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Closed Loop Phase Diagrams in Liquid Mixtures: From Theory to Simulations

Boris Veytsman*

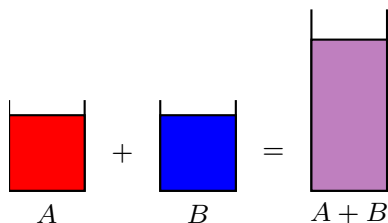
September 20, 2004

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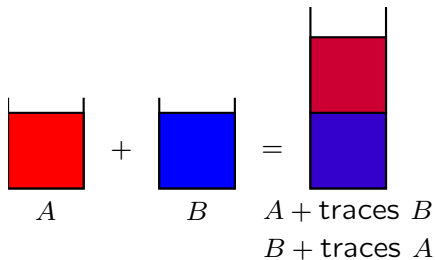
1. Thermodynamics of Mixing

A typical situation (polymers etc.):

High temperatures: mixing

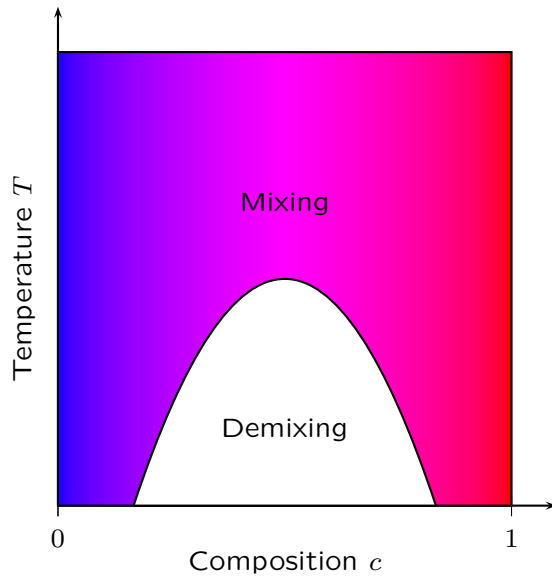


Low temperatures: phase separation



Phase diagram

Plot the points corresponding to mixed liquids



Minimization Condition

Why does demixing happen?

The system wants to minimize free energy

$$F = E - TS \rightarrow \min$$

Estimates for E and S

Energy E depends on c because of Van der Waals interactions: molecules attract like molecules *more* than unlike ones. E favors *demixing*. Estimate:

$$E \propto c(1 - c)$$

Entropy S favors disorder, i.e. *mixing*. Estimate:

$$S \propto k \ln c + k \ln(1 - c)$$

Resulting behavior

We minimize

$$F = E - TS$$

demixing mixing

Result:

- High T : entropy wins. Mixing
- Low T : energy wins *unless* c or $1 - c$ is small. Demixing in the middle, mixing on the edges. Traces of A in B , traces of B in A .

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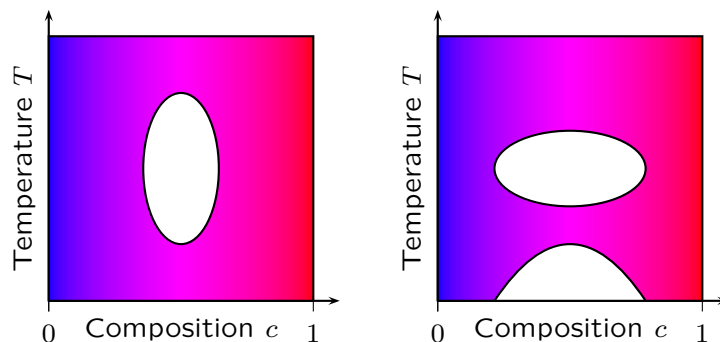
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2. Closed Loop Phase Diagrams

Guiacol-glycerol; β -picoline-water, many polymers¹:



Van der Waals forces cannot produce this—there must be something else

¹T. Narayanan and A. Kumar, "Reentrant Phase Transition in Multicomponent Liquid Mixtures," *Phys. Reports* 249 (1994): 136–218.

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Physics of Hydrogen Bond

- Covalent bonds: two atom share electrons A:B.
 - Strong selective bond ($E \gg kT$)
 - (Almost) unbreakable at room temperatures
- Hydrogen bond: two atoms (usually oxygen) share a proton: O–H...O. Proton is *much* heavier than electron—weaker quantum effects.
 - *Weak* selective bond ($E \sim kT$)
 - Constantly breaking and reappearing at room temperatures.

