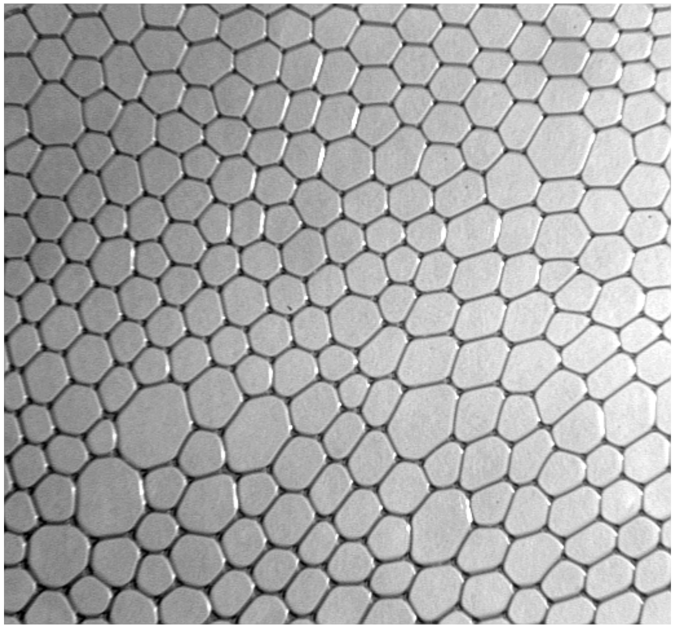
Les Houches School of Foam: Introduction to Coarsening



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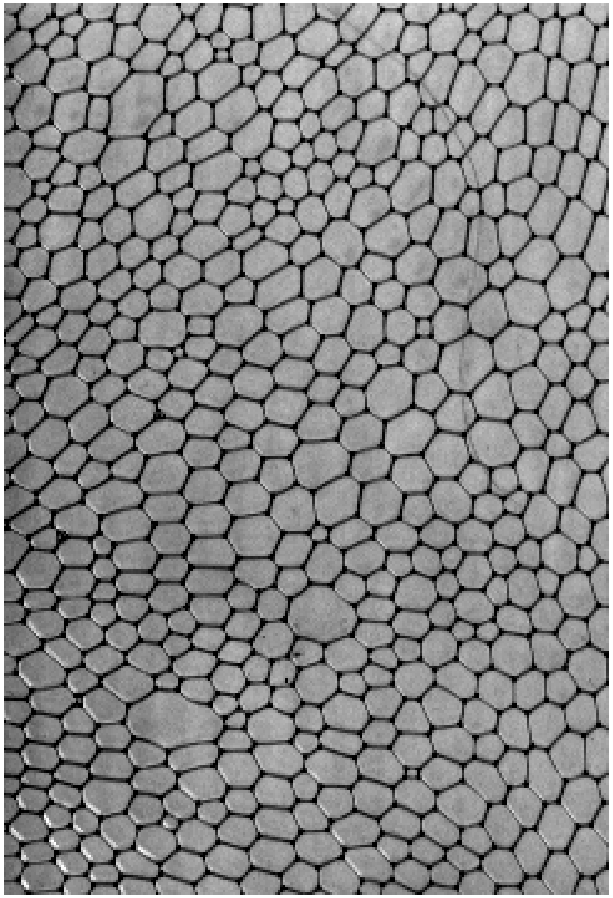
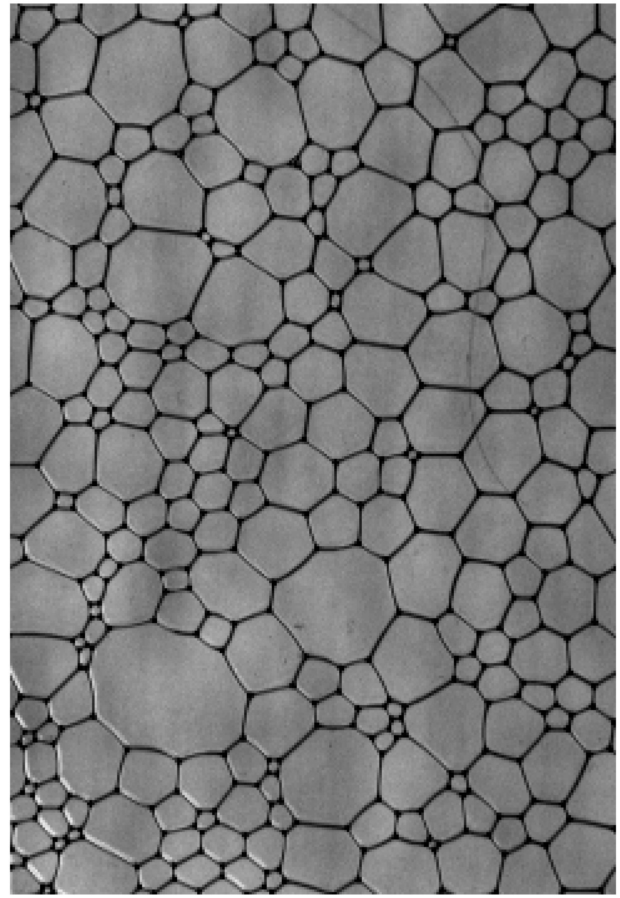
What is Coarsening?

(for a foam)





Initial foam between parallel plates at 17h00, and "coarser" foam the next morning at 9h00 (16 hrs later) - *Skach & Belmonte, 2002*

Coarsening in General

Foam is not the only physical system which coarsens. What is required to say that there is coarsening?

My answer:

- some sort of cellular or periodic structure
- that the lengthscale of the system increases with time
- (optional) this increase leads to fewer structures

Today we will discuss some of the other systems which coarsen, typically diphasic systems. How similar? How different?

How many ways of coarsening are there?

