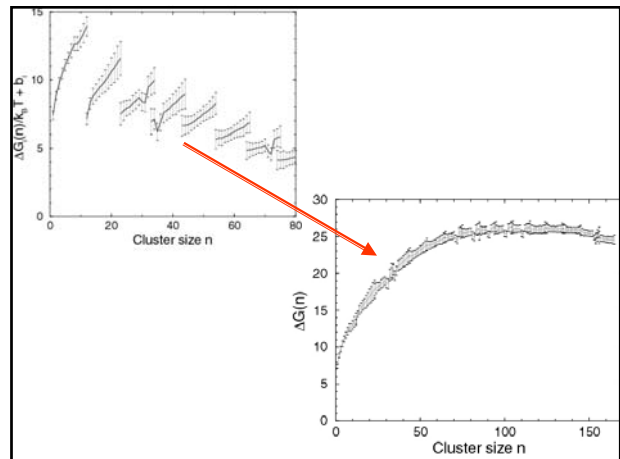


The only remaining problem is that the different parts of $F(Q)$ are shifted with respect to each other.

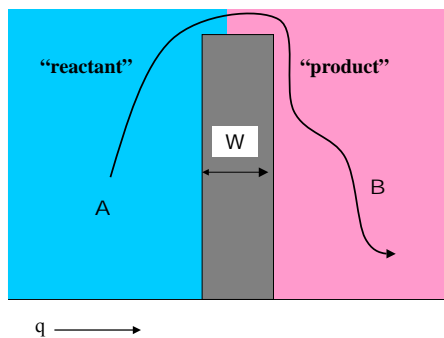
Solutions:

1. Fit to a single curve (not very elegant, but effective)
2. Use Ferrenberg-Swendsen scheme to combine different parts of the histogram (more elegant, but more sensitive to noise)

Result:



Simulating rare events.



How do concentration fluctuations decay?

$$\Delta c_A(t) = \Delta c_A(0) \exp(-t/\tau_R)$$

If the concentration increase on the left side of the barrier is $\Delta c_A(0)$, then the concentration increase on the top of the barrier is, on the left side:

$$\Delta c_A^* = \Delta c_A \exp(-\beta \Delta G)$$

And, on the right side: 0 ("absorbing boundary")

The diffusive flux across the barrier is:

$$j_A = D(\Delta c_A^*/W)$$

Therefore

$$\Delta \dot{c}_A(t) = -(D/W) \Delta c_A(t) \exp(-\beta \Delta G)$$

The solution is

$$\Delta c_A(t) = \Delta c_A(0) \exp(-t/\tau_R)$$

with

$$\frac{1}{\tau_R} = \frac{D}{W} \exp(-\beta \Delta G)$$

In practice, is only slightly more complex.

To compute the rate of an activated process, we must compute:

1. The free energy barrier (ΔG)
2. The diffusion constant at the top of the barrier (D)
3. The "effective" width of the barrier (for a square barrier, this is W – in other cases it is a bit different)

Comment:

For nearly ballistic barrier crossings, there are other expressions (Bennett-Chandler)

Applications typically combine many different techniques...

Example:
Crystal Nucleation

Intro:

Why is Nucleation important?

Holy grail:

TO FORM COMPLEX, ORDERED STRUCTURES
("CRYSTALS")
VIA SELF ASSEMBLY.

Steps required:

1. Design the "building blocks" (e.g. colloids) such that the desired structure is stable.
2. Verify that the stable structure can form within a reasonable time.

i.e.: Control nucleation and growth...

What could go wrong?

1. The system gels ⇒ No crystal
2. The crystal grows too fast ⇒ Many defects
3. The crystal is stable – yet never appears
4. Another, metastable phase forms
5. ...

Nucleation is too slow

Ostwald's rule

Ostwald's Rule(1897)

"The phase that nucleates need not be the stable phase, but the one that is closest in free energy to the parent phase..."

The more complex the building blocks, the more serious this problem becomes
("the polymorph disaster" – e.g. Ritonavir)

What could go wrong?

