

# Non-equilibrium phenomenon in CO<sub>2</sub>/Hexadecan: towards micro-cellular polymer foams

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## Introduction



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## Introduction

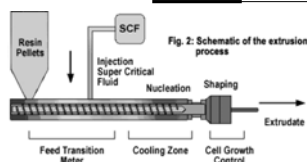


Fig. 2: Schematic of the extrusion process

1. SCF Injection/Dissolution
2. Cell Nucleation
3. Cell Growth
4. Shaping

• Supercritical fluids (SCF) of atmospheric gases are injected into a polymer melt under specified pressure profiles

• A massive thermodynamic change in the polymer melt is effected by pressure drop

• A large number of nucleation sites homogeneously distributed throughout the polymer melt is created

• Growth is controlled in the die as well as post die by temperature and rheological conditions

• Manage the nucleation driving force to dominate the heterogeneous nucleation process in order to create a vast number of cells, even when heterogeneous nucleation sites are available

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## Goals

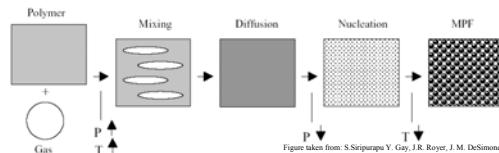


Figure taken from: S. Srijungro V. Gao, J.R. Royer, J. M. DeSimone, S. A. Khan and R. J. Spontak Mat. Res. Soc. Symp. Vol. 629

- Understand the production process
- Give indications for conditions for micro-cellular foams

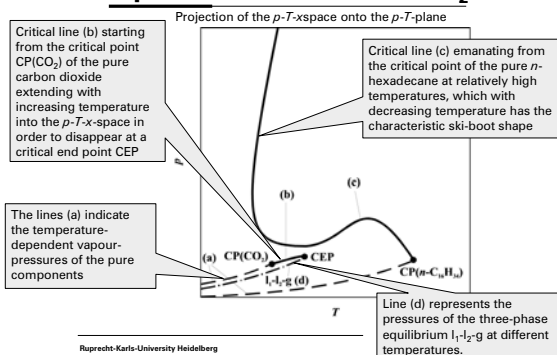
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## Approach

- Reduce complexity: Study instead of PS/CO<sub>2</sub> Hecadecan/ CO<sub>2</sub>
- Provide experimental data on the phase diagram
- Provide experimental data on the nucleation rates
- Provide mean-field results
- Model the system atomistically
- Model the system on a coarse-grained scale

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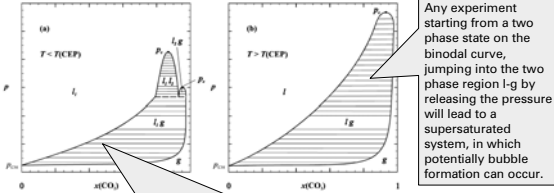
## Experiments on Hexadecan/CO<sub>2</sub>



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# Experiments on Hexadecan/CO<sub>2</sub>

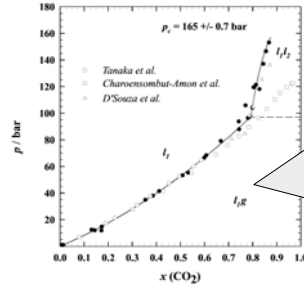
Schematic representation of p-x-diagrams for two different temperatures.



Any experiment starting from a two phase state on the binodal curve, jumping into the two phase region l-g by releasing the pressure will lead to a supersaturated system, in which potentially bubble formation can occur.

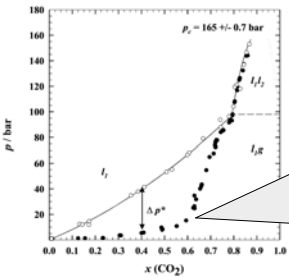
The for this work important finding was that the miscibility gap  $l_1-l_2$  has replaced the expected l-g miscibility gap of Figure (b). The striking feature of this miscibility gap  $l_1-l_2$  is that - as frequently found for liquid mixtures - hardly any supersaturations can be generated in experiments, if one jumps from the binodal curve into the two-phase-region  $l_1-l_2$ .

