Phase-separating colloidal mixtures: lattice-gas model, composition heterogeneities, and secondary quench

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1: Intro and Overview

- **Is *composition relaxation* really slower than *density relaxation* in *dense* mixtures?**

- Take colloidal fluid with two species in a solvent;
- From mixed state, drop temperature T to coexistence;
- Two relaxations begin: composition & total concentration;
- *P. Warren*: in **dense** systems, composition relaxation is much slower;
- It requires different species to 'push past each other' in opposite directions;
- **Our results support two-stage proposal and predict consequences**.

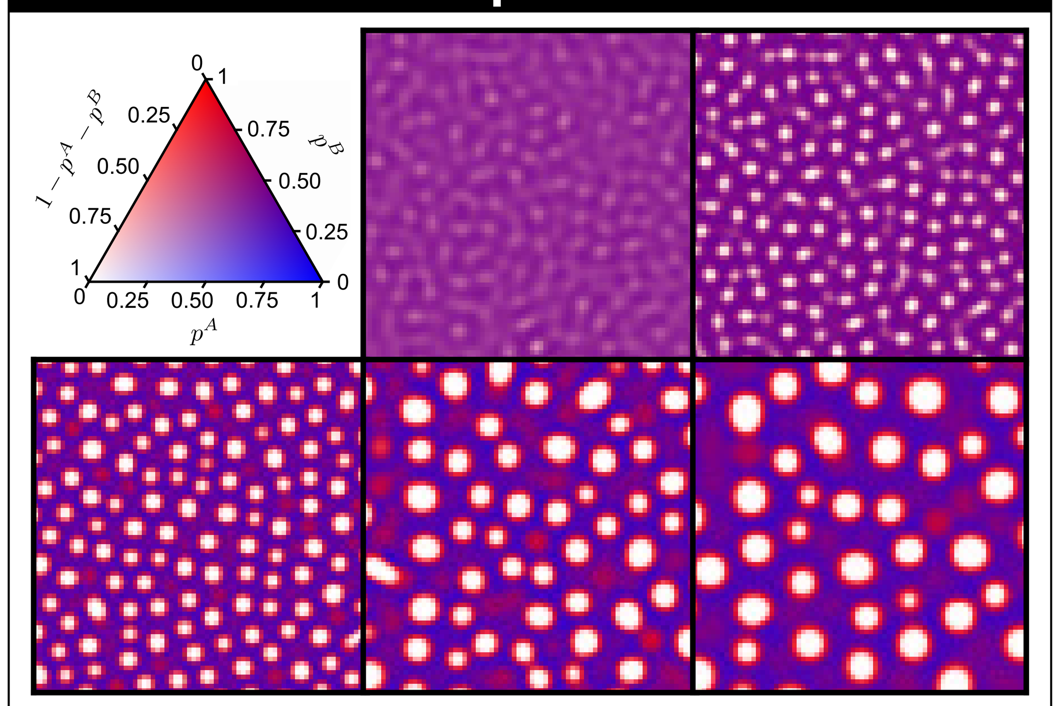
2: Model

- Consider L^2 sites. Define Hamiltonian as

$$H = -\sum_{\langle i,j\rangle}\sum_{\alpha,\beta}\sigma_\alpha\sigma_\beta n_i^\alpha n_j^\beta \qquad (1)$$