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Nucleation is too slow

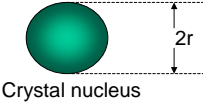
A brief review of Classical Nucleation Theory

Homogeneous nucleation

(e.g. Liquid \Rightarrow Solid)

Crystallization requires supercooling

($\mu_{\text{solid}} < \mu_{\text{liquid}}$)

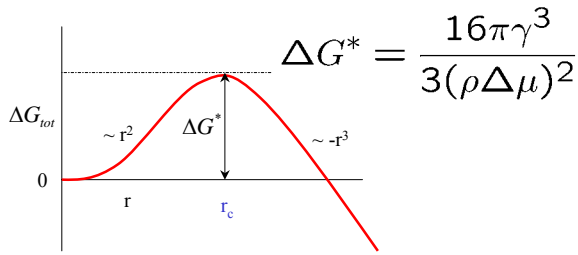


Free - energy gain

$$\Delta G_{\text{Bulk}} = \frac{4\pi}{3} \rho r^3 \Delta\mu_{s,l} < 0$$

Free - energy loss :

$$\Delta G_{\text{Surface}} = 4\pi r^2 \gamma_{s,l} > 0$$



Nucleation Rate = prefactor \times exp $[-\Delta G^*/kT]$

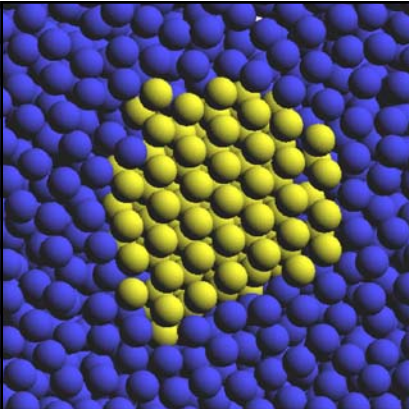
SURFACE FREE-ENERGY DENSITY ("SURFACE TENSION")

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\rho\Delta\mu)^2}$$

SHAPE

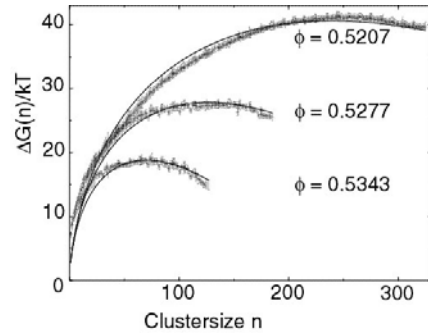
THERMODYNAMIC DRIVING FORCE

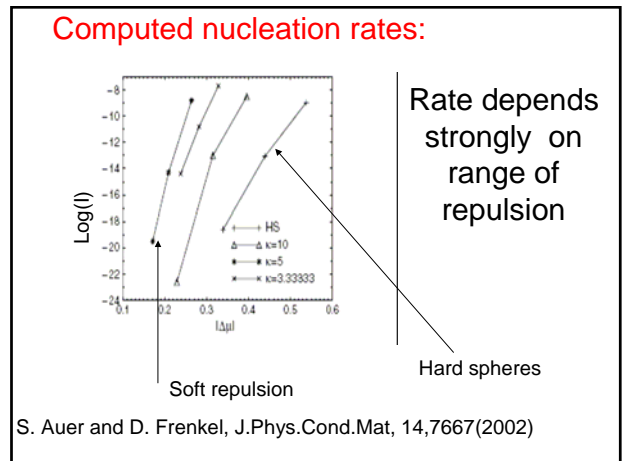
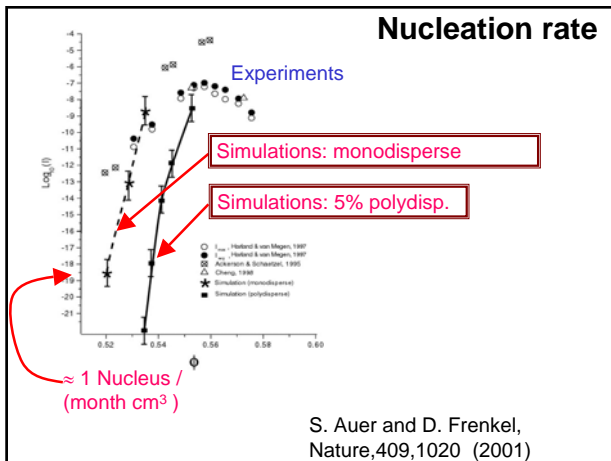
Nucleation Rate = prefactor \times exp $[-\Delta G^*/kT]$