# Experiments on Hexadecan/CO<sub>2</sub>



While the p-x-curve at low mole fractions of CO<sub>2</sub> is well described up to 0.6 by a common slightly curved line, the experimental data points of Charoensombut-Amon et al. significantly deviate from our findings at mole fractions of 0.8 to 0.9. Our findings suggest that differently than Charoensombut-Amon et al. supposed to see a diagram of the type of Figure (b) from the previous slide, we in reality have at 40 °C a diagram of the type shown in Figure 2(a).

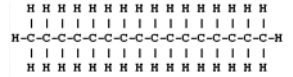
# Experiments on Hexadecan/CO<sub>2</sub>



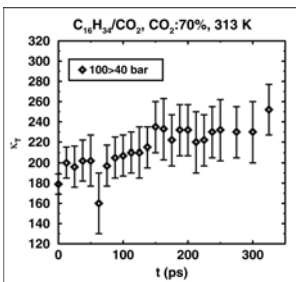
We believe the data can be divided into three characteristic regions: Data below  $x = 0.6$  are characterized by spurious nucleation and are clearly heterogeneous in nature. Experiments starting at 100 bars and below, but with  $x$  larger than 0.6, show characteristic features of truly homogenous nucleation. Data above  $p = 100$  bars and with mole-fractions above 0.78 are characterized by very small onsets of nucleation of the order of 5 bars or less. Experiments starting on the binodal curve in this high pressure- and mole-fraction-range show immediately, i.e. after only slight release of pressure, an extremely strong light scattering and high turbidity. These ranges are presumably governed by spinodal decomposition, in which two CO<sub>2</sub>-rich liquid phases separate from each other.

# Atomistic Modelling

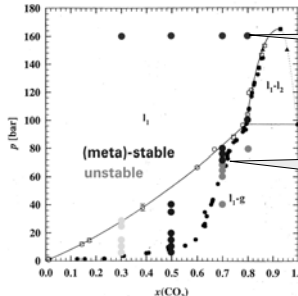
- Model the atomistically
- Use Molecular Dynamics
- Use a thermostat
- Follow the observables:
  - Average cluster number
  - Compressibility
  - Scattering intensity



# Atomistic Modelling



# Experiment and Atomistic Modelling



The red dots are the starting points for the quenches

The decision whether a point is unstable or metastable was made on the basis of the time behaviour of the compressibility

## Coarse-Grained Modelling

- Chain molecules and solution
- Apply a thermodynamic perturbation theory to derive the equation of state
- Start with the free energy of the chain mixture

$$\frac{A}{Nk_B T} = \frac{A^{ig}}{Nk_B T} + \frac{A^{mono}}{Nk_B T} + \frac{A^{chain}}{Nk_B T},$$

where  $A^{ig}$  is the free energy of the ideal gas of chains  
 $A^{mono}$  the free energy of a mixture of non-bonded monomers  
 $A^{chain}$  the free energy required to the chain fluid from the monomer fluid

## Coarse-Grained Modelling

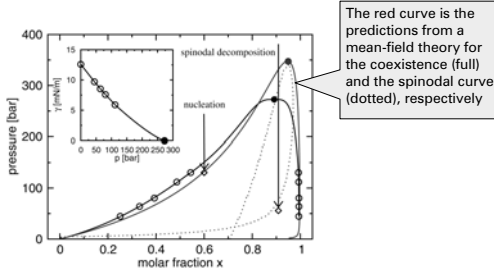
- represent  $\text{CO}_2$  by a single pseudo-atom
- represent  $\text{C}_{16}\text{H}_{34}$  by a flexible chain of 5 subsequent effective segments, each of which then contains roughly 3 successive C-C bonds.
- All such effective monomeric units interact with a truncated and shifted Lennard Jones (LJ) potential

$$V_{LJ}(r) = 4\epsilon_{hh} \left[ \left( \frac{\sigma_{hh}}{r} \right)^{12} - \left( \frac{\sigma_{hh}}{r} \right)^6 + \frac{127}{16384} \right], \quad r \leq r_c = 2 \cdot 2^{1/6} \sigma$$

- Subsequent effective monomers along a chain are in addition exposed to a finitely extensible nonlinear elastic (FENE) potential

$$V_{FENE}(r) = -33.75 \epsilon_{hh} \ln \left[ 1 - \left( \frac{r}{1.5 \sigma_{hh}} \right)^2 \right]$$

## Coarse-Grained Modelling



## Conclusions

- Experiment and theoretical approaches show consistent results for the hexadecan/ $\text{CO}_2$ -System**
- The phase diagram has been established**
- Regime for nucleation has been traced out**