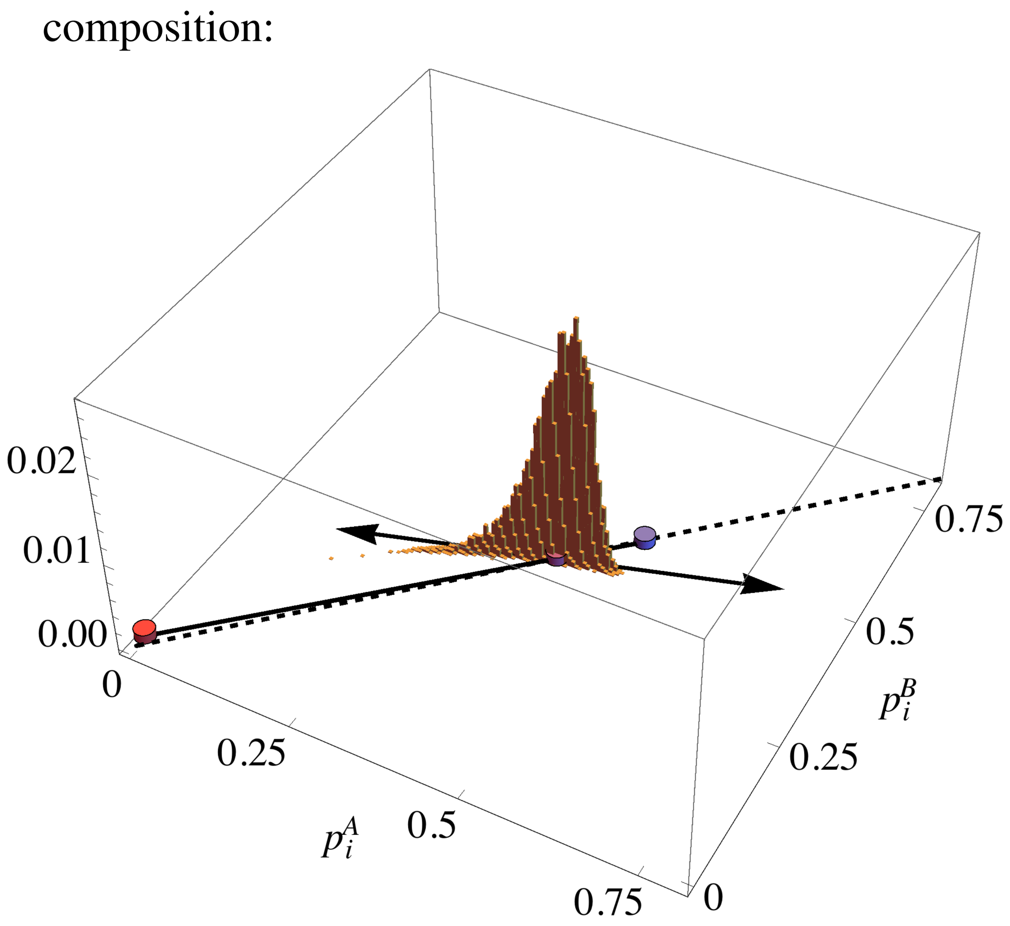
- Species are characterized by $\sigma_A = 1+d$ and $\sigma_B = 1-d$
- The number of α-particles at site i is n_i^α;
- Solvent has $\sigma = 0$; a max. of 1 colloid per site is allowed;
- Kinetics proceeds via jumps to "empty" sites;
- Jump rates depends on T and associated $\Delta H_{ij}^{\alpha\beta}$
- Derive *deterministic* **mean-field** eqns for $p_i^\alpha(t) = \langle n_i^\alpha\rangle(t)$

