The coexistence region in the Van der Waals fluid and the liquid-liquid phase transitions[1]

Dinh Quoc Huy Pham, Mateusz Chwastyk, and Marek Cieplak

Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

Abstract

Cellular membraneless organelles are thought to be droplets formed within the two-phase region corresponding to proteinaceous systems endowed with the liquid-liquid transition. However, their metastability requires an additional constraint—they arise in a certain region of density and temperature between the spinodal and binodal lines. Here, we consider the well-studied van der Waals fluid as a test model to work out criteria to determine the location of the spinodal line for situations in which the equation of state is not known. Our molecular dynamics studies indicate that this task can be accomplished by considering the specific heat, the surface tension and characteristics of the molecular clusters, such as the number of component chains and radius of gyration.

Phase separation at different densities

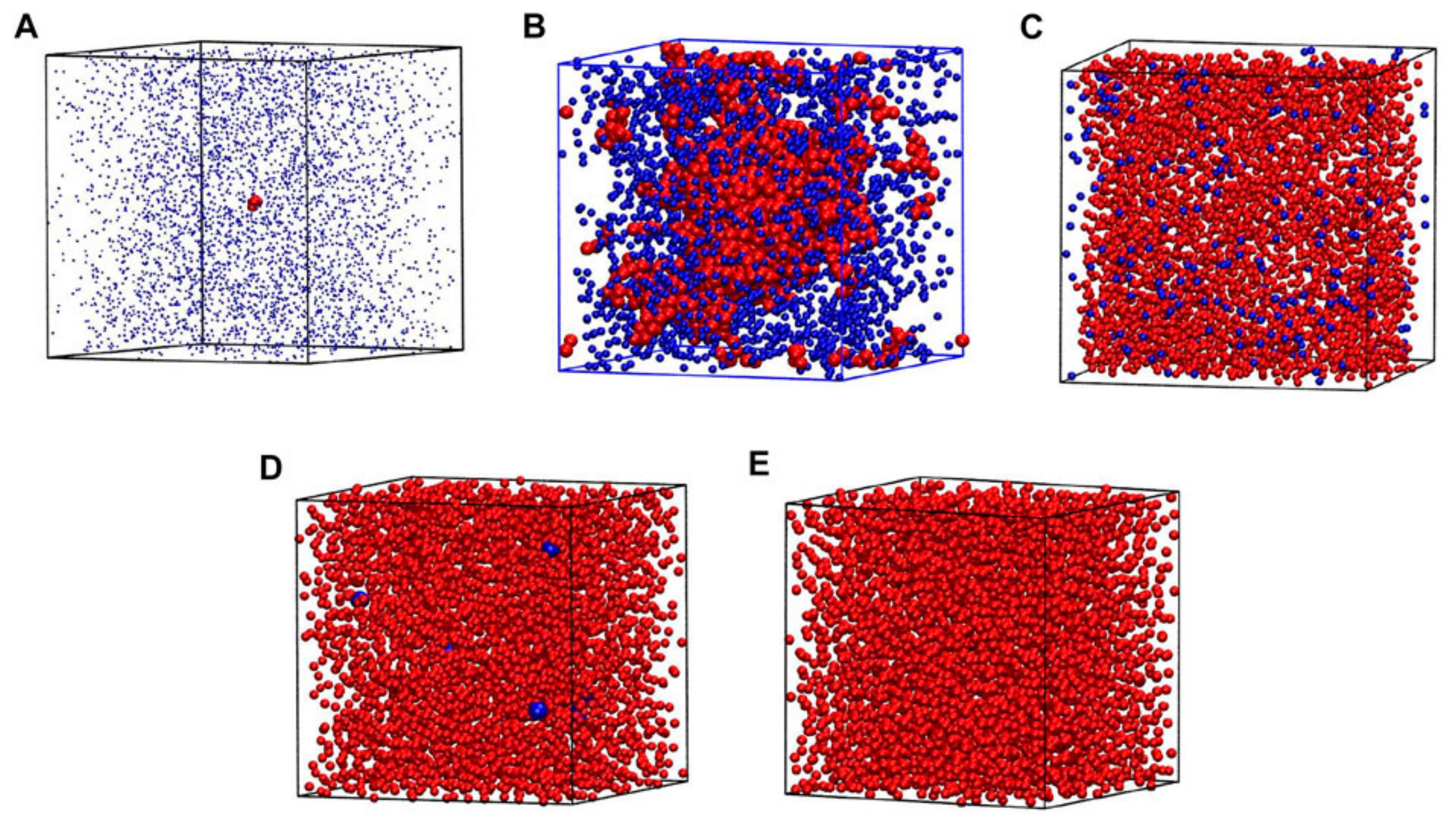

Fig. 3: T^* = 1.1. ρ^* = 0.01, 0.11, 0.35, 0.58 and 0.80 for A, B, C, D, and E, correspondingly.