In This Lecture

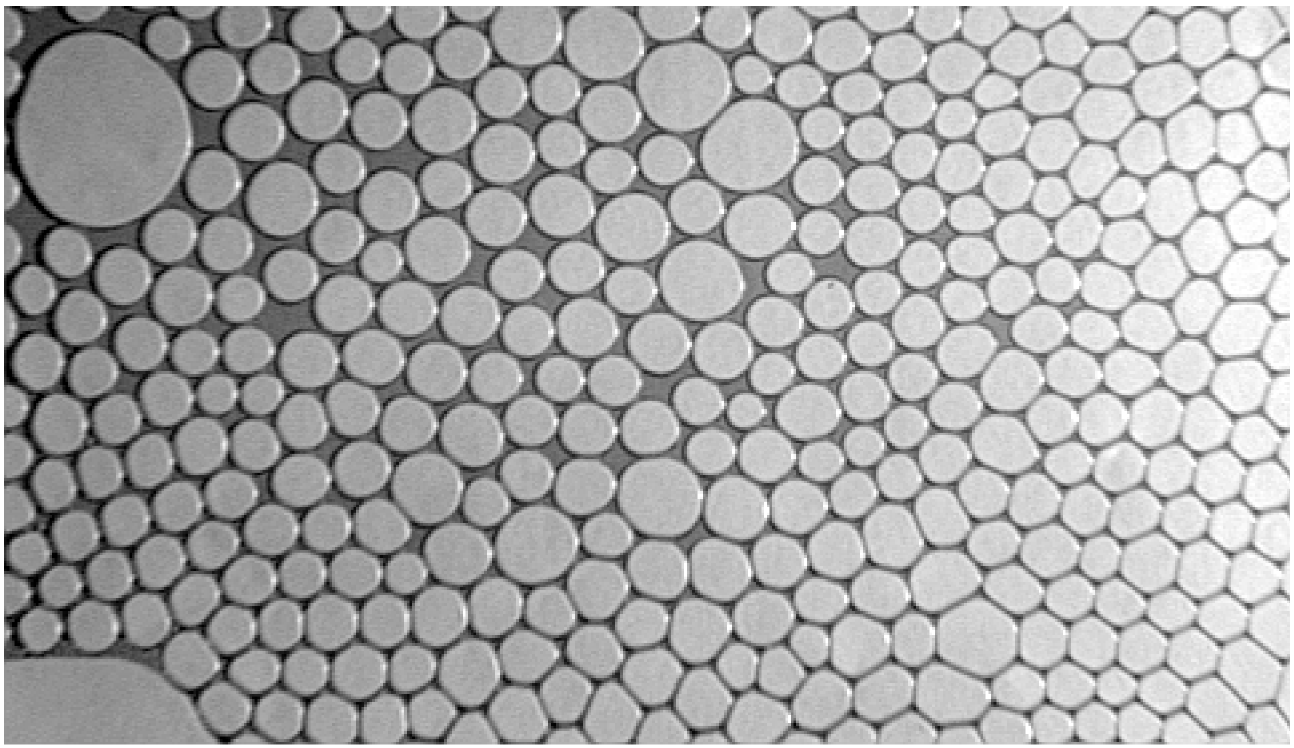
An Overview of the Physics of Coarsening - Systems and Mechanisms

- Survey of Experimental Systems - ‘Ostwald Ripening’ (1901)
- Refresher on Thermodynamic Transitions & Phase Separation
- Dicussion of mechanisms and scaling laws

