Spinodal-Assisted Crystallization in Polymer Melts

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Outline

1. Summary of experiments
2. Hypothesis of Liquid-Liquid Separation
3. Model and Predictions
4. Relation to other systems
5. Consequences/future work

"Be Bold!!!"

Experimental Suggestions

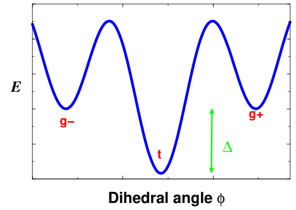
Simultaneous SAXS and WAXS scattering on PEO, PE, *i*-PP (Ryan, *et al.*):

- WAXS pattern appears after SAXS pattern.
- SAXS has a characteristic length $\ell = q_*^{-1} \sim 50 - 200$Å.
- SAXS pattern $S(q,t)$ obeys Cahn-Hilliard kinetics to a good approximation.
- $\ell(t)$ grows, stopping when crystallization (WAXS) begins.

$\Longrightarrow$ *Spinodal decomposition (phase separation) occurs in the supercooled melt **before** primary (or secondary) crystallization?*

Interpretations

1. Detector sensitivity/form factor (Hanna *et al.*)
   Incorrect shape/dynamics of SAXS pattern $S(q,t)$.
2. Junk (dirty samples)
   Not enough for macroscopic phase separation?
3. Length polydispersity
   Small signal: ($\delta\rho$ determined by end density)
4. Comonomer/sidegroup (chemical) disorder)
   Too many systems? (PE, *i*-PP, PEO, PET, ...). Worth investigating further!
5. Conformation $\leftrightarrow$ density coupling?
   - Generic to all polymers.
   - Driving force for polymer crystallization
   - Intermediate phases quite common (*e.g.* liquid crystals)

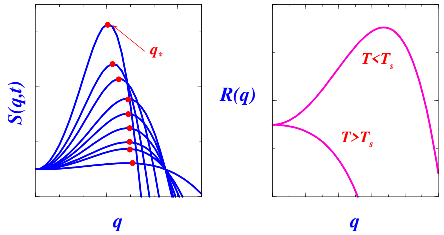


Cahn-Hilliard Theory

For a **two component blend**, with ψ a **composition** fluctuation:

$$\langle \psi(q,t), \psi^*(q,t) \rangle \equiv S(q,t) = S(q,0) e^{2R(q)t}$$

$$R(q) = -Mq^2 \left[a\,(T - T_s) + g q^2 \right]$$



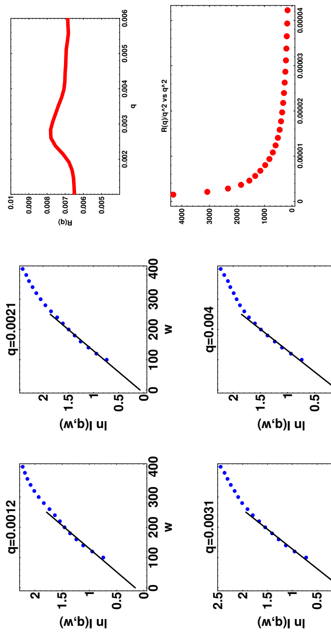
For a **one component liquid near a critical point** we need:

$$\partial_t \rho = \ldots \qquad \text{(mass flow)}$$
$$\rho \partial_t \mathbf{v} = \ldots \qquad \text{(momentum)}$$
$$\partial_t q = \ldots \qquad \text{(heat flow)}$$

$\Longrightarrow$ equivalent dynamics; Model H.

$$\psi \Longrightarrow \delta\varepsilon - \frac{\varepsilon + p}{\varepsilon \rho}\delta\rho \qquad \text{(entropy density)}$$

Hanna Calculations

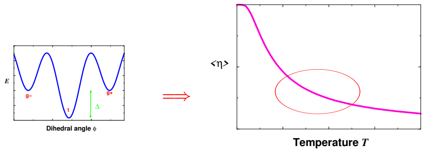


Model Free Energy

Density $\rho(\mathbf{r}) = \bar{\rho} + \sum_{q \neq 0} \rho_c(q)\, e^{i\mathbf{q}\cdot\mathbf{r}}$

$$\begin{cases} \bar{\rho} & = \text{mean density} \\ \rho_c(\mathbf{q}) & = \text{Bragg peaks} \end{cases}$$