3: Separation

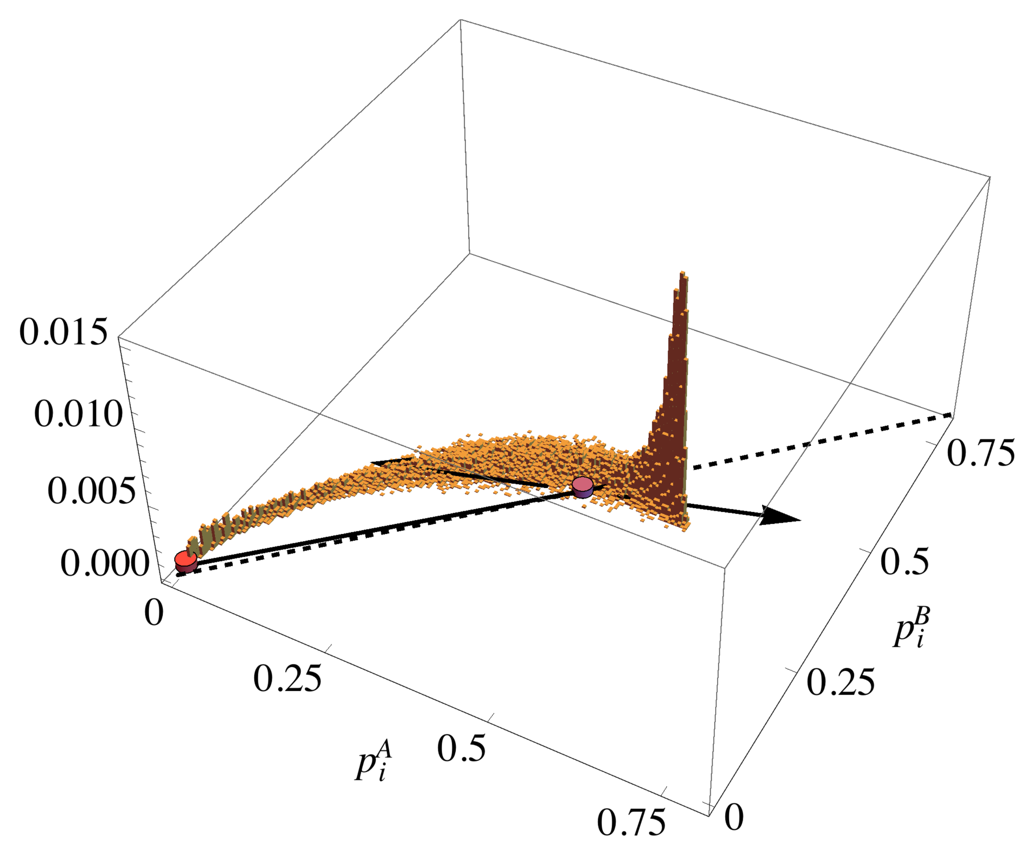


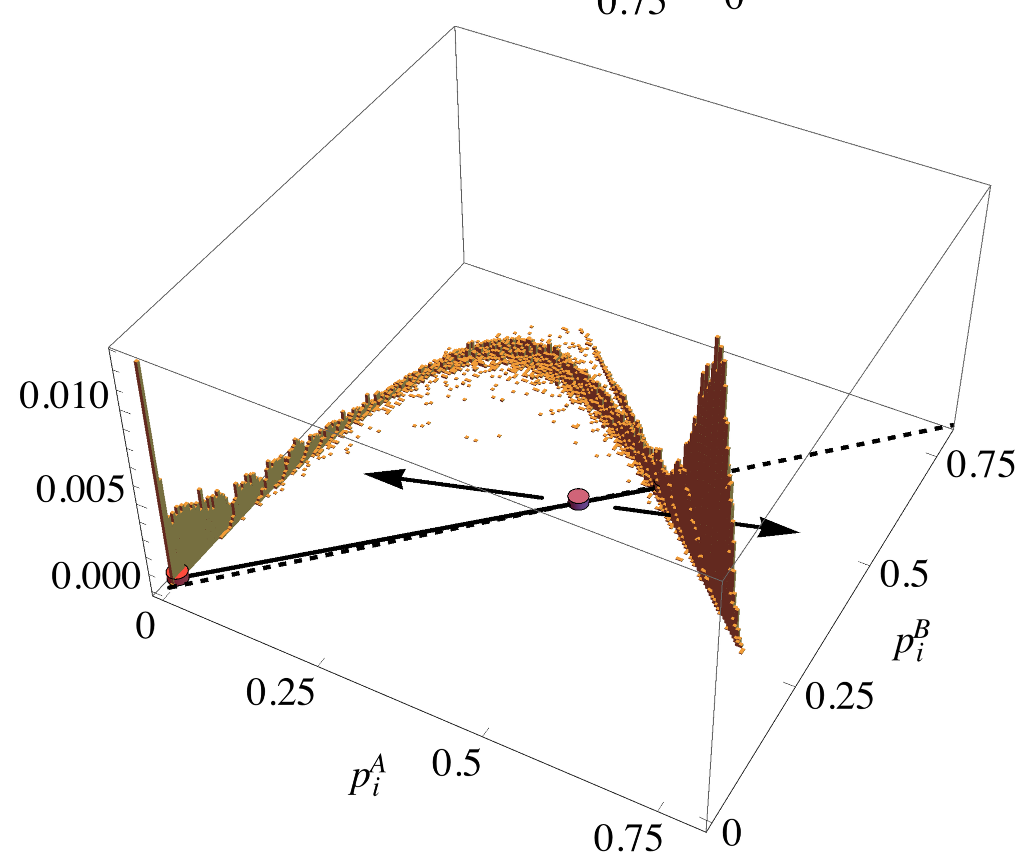
B-rich interface separates gas bubbles from A-rich continuous liq. Param: $p^A = p^B = 0.41$, $d = 0.25$, $T = 0.3$, and $L = 75$.