Cut through critical nucleus of hard-sphere colloidal crystal

NUCLEATION BARRIER for Hard-sphere colloids





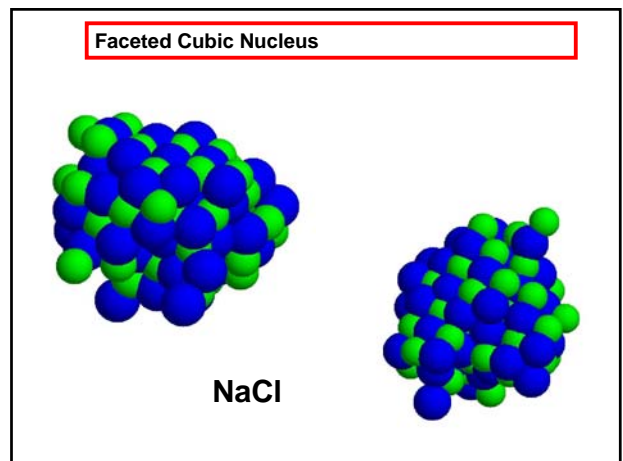
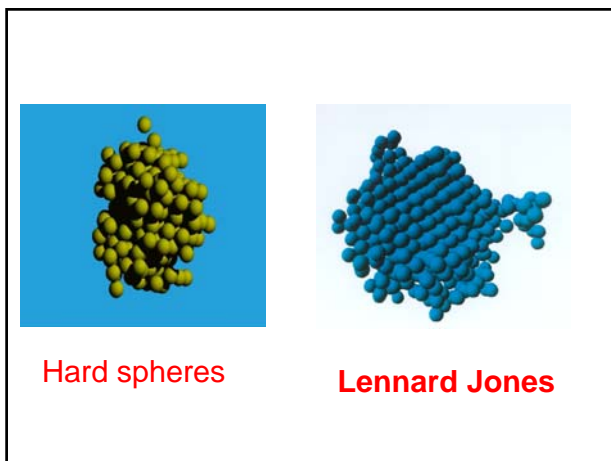
Old Question:
What is the structure of critical nuclei?



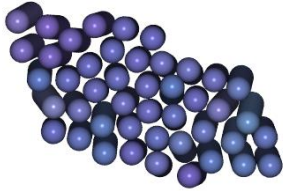
Wilhelm Ostwald

Ostwald's Rule(1897)
 "The phase that nucleates need not be the **stable phase**, but the one that is **closest in free energy** to the parent phase..."

Stranski & Totomanov (1930's)
 "The phase that nucleates is the one with the **lowest nucleation barrier..**"



Oblate Nucleus:



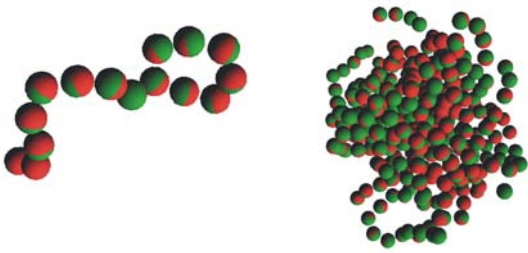
Rodlike Colloids

Hardly surprising, but...

Most experiments are fitted to CNT assuming a spherical nucleus →

Incorrect surface free energy estimates

Incidentally,
even LIQUID nuclei are not always spherical!



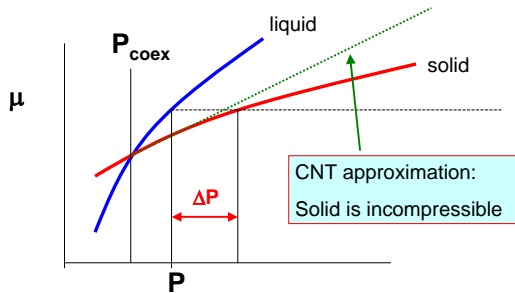
L-V Condensation of Polar Molecules

Ostwald's rule, is a RULE not an EXPLANATION

Why would a metastable phase nucleate?

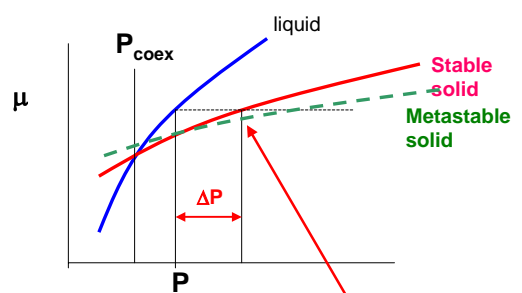
Consider the thermodynamic **droplet** model for nucleation (more general than Classical Nucleation Theory)

Metastable liquid and crystal nucleus have the same chemical potential



$\Delta P = 2\gamma/r$ (Laplace pressure)