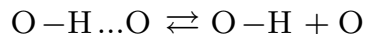
These properties make hydrogen bonds *fundamental for biology*. Life is a way of arranging hydrogen-bonded molecules.

Thermodynamics of Hydrogen Bonds

When the system forms a hydrogen bonds, it wins energy *and* loses translational entropy. \Rightarrow The number of bonds depends on the temperature.

Mean field estimates²:

Dynamic equilibrium:



Equilibrium condition:

$$n_{\text{bonds}} = K(n_{\text{donors}} - n_{\text{bonds}})(n_{\text{acceptors}} - n_{\text{bonds}})$$
$$K \propto \exp(-E_H/kT)$$

If T increases, K and n_{bonds} *decrease*!

Free energy:

$$F = E_{\text{vdW}} - TS + F_H, \quad F_H \propto -kTn_{\text{bonds}} \ln K$$

²B. A. Veysman, "Are Lattice Models Valid for Liquids with Hydrogen Bonds?" *J. Phys. Chem.* 94 (1990): 8499–8500.

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Hydrogen Bonds and Mixing

Suppose that A and B want to make hydrogen bonds between each other. $\Rightarrow F_H$ favors mixing.

1. High temperatures. $-TS$ dominates. Mixing.
2. Lower temperatures. E_{vdW} dominates. Not many hydrogen bonds. Demixing.
3. Even lower temperatures. Many hydrogen bonds. $F_H - TS$ dominates. Mixing again.
4. Even lower temperatures. Mixing or demixing depending on E_H and E_{vdW} .

We reproduced closed loop phase diagram!

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3. Computer Simulations

Goals

We have a theory for closed loop phase diagrams caused by hydrogen bonds.

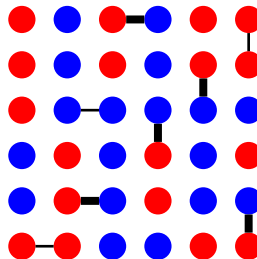
1. Verify the theory on a computer experiment
2. Look at the structure of the mixture

Since we understand what is going on, we can use a very simple (even simplistic) model.

Lattice Model

A simple lattice model of binary hydrogen-bonded solution³.

1. Simple cubic lattice.
2. In each cell either an A or a B (no holes).
3. Molecules attract neighbors; $AB < AA = BB$.
4. Molecules can form hydrogen bonds (one donor and one acceptor). $K_{AB} > K_{AA} = K_{BB}$.



³Michael Kotelyanskii, Boris Veytsman, and Sanat K. Kumar, "Phase Behavior of Associating Liquid Mixtures," *Phys. Rev. E* 58/1 (1998): R12–R15.

Elementary Operations

1. Change A for B or B for A
2. Create a bond or break a bond

The number of A or B is *not* constant. How do we control composition?

Introduce a penalty μ for substituting B for A .

1. $\mu = 0$ —symmetric mixture
2. $\mu > 0$ —more A
3. $\mu < 0$ —more B

Probability for a step:

$$P \propto \exp(-\Delta E/kT + \mu\Delta N_A/kT)$$

This is a μPT ensemble. μ is the *chemical potential*⁴.

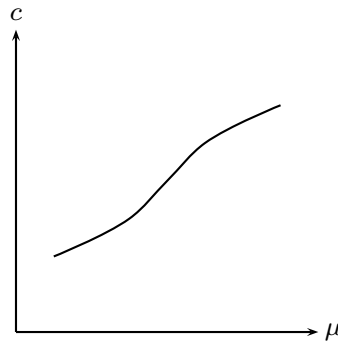
⁴Actually, the difference between μ_A and μ_B

Phase Transitions in μPT Ensemble

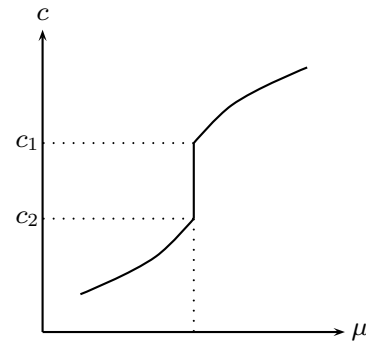
Phase equilibrium between c_1 and c_2 :

$$\mu(c_1) = \mu(c_2)$$

Let us plot $c(\mu)$:



One phase



Phase separation

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Thermodynamics . . .