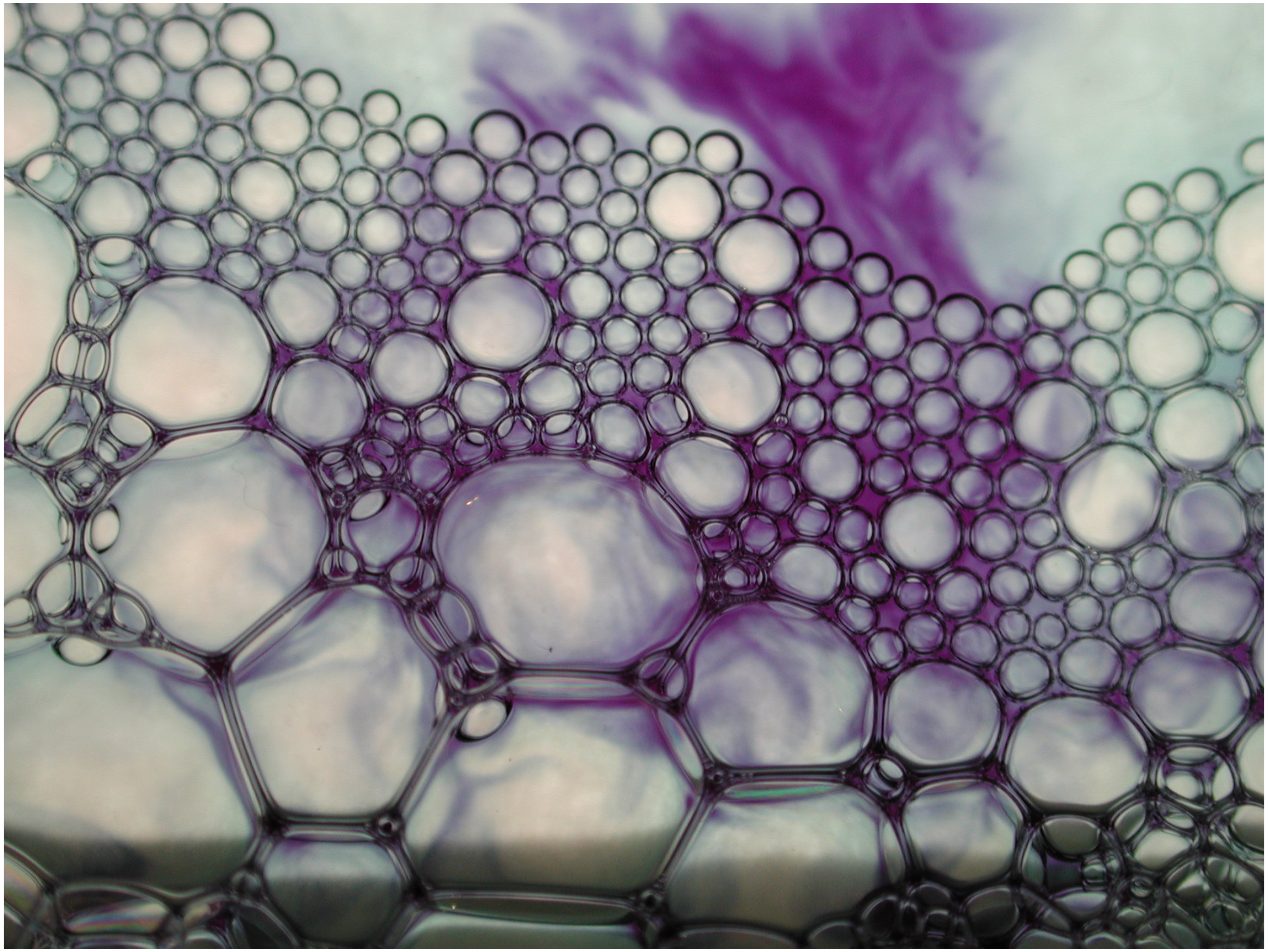
In This Lecture

An Overview of the Physics of Coarsening - Systems and Mechanisms

NOTE: from the foam side, think Wet Foams

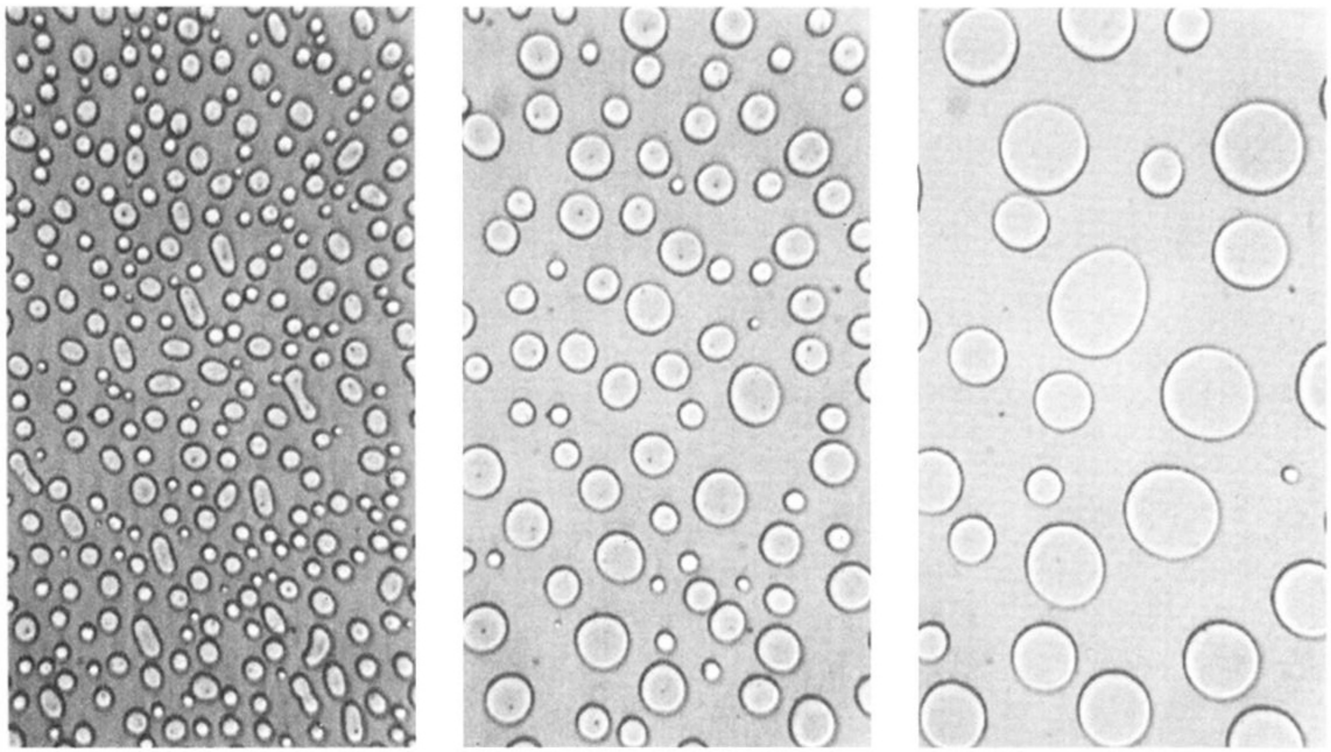


($1/8''$-thick quasi 2D soap bubbles and foam)



(Antje's 3D bubbles and foam, from the Gallery)

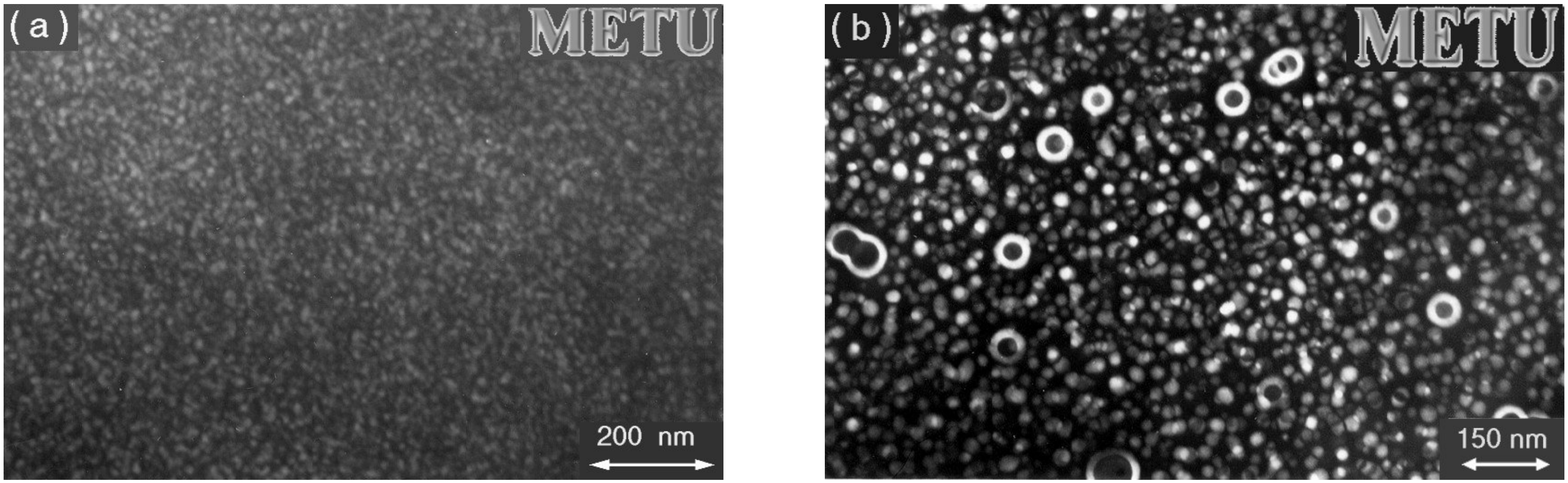
Coarsening in Various Physical and Model Systems



growth of liquid-solid coexistence domains in succinonitrile plastic
- 16, 145, and 1440 min ($T = 54°$C, $\phi = 0.3$)

