Stability of supercooled binary liquid mixtures.

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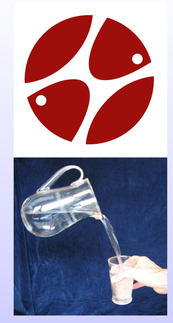
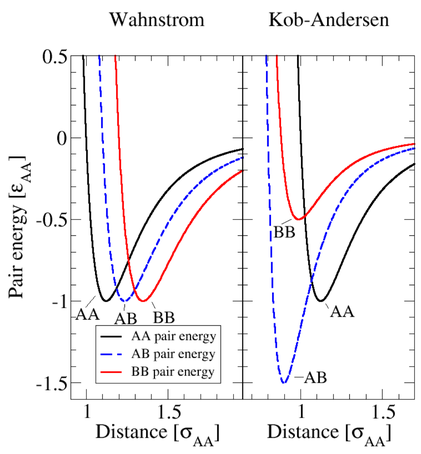


Models for supercooled mixtures

Molecular Dynamics models for supercooled mixtures



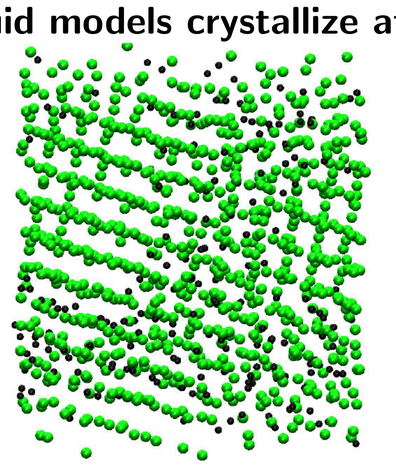
- The Kob-Andersen model disobeys the Lorentz-Berthelot mixing rules by having a strong covalent-like AB attraction

Lorentz-Berthelot (LB) mixing rules

- $\sigma(AB) = (\sigma(A) + \sigma(B))/2$ and $\epsilon(AB) = \sqrt{\epsilon(A)\epsilon(B)}$

Crystallization

Both binary fluid models crystallize at supercooling



- Particle positions projected onto a plane for the Kob-Andersen (standard) system. A: large solvent green particles in a fcc lattice order and small B-particles are black. The binary mixture consists of 800 A-particles and 200 B-particles

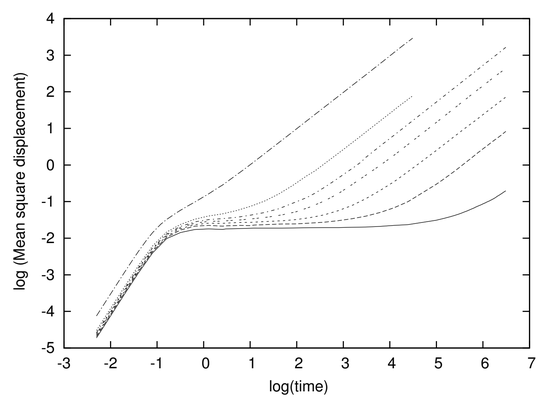
Theory for crystallization

- Equilibrium (at constant pressure) between a crystal of A and a mixture with particle fraction x(A):
  $\Delta G_{\mathrm{trans,A}} = \Delta G_{\mathrm{fus,A}} + \Delta G_{\mathrm{mix,A}}(x(A)) = 0$
  where the total change in Gibbs free energy is divided into a melting (fus) and a dilution (mix)
- Real mixture: $\frac{\Delta T_{fus,A}}{T^*_{fus,A}} \approx \frac{\Delta_{\mathrm{A,mix}} u_{pot}(A) + k_B T_{fus,A} ln(x(A))}{\Delta H^*_{fus,A}}$
- The creation of a critical crystal nucleus of N_A A particles in the mixture can be divided into two steps
  $N_{\mathrm{A}}(\mathrm{mix}) \rightarrow N_{\mathrm{A}}(\mathrm{liquid}, x_{\mathrm{A}} = 1)$
  $N_{\mathrm{A}}(\mathrm{liquid}, x_{\mathrm{A}} = 1) \rightarrow N_{\mathrm{A}}(\mathrm{crystal}, x_{\mathrm{A}} = 1)$
- $\delta N^*/N^* \approx -3(\Delta_{\mathrm{A,mix}} u_{pot}(A) + k_B T_{fus,A} ln(x(A)))/\Delta\mu$
  where $\Delta T_{fus,A}$ is the freezing point depression and δN^* is the change in number of particles in the critical nucleus due to the mixing energy. Ideal mixing and classical nucleation theory ignores $\Delta_{\mathrm{A,mix}} u_{pot}(A)$; but the KA mixture has a neg. $\Delta_{\mathrm{A,mix}} u_{pot}(A)$ which stabilizes the supercooling mixture.

A modified model not prone to crystallization

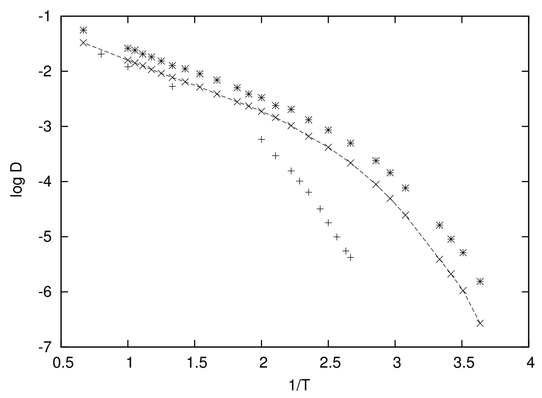
- Accordingly to the theory the stability of the supercooled state is increased by increasing the strength of $\Delta_{\mathrm{A,mix}} u_{pot}(A) < 0$. In the case of Lennard-Jones like interaction one can simply remove the attraction between the solvent particles (and the solute particles); but remain the attraction between the solvent A- and solute B-particles. The structure (distribution functions) are given by the repulsive part of the pair-potentials and in practice unchanged. But the resulting mixture is prone against crystallization.
- And faster to simulate. We have simulated it what corresponds to $t \approx 0.1ms$.

The ballistic- and diffusive regime



- $log - log$ plot of the mean square displacement for A-particles as a function of time and for the temperature T=1.00, 0.40, 0.35, 0.325, 0.30, 0.275 and 0.25.

The self-diffusion constants



- An Arrhenius plot, logD(1/T), of the self diffusion constants D. With $+$ is D(A) for the KA-mixture, and the points given by $\times$ and connected with lines are D(A) for the modified mixture. D(B) for the smaller B-particles in the modified mixture are shown with *

Summary

- The theory for real mixture gives a recipe for modelling stable supercooled mixture, not prone to crystallization
- A simple modification of the Kob-Anderson mixture does not crystallize and can be simulated over longer times.
- Reference: Søren Toxvaerd, Ulf R. Pedersen, Thomas B. Schrøder, and Jeppe C. Dyre, *preprint*