Simulations

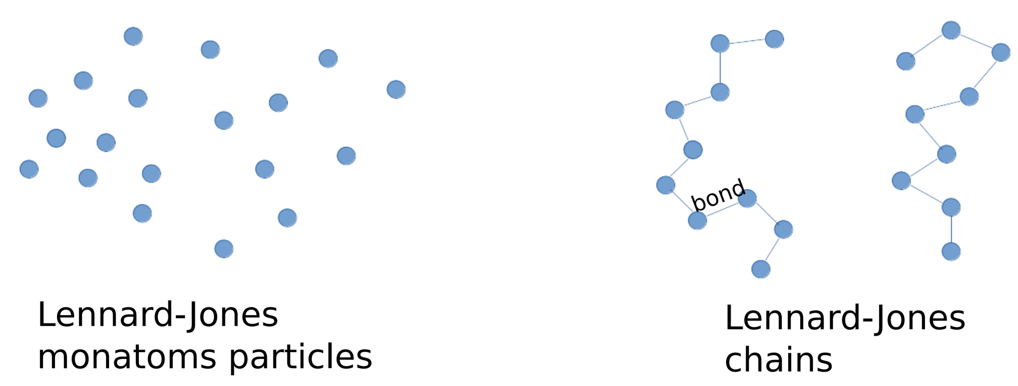

Fig. 1: Simple Lennard-Jones fluids

$$\Phi_{LJ}(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] \quad (1)$$

$$U_{bond}(r) = k_b(r-\sigma)^2 \quad (2)$$

- Simulation machine: LAMMPS
- System size: 4000 particles or 200 X 20-bead chains
- Cutoff=6.85σ, simulation time = 5000τ
- k_b = 75000(ϵ/σ^2)
- Canonical ensemble
- Nose-Hoover thermostat
- Home-made codes used for all analyses