Krichevsky & Stavans, Phys Rev E ***52****, 1818 (1995)*

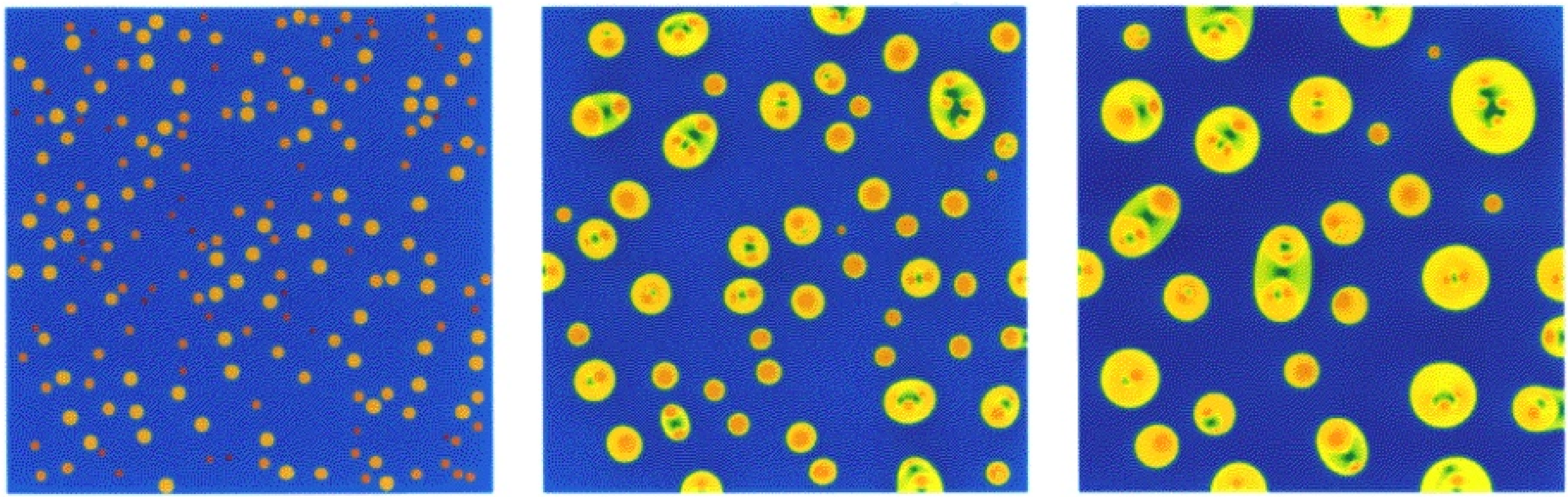
Coarsening in Various Physical and Model Systems



growth of Al_3Li precipitates in solution - 3,600 s and 32,400 s (473 K)

Metallurgical Engineering Dept, Middle East Tech Univ, Ankara, Turkey

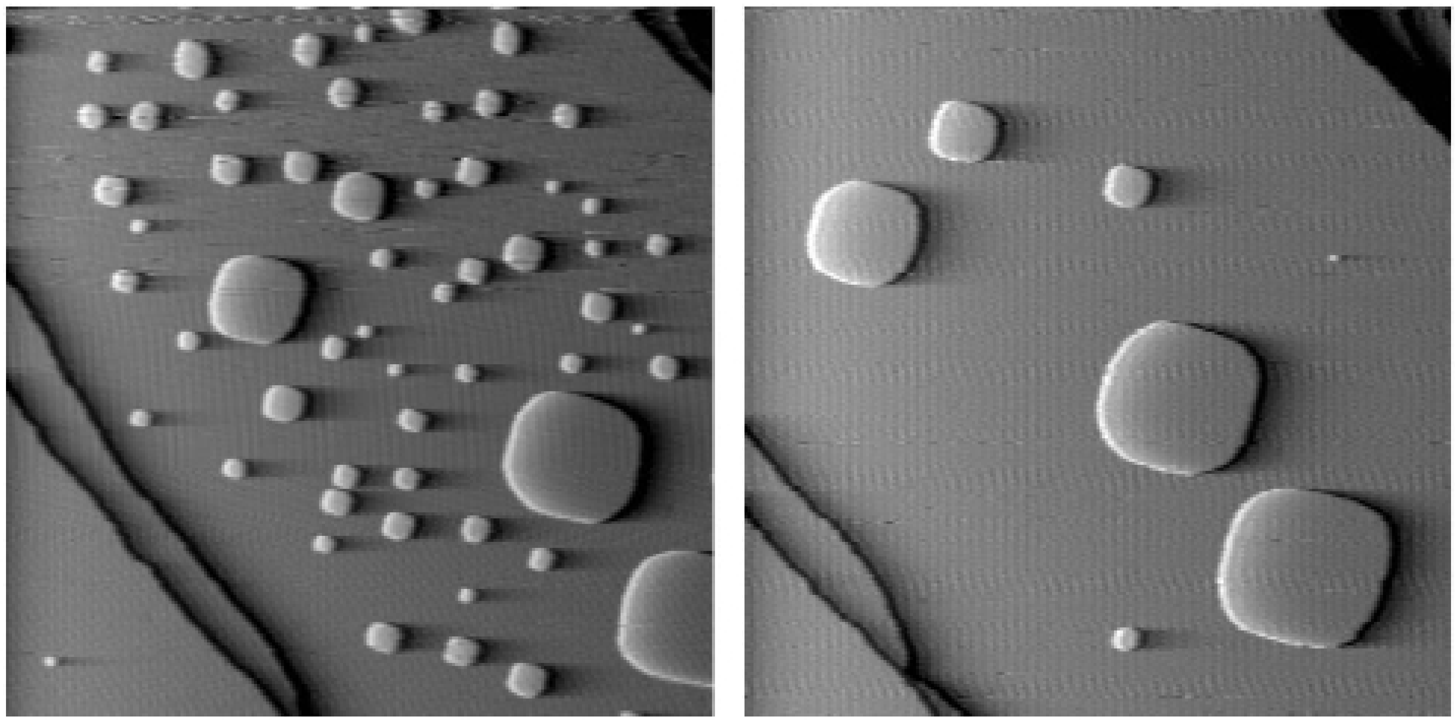
Coarsening in Various Physical and Model Systems