- Colours: A's are blue, B's are red and solvent is white;
- Histograms count the fraction of sites with a certain composition:



3: Separation (cont.)

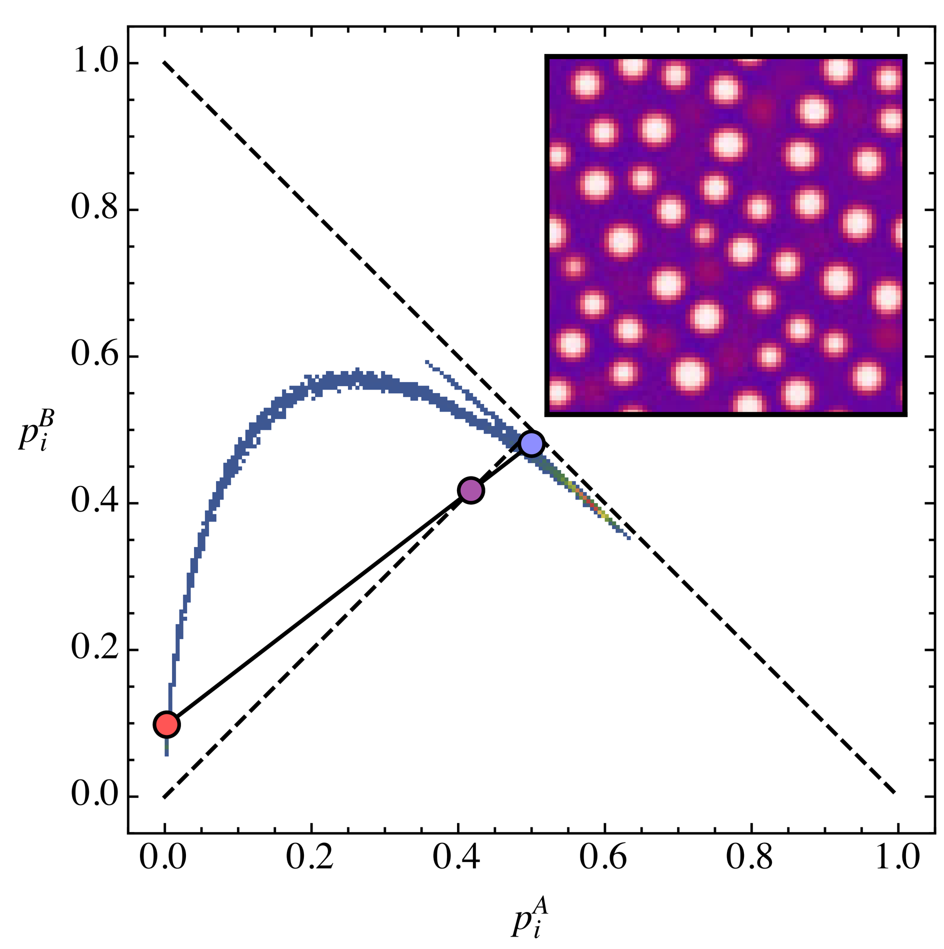




For $p^A = p^B = 0.41$, $d = 0.25$, $T = 0.3$, and $L = 75$, at $t = 8$, 16, and 316.

4: Composition heterogeneities

- Top-view:
  - ⋆ An 'arm' is formed, corresponding to long-lived heterogeneities in the liq.
  - ⋆ Origin: evaporation of gas bubbles.
- Interfacial remnants rapidly match liq. density;
- But only slowly they relax composition, producing B-rich patches.