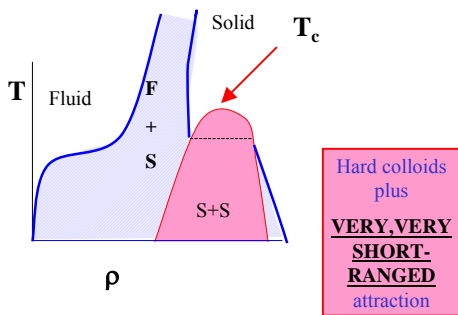
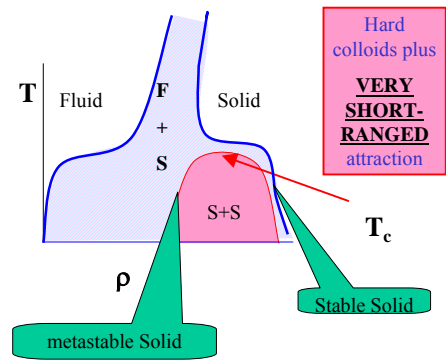
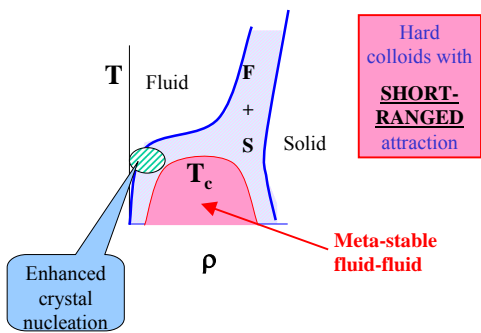
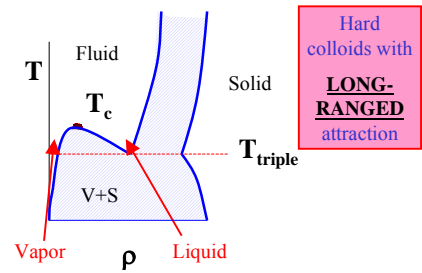
Now with a metastable phase:



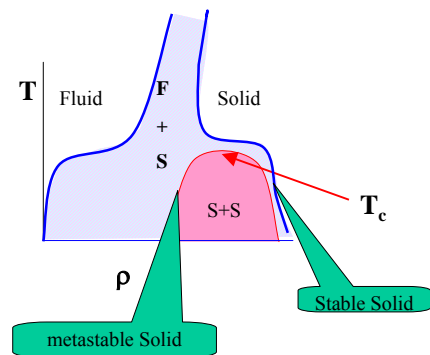
At the pressure inside the nucleus, the metastable phase is, in fact, **stable**.

So we should study a system with a stable and a meta-stable solid phase...

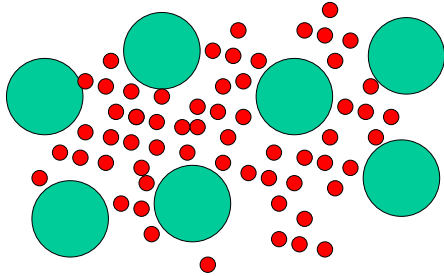
Intermezzo:
Phase behavior of colloids with short-ranged attraction...