binary alloy domain growth - phase coexistence with interface energy term

Warren & Murray, Modelling Simul Mater Sci Eng ***4****, 215 (1996)*

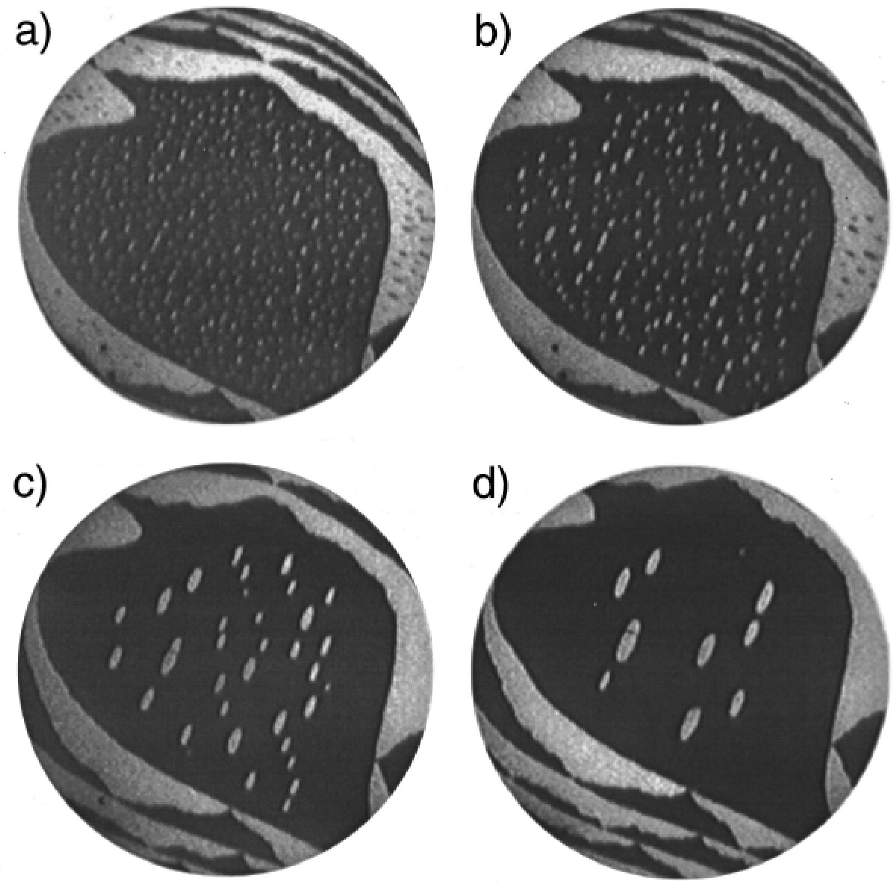
Coarsening in Various Physical and Model Systems



surface growth via 'island ripening' on Cu(001) - 300 nm $\times$ 300 nm

Hannon et al, Phys Rev Lett ***79****, 2506 (1997)*

Coarsening in Various Physical and Model Systems



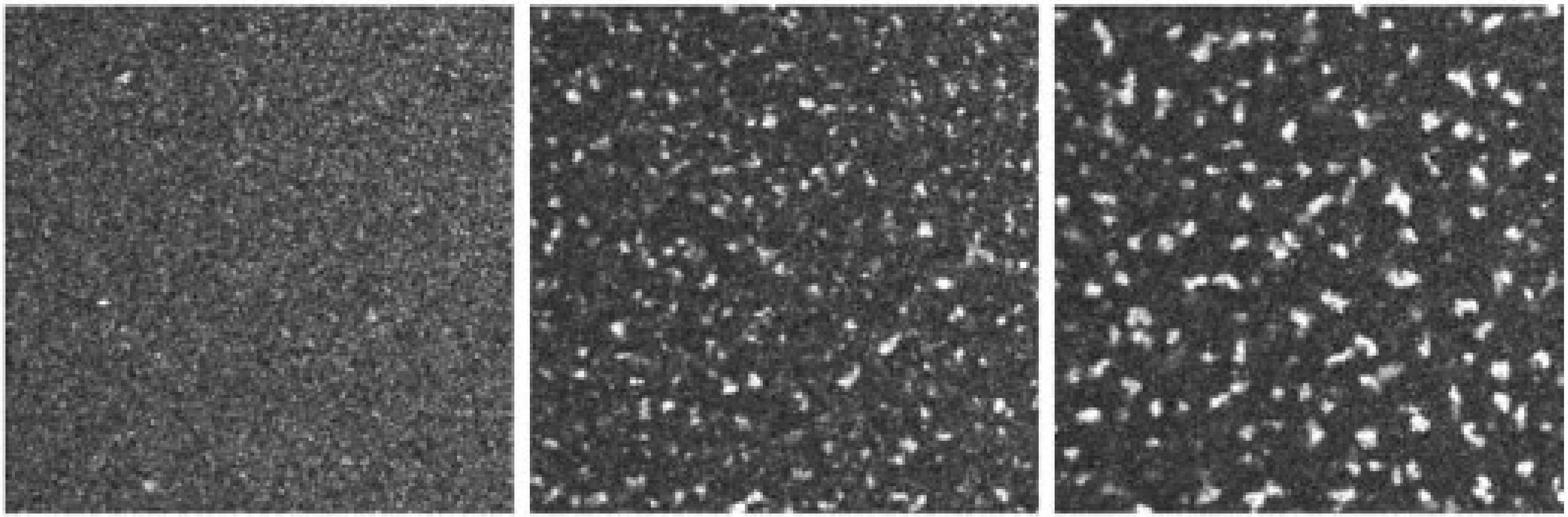
different anisotropy effect in single atom island ripening on Si(001)

*Bartelt et al, Phys Rev B **54**, 11741 (1996)*

But the first thing you (or at least I) think of when discussing ripening...

cheese - (cantal AOC)

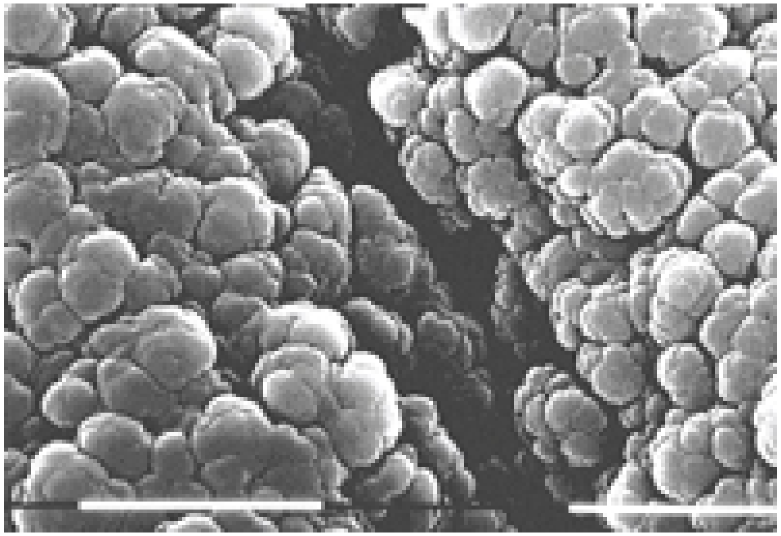
Coarsening in Various Physical and Model Systems



Aggregation of casein particles in milk protein / enzyme mixtures - 0, 10 and 30 min after stirring was stopped

de Bont et al, Food Hydrocolloids ***18****, 1023 (2004)*

Coarsening in Various Physical and Model Systems

Emulsions - usually we don't want them to coarsen!
(add stabilizing agents - surfactants, etc)

Thermodynamics of Phase Transitions

Start with the Ideal Gas law:

$$pV = nRT$$

in fact this is already material science...