Coexistence curves

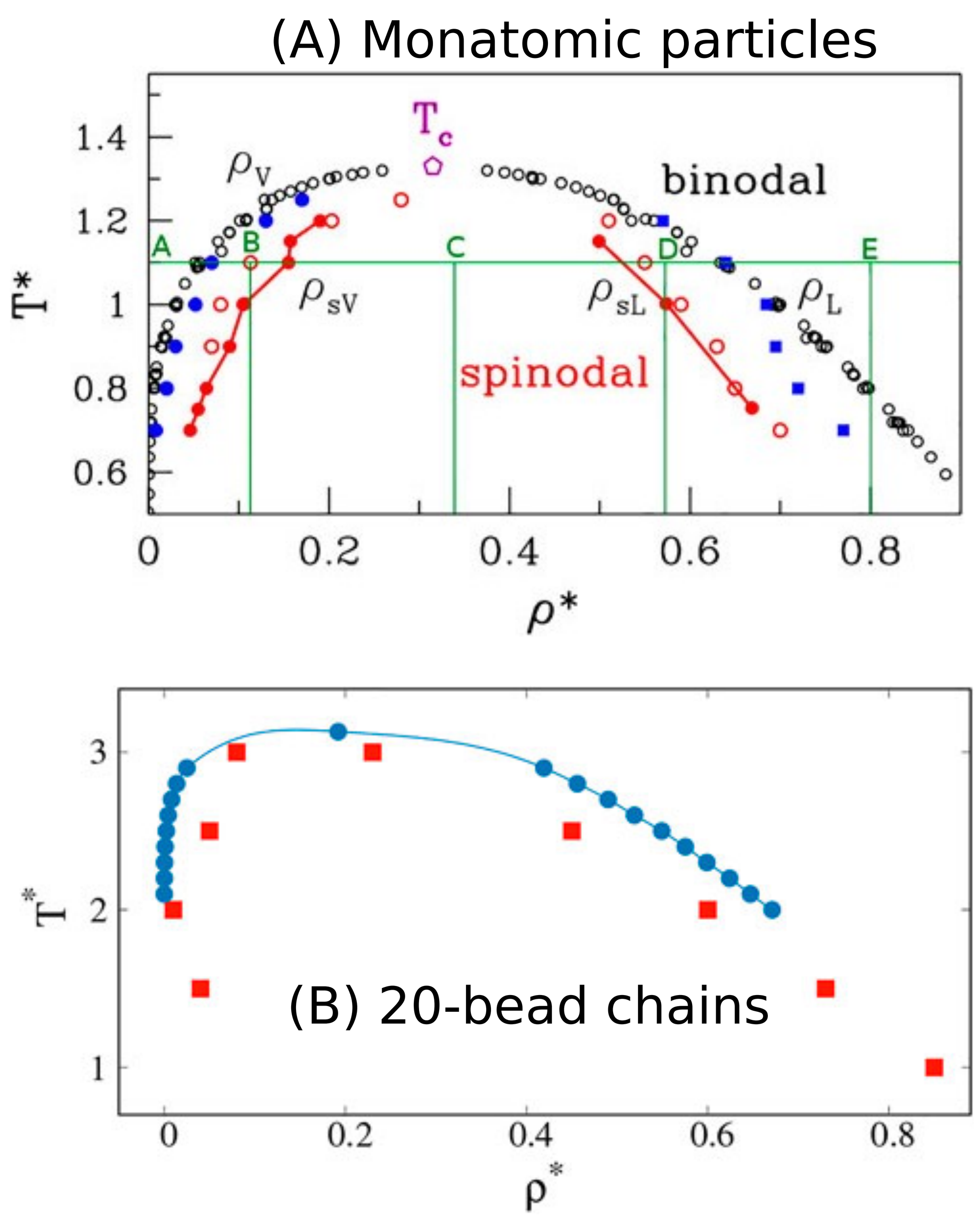

Fig. 2: Coexistence curves. (A) Monatomic particles: open black and solid red circles extracted from Stephan *et al.* (2019)[2]. (B) 20-bead chains: binodal data taken from Silmore *et al.* (2017)[3].

Binodal, spinodal finding

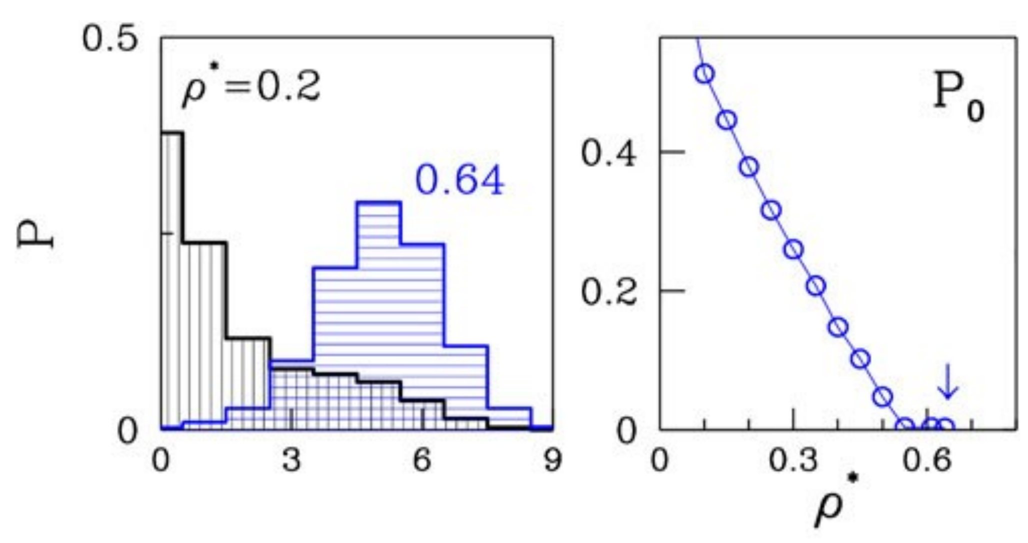

Fig. 4: Obtaining ρ_L. System is divided into cubes of which size is 2σ and number of particles inside the cubes are coundted. P_0 is probability of emty cubes.