But now we focus on system with meta-stable solid-solid transition

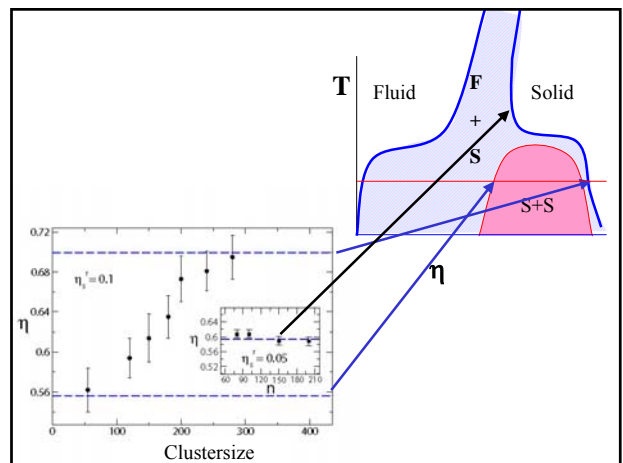
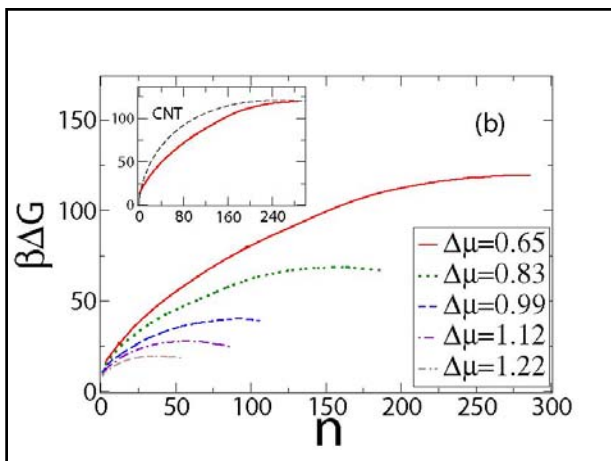
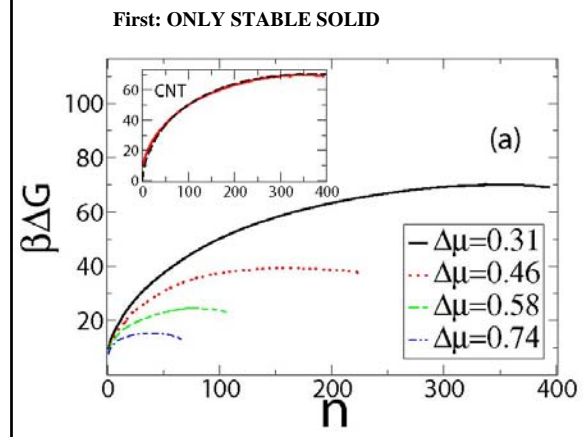
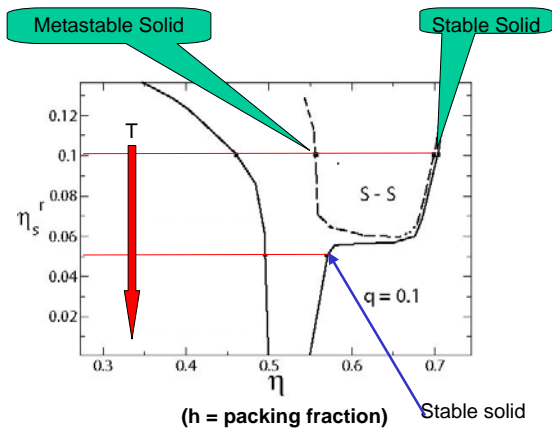
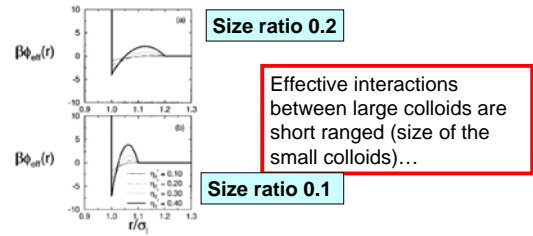


Realization: Mixtures of large and small hard colloids



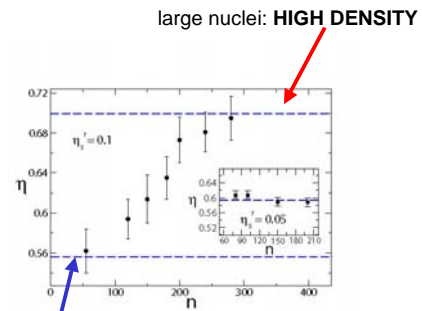
Phase diagram:

Dijkstra, van Roij and Evans PRL, **81**, 2268 (1998)



So, indeed, the metastable phase (if present) forms first.

But there is something strange....



Small nuclei: **LOW DENSITY**

How can that be?

At the pressure of the metastable liquid, the low density phase is **MECHANICALLY UNSTABLE**.

How can it be stabilized by an **ADDITIONAL Laplace pressure?**

It turns out that the entire analysis (CNT, Droplet model) is **wrong** for crystals.

For solids, the surface free-energy density is **NOT** the same as the surface stress.

Hence the Laplace pressure

$$\Delta P \neq \frac{2\gamma}{r}$$

But

$$\Delta P = \left(\gamma - \frac{3}{2} \rho \frac{d\gamma}{d\rho} \right) \frac{2}{r}$$

$$\Delta P = \left(\gamma - \frac{3}{2} \rho \frac{d\gamma}{d\rho} \right) \frac{2}{r}$$

For hard particles with attraction, the second term can be much larger than the first and the Laplace pressure can even become **negative!**

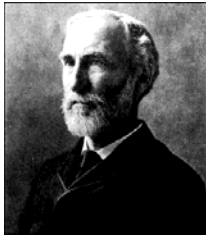
THAT IS WHY THE SMALL NUCLEI ARE IN THE LESS DENSE PHASE

NOTE TO EXPERIMENTALISTS:

The expansion of small crystal nuclei should be **DIRECTLY** observable in colloidal systems! Not just near a solid-solid transition

Are all old theories about crystal nucleation wrong?

NO: one man was right all along...



J. Willard Gibbs

$$\Delta G^* = \frac{A\gamma}{3}$$

The Gibbs expression for the barrier height **predates** Classical Nucleation Theory and it **survives** it...

(and he knew about surface stress)

References:

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