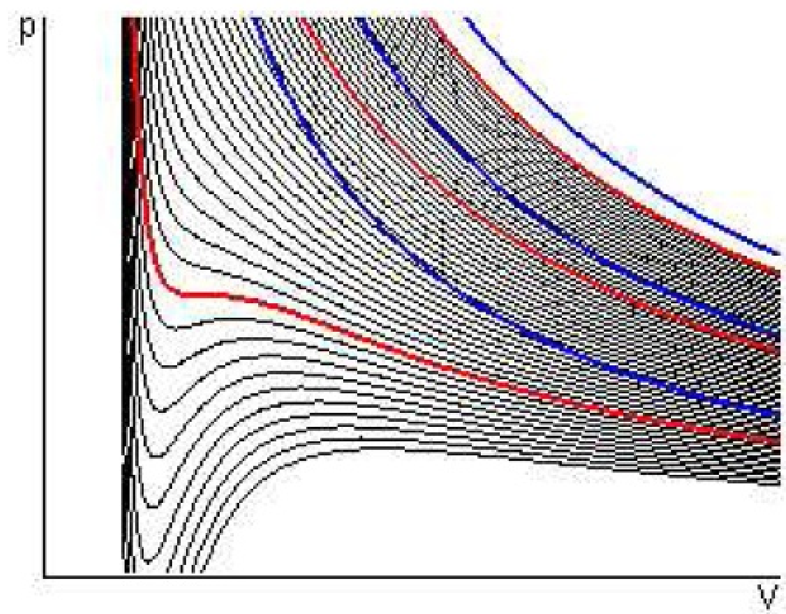
- discuss equation of state
- definition of thermodynamic equilibrium
- p, V isotherms are hyperbolic

Much that the ideal gas law is missing (life is not so ideal)

Improving the Ideal Gas equation of state

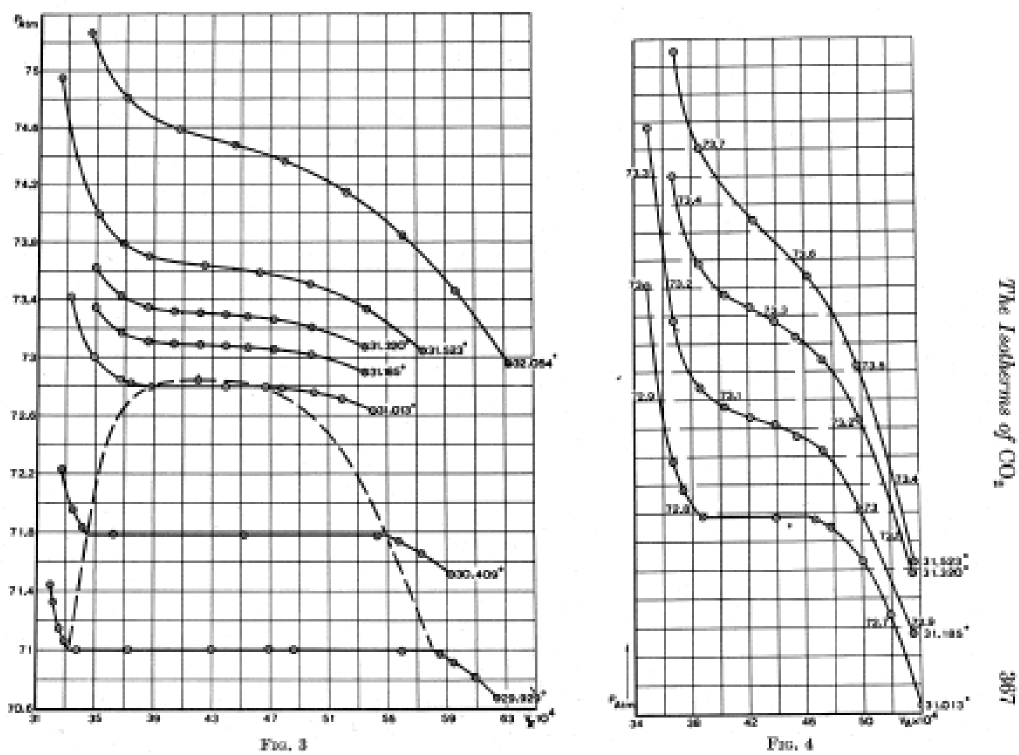
$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

the van der Waals equation of state, which includes excluded volume effects and an attractive interaction



Phase Coexistence

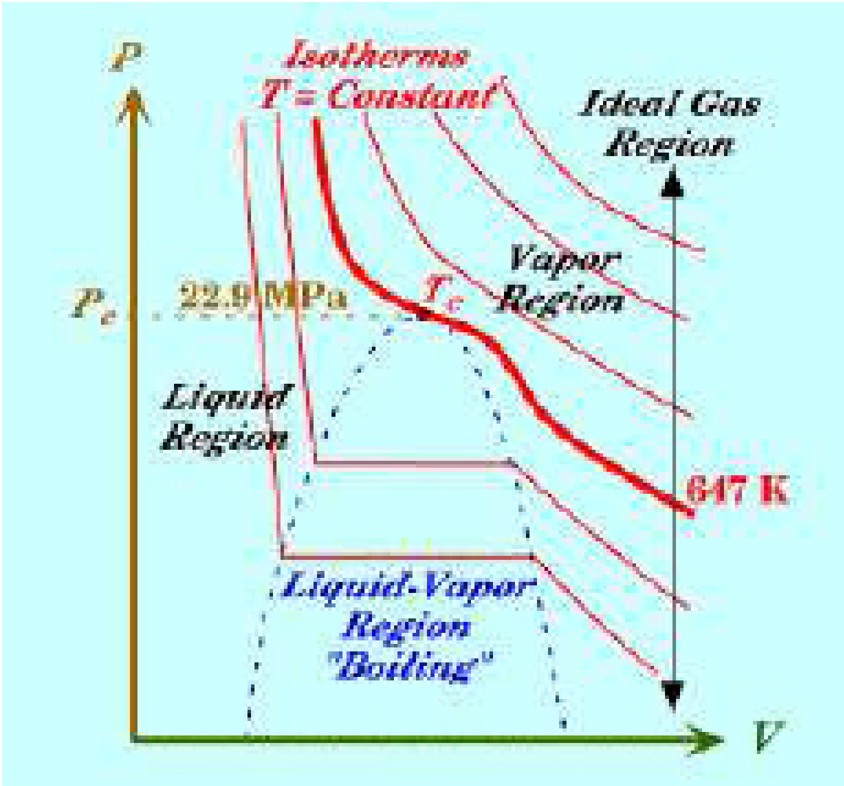
This region of the phase diagram (p, v plane) where $dp/dv < 0$ leads to instability $\rightarrow$ first-order phase transition. Seen experimentally in CO_2:



Michels, Blaisse, & Michels, Proc. Royal Soc. London A ***160****, 358 (1937)*

Phase Coexistence

Coexistence diagram for water:



The apparent plateau is not a single point but *two points* on the diagram: the material is two phase!

Phase Coexistence

So where are the two phases?