Conformation η fraction of preferred isomeric states



(Landau) Free Energy Density:

$$\boxed{\begin{aligned} f = \; & f_0(\bar{\rho}, T) && \text{(high } T \text{ eq. of state)} \\ & + \bar{\rho}\, V(\rho_c, T, \bar{\rho}) && \text{(crystal free energy)} \\ & + \bar{\rho}\, f_\eta(\eta, \bar{\rho}) && \text{(density-conformation coupling)} \end{aligned}}$$

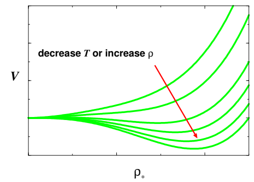
Free Energies

Equation of State $f_0 = Rk_BT\bar{\rho}\ln\left[\frac{1}{\bar{\rho}} - w\right]$

(high temperature equation of state)

Crystal Free Energy $V = \frac{1}{2}a\,(T - \alpha\bar{\rho})\,{\rho_*}^2 - \frac{1}{3}b{\rho_*}^3 + \frac{1}{4}c{\rho_*}^4$

(assume a single wavevector $\rho_* \equiv \rho_c(\mathbf{q})$)



Conformation $f_\eta = \frac{k_BT}{2M_b}\left[\eta^2 \cosh^2\frac{\Delta}{2k_BT} - \eta\sinh\frac{\Delta}{k_BT}\right]$

(simplest version of Flory's RIS model)

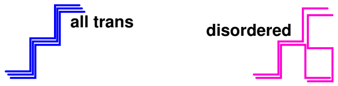
Gap Renormalization $\boxed{\Delta = \Delta_0 + v\bar{\rho} + \lambda\rho_*^2}$

Conformation-Density Coupling

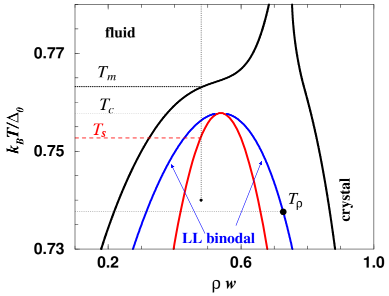
Gap Renormalization $\boxed{\Delta = \Delta_0 + v\bar{\rho} + \lambda\rho_s^2}$

v :
- RIS energy gap depends on density (Flory's RIS calculation a single-chain calculation).
- *"Things that look the same pack more efficiently"*: Reduce excluded volume interaction.
- Density increase at isotropic-nematic transition.

λ :
- Crystalline ordering prohibits further non-crystalline (*i.e.* gauche) sequences.
- Easier to crystallize (come into registry) once straightened.



Phenomenological Phase Diagram



$T_s < T < T_m$	metastable supercooled melt
$T_\rho < T < T_s$	"spinodal decomposition", then enhanced nucleation (heterogeneous or homogeneous).
$T < T_\rho$	"spinodal decomposition" with rapid nucleation (barrier in dense phase of order k_BT.)

Induction Time: $\tau \simeq \tau_{phase\ sep} + \tau_o e^{E_{nuc}/k_BT}$

i-PP: $T_m^\infty \simeq 190°\,\mathrm{C}, T_s \simeq 140°\,\mathrm{C}, T_\rho \simeq 129°\,\mathrm{C}$.

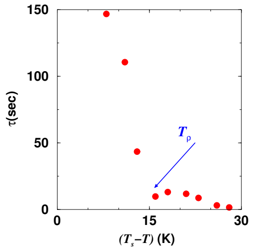
Growth Process

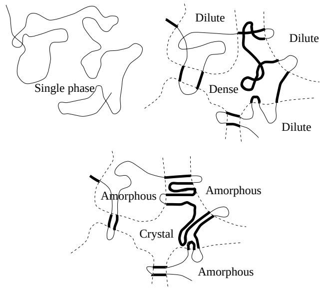
(from Ryan *et al.*)

$T_m^\infty \simeq 190°\,\mathrm{C}$

$T_s \simeq 140°\,\mathrm{C}$

$T_\rho \simeq 129°\,\mathrm{C}$.