Closed Loop . . .

Computer . . .

Conclusions

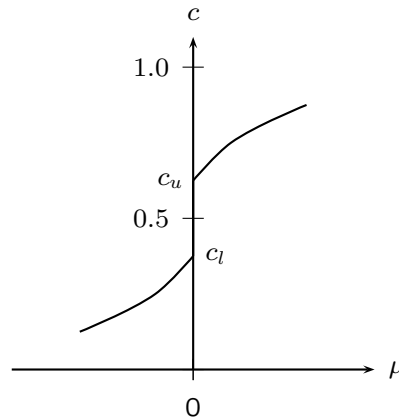
Phase Transition in Symmetric System

Our system: symmetry for substitution $A \leftrightarrow B$. Therefore

$$c(-\mu) = 1 - c(\mu)$$

Consequences:

1. Phase transition at $\mu = 0$
2. Phase coexistence between c_u and $c_l = 1 - c_u$



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Recipe for Phase Diagram

1. Equilibrate the system for several values of $\mu > 0$
2. Determine

$$c_u = \lim_{\mu \rightarrow +0} c(\mu)$$

3. If $c_u = 1/2$ —one phase
4. If $c_u > 1/2$ —phase coexistence between c_u and $c_l = 1 - c_u$.

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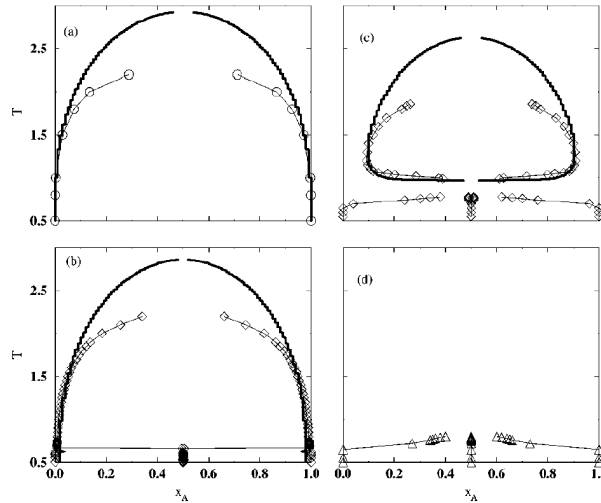
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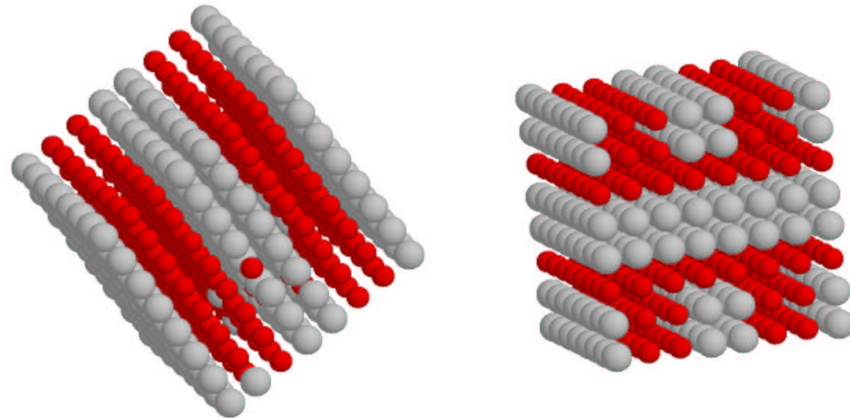
Results

Phase Diagram



Good agreement between theory and simulations. *But* at low T we see *three* phases, not two!

Low Temperature Ordered Phase



This looks like a liquid crystal. Lattice model artifact—or a nano-structure?

4. Conclusions

1. Hydrogen bonds cause rich and interesting phase diagram.
2. Combination of statistical physics *and* simulations is a powerful tool.
3. There is much to discover about ordered hydrogen-bonded structures.

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- Michael Kotelyanskii, Boris Veytsman, and Sanat K. Kumar. "Phase Behavior of Associating Liquid Mixtures." *Phys. Rev. E* 58/1 (1998): R12–R15.
- T. Narayanan and A. Kumar. "Reentrant Phase Transition in Multicomponent Liquid Mixtures." *Phys. Reports* 249 (1994): 136–218.
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