- discuss this ambiguity
- how long until we are in thermodynamic equilibrium?
- is it all transient?
- interface energy needs to be included in our equation of state...

$\rightarrow$ Minimizing the energy of the system typically implies that the total interface should be as small as possible; but *how* to do this??

Ostwald ripening (coarsening) appears in the transient approach to coexistence in equilibrium - trying to minimize the surface when the domains are separate!

Transients: Fast and Slow

The time evolution of a first-order phase transition can be divided into several different stages:

1. *Quench*

Starting with a homogeneous system in ‘equilibrium’, experimental knobs are turned until the parameters are in the coexistence region

2. *Nucleation and growth*

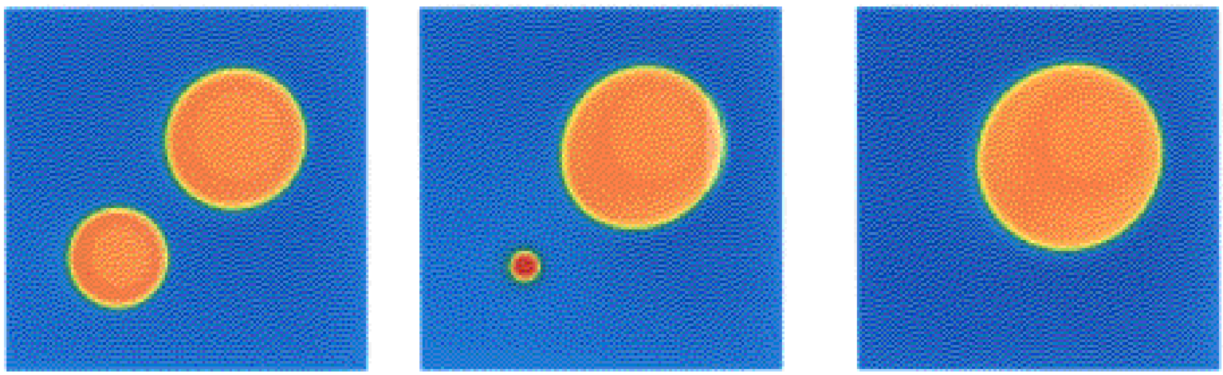
Fluctuations in the old metastable phase lead to the formation of the new phase throughout space (cluster formation). These clusters grow rapidly until the volume fraction of the two phases is close to the new equilibrium value

3. *Ripening or coarsening*

The coexisting phases evolve further to minimize total energy, but against limiting processes such as diffusion or coagulation. Some regions become larger, some disappear

Coarsening Mechanisms: Diffusive Flux

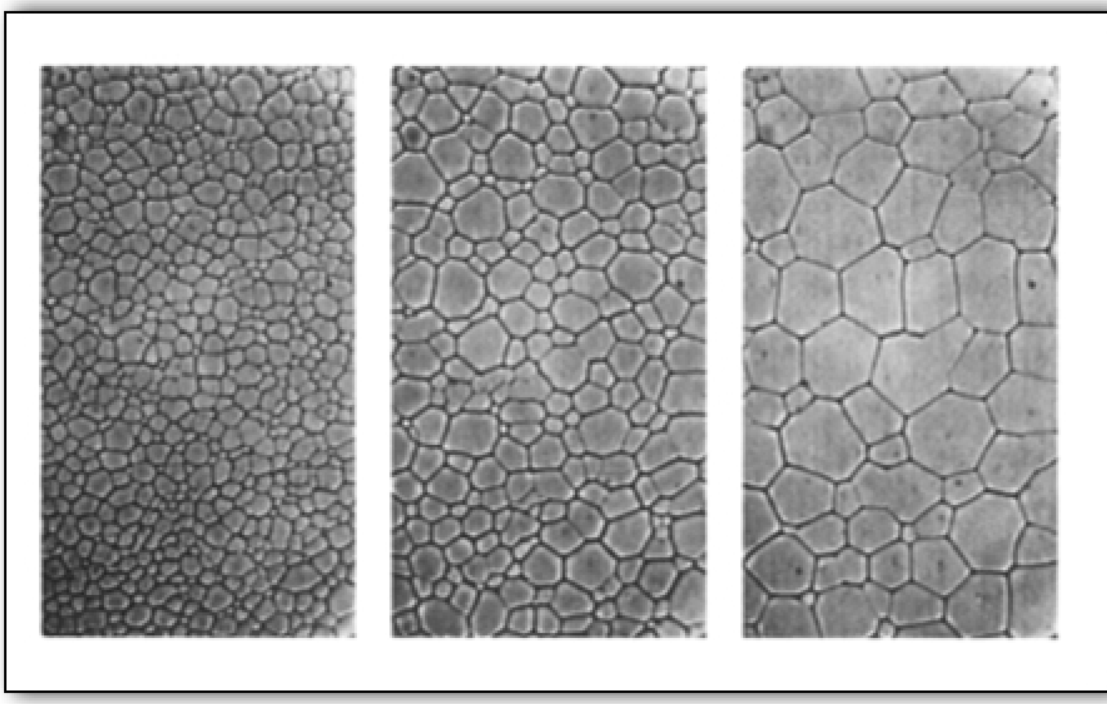
How do drops coarsen if they are far apart? One mechanism is the diffusion of minority species through the bulk material in between. For example:



phase field model simulation for binary alloys, two drops - $t/\Delta t = 1, 50, 73$