Param.: as before but $T = 0.5$ and $t = 1110$

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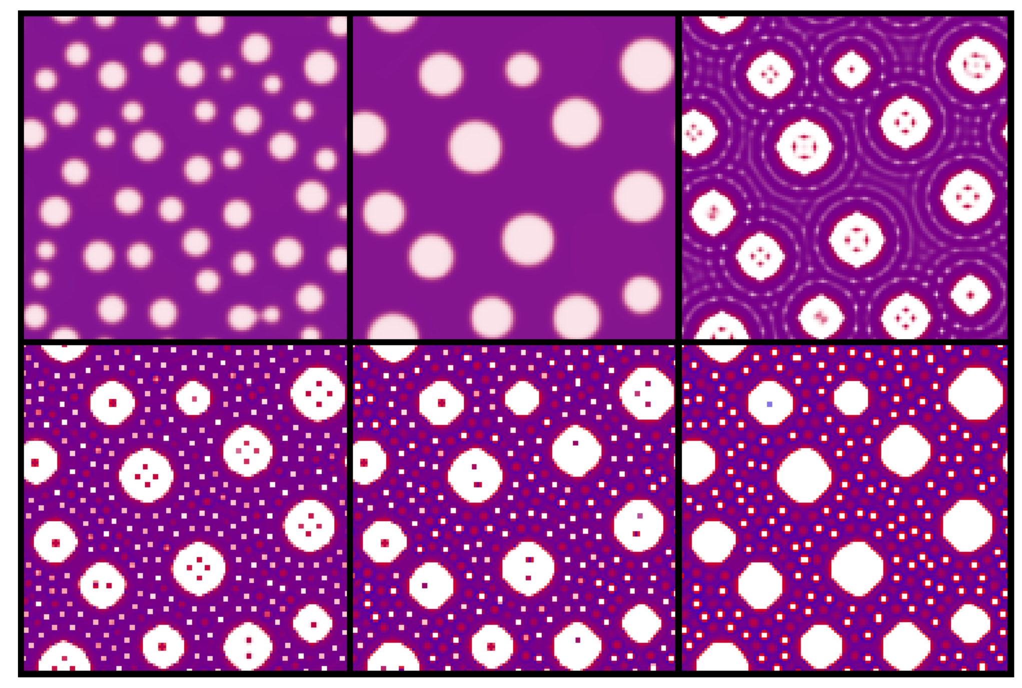
- When adding colloid-colloid direct interchanges, heterogeneities (and 'arm') do **not** form;
- Similarly found for **arbitrary** number of species

5: Second quench

- After equilibration at $T = T_1$, change to lower $T = T_2$
- Secondary domains grow inside primary phases, being eventually reabsorbed;
- For low T_2, the primary domain coarsening stops;
- Shrunk bubbles trap material that could go to other secondary bubbles;
- Liberated gas slowly goes to the primary bubbles;
- Regular arrangement of secondary bubbles is long-lived;



For $p^A = p^B = 0.375$, $T_1 = 0.7$, $T_2 = 0.1$, $d = 0.15$, $L = 128$, and second quench at $t = t_2 = 4\times10^4$. Top left to bottom right: $t = 5\times10^3$, 4×10^4, 40009, 5×10^4, 2.4×10^5, and 3.4×10^6. Symmetries result from lattice structure and low T.

6: Conclusions

- Linear analysis supports two-stage proposal (see refs.);
- Via histograms, slow composition changes effects become clear;
- Interface composition is strongly distinct from 'parent' state;
- Long-lived composition heterogeneities exist in the bulk liquid;
- Single-quench results validated for arbitrary numbers of species;
- With low 2nd temperature, primary coarsening stops;
- Morphology of liq. changes with composition kinetics;
- Long-lived regular arrangement of the secondary domains;
- Additional conclusions and phase diagram in thesis and refs. (see below);
- Predictions may be amenable to experimental verification in dense mixtures.

Further info

- **Contact:**

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- **References:**

- ***PCCP***, 2017, **19**, 22509-22527
- ***Soft Matter***, 2019, **15**, 9287-9299

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