Numbers

- High Temperature equation of state: look up w, R.
- RIS model (*e.g.* PE): look up bare energy gap Δ.
- **Dimensionless Number** RM_b (mass of a bond)

$$\hat{v} = \frac{v}{\Delta_0 w}.$$

T_s for a characterized system (w, M_b, R, Δ_0) determines $\hat{v}$.

Polyethylene: $\hat{v} \simeq 1.4$.

n-butane: (2 bonds) [Pratt, Hsu, and Chandler, J Chem Phys **68** (1978) 4202. RISM theory calculation of *gauche-trans* activity,

$$K = \exp\left\{\frac{-\Delta}{k_BT}\right\}:$$

$$\hat{v} = \frac{k_BT}{\Delta_0}\frac{1}{V_b}\frac{\partial \ln K}{\partial \bar{\rho}}\bigg|_T \simeq -2.9.$$

- Small molecules collapse!.
- Long chains: examine perturbations about melt (Gaussian) behavior (many-body effects).

Phase Diagram: Landau coefficients λ, b, c, α to obtain phase diagram (crude!!).

Discussion

Kinetics

Liquid Crystalline Point of View

- Imai *et al.* Chain stiffening a dynamical variable (orientational degree of freedom). Coupling to density allows for a spinodal.

Related Calculations

- Flory Theory [Proc Roy Soc Lon Ser A **234** (1956) 60]. Entropy vs. packing $\Rightarrow$ crystallization: no density change.
- McCoy *et al.* [J Chem Phys **95** (1991) 9348]. DFT calculation, RIS and ρ separate: manipulate to get melt conformation.
- Liu and Muthukumar [J Chem Phys. **109** (1998) 2536]. Simulation of few-chain crystallization (in solution): structure not inconstistent with a spinodal like pattern.
- Fujiwara and Sato [J Chem Phys. **110** (1999) 9757]. Simulation of short alkane chains: growth of conformational order proceeds before crystallization

Related Work

Polymers

- Imai *et al.* [Macromolecules **27** (1994) 7101]. PET annealed from glassy state
- Ezquerra *et al.* [PRE **54** (1996) 989]. annealed PEKK
- Gelation/Crystallization in biopolymer solutions (*e.g.* gelatin) [Keller, Far. Disc. **101** (1995) 1].

Colloids

- K. Schätzel and B. J. Ackerson [PRE **48** (1993) 3766]. Spinodal-like pattern in hard sphere crystallization.
- Poon *et al.* [Far. Disc. **101** (1995) 65., PRE **55** (1997) 3762.] Hidden L-L spinodals in colloid-polymer mixtures and protein crystallization.

Other Molecular Liquids

- **Water:** clusters in supercooled water (simulations). [Harrington *et al.* PRL 78 **1997** 2409]; hidden liquid-liquid critical point [Mishima & Stanley *et al.* Nature **396** (1998) 329]; experimental "critical-like" singularities [P Debenedetti *Metastable Liquids* (1996)].
- Fischer *et al.* [Acta Poly. **45** (1994) 137] long lived (slow) density fluctuations in molecular liquids near a glass transition.

Conclusion/Future Directions

Main Points

- Conformation-density coupling can induce liquid-liquid phase separation, which enhances (assists) nucleation.
- (the dynamics is that of a one-component fluid)
- Generic emerging themes: hidden metastable phases, coupling internal structural order to density (*"compressible Ising model"* [Bergmann *et al.* 1970's]).

Theoretical Challenges

- Density functional (or other) more precise theory.
- Landau-type theories of strain-induced crystallization:

$$f \longrightarrow f - \sigma\eta$$

Effects: enhance spinodal; induce metastable phase for non-*trans* crystal ground states?
- Implications for secondary nucleation and growth, crystal front speed, morphology.
- Surface effects [RA Jones]?

Experimental Challenges

- Effects of molecular weight, polydispersity, side-branching, impurities.
- Independent measures of conformation (NMR, Raman)
- Heat capacity, Pressure, Strain effects?