Warren & Murray, Modelling Simul Mater Sci Eng ***4****, 215 (1996)*

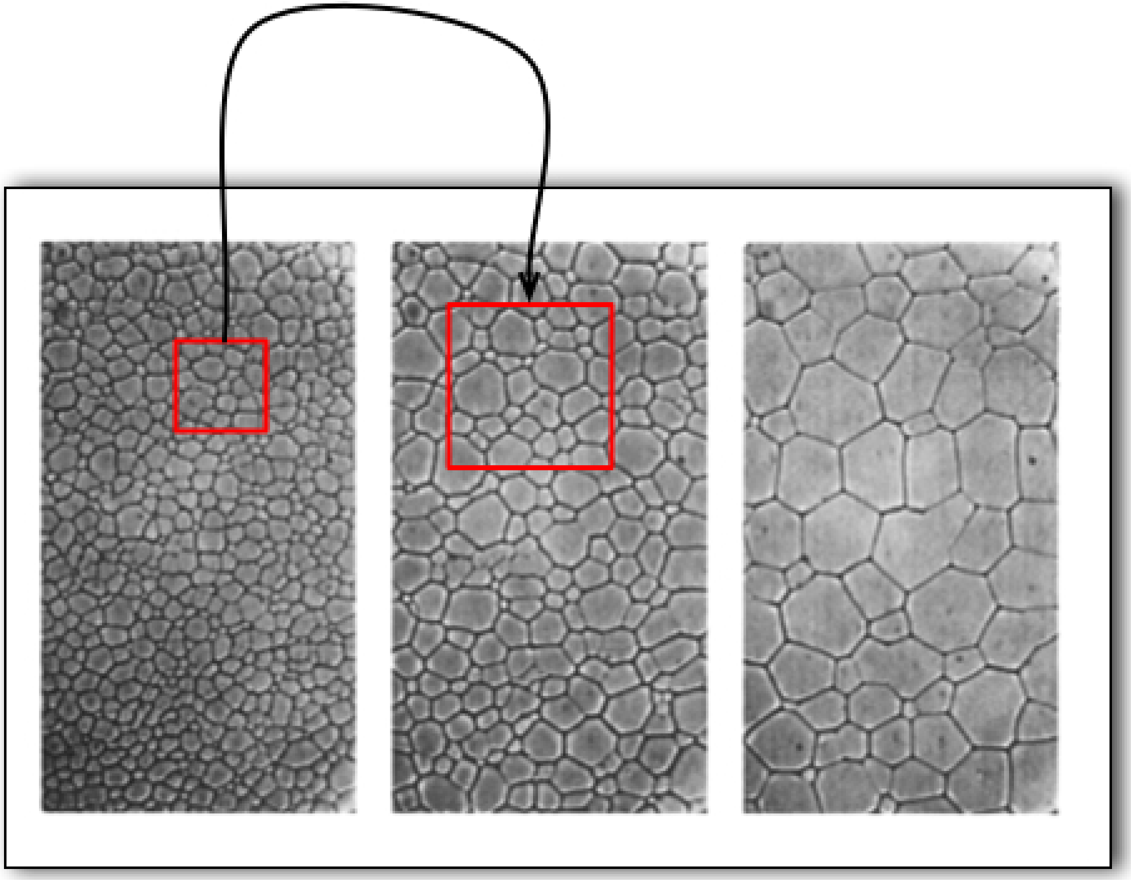
The Scaling Regime in Coarsening



liquid-solid coexistence of succinonitrile plastic ($T = 38°$C, $\phi \simeq 1.0$)

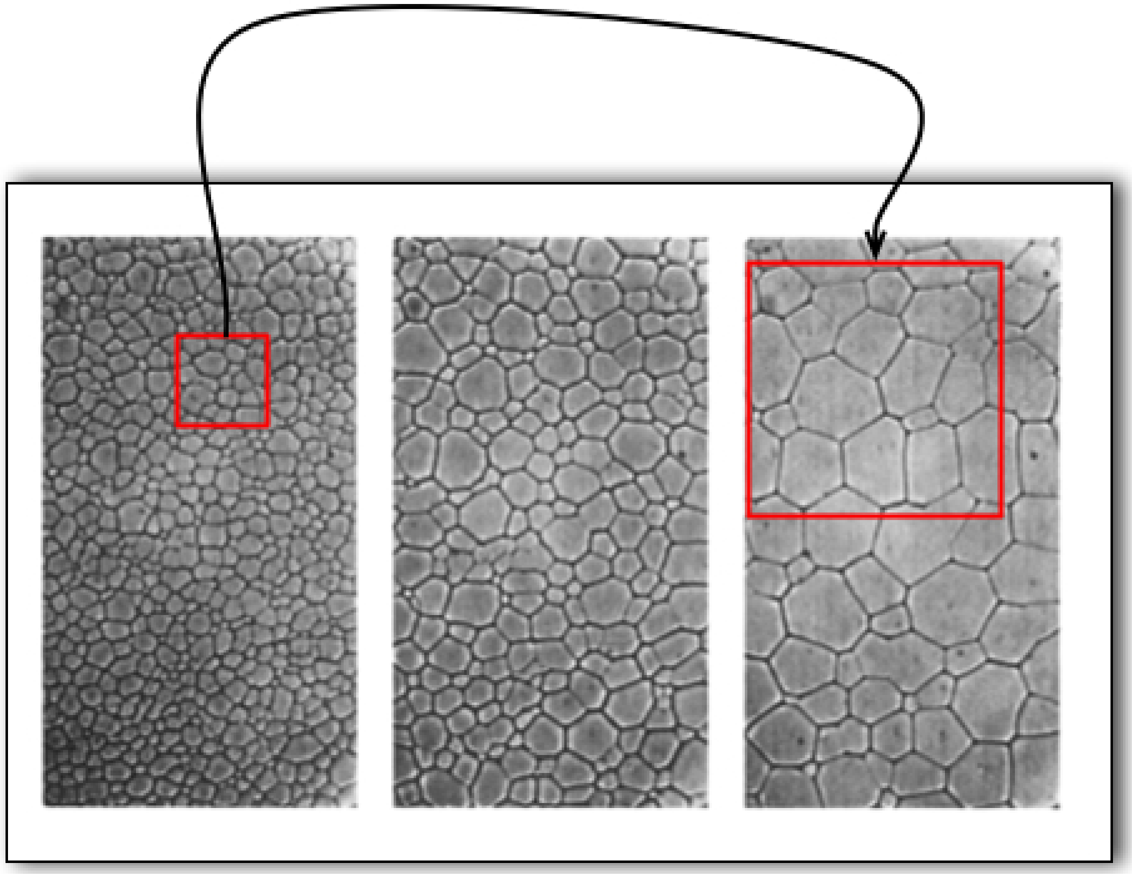
Krichevsky & Stavans, Phys Rev E ***52****, 1818 (1995)*

The Scaling Regime in Coarsening



In coarsening systems, the scaling hypothesis means that - statistically speaking - larger regions at later times look like smaller regions at earlier times...

The Scaling Regime in Coarsening



The question is:

given a certain time interval, how to rescale the size of the region?

Scaling Laws in Coarsening

Model dependent, and suffers from usual nonuniqueness of scaling laws!

Here mention only the simplest case:

based on dimensional analysis, given an average domain size R, in the mean field limit (each domain is alone) with diffusion the only physical limitation, the growth law scales as

$$\frac{dR}{dt} \sim \frac{D}{R}$$

which is curvature limited diffusion. This leads to

$$R \sim t^{1/2}$$

Summary and Foam Connections

Coarsening can occur in many slightly-out-of-equilibrium systems, with different mechanisms. Already not so easy even with few domains far apart...

Returning back to foam:

- topology enters as domains encroach on and deform each other; domain loss in this situation may cause long-range rearrangements
- diffusion or other effects driving flux may be modified $\rightarrow$ von Neumann's law
- domain walls subject to new forces (e.g. cell walls meet at 120°)
- unlike particle preciptates, collisions and sedimentation may not play a role - unless the foam is shaken...