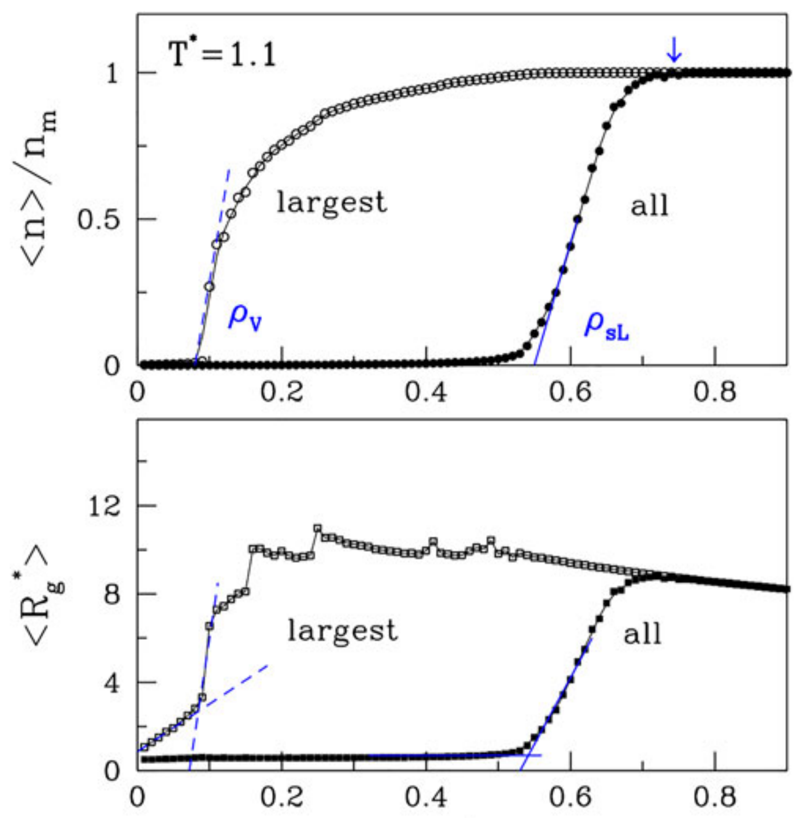

Fig. 5: ρ_V, ρ_{sL}, and ρ_L are obtained by cluster size analysis (upper panel)and R_g analysis bottom panel.

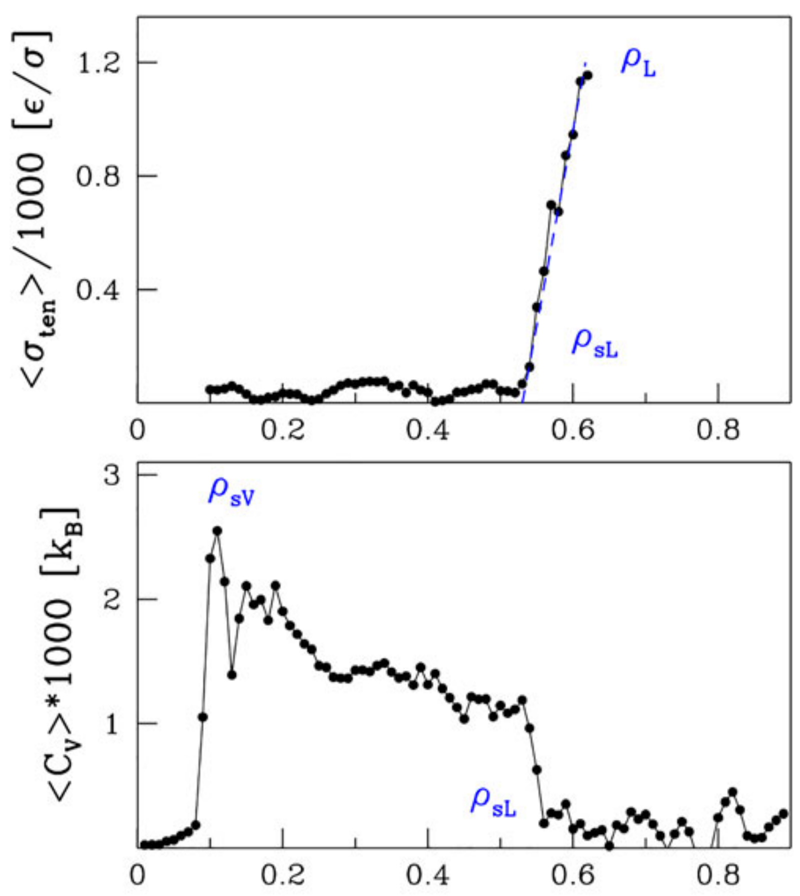

Fig. 6: ρ_{sL} and ρ_L are obtained by surface tension analysis (upper panel). Spinodal line is obtained by constant volume specific heat (bottom panel).

Conclusions

In principle, a precise determination of both the binodal and spinodal line requires procedures of finite-size scaling. Our purpose here, however, was to determine quantities to accomplish the task of determining the region in which the metastable droplets could be studied theoretically. We proposed the techniques for determining the binodal and spinodal line positions for fluids of complex composition.

Acknowledgments

- This research has received support from the National Science Centre (NCN), Poland, under grant No. 2018/31/B/NZ1/00047 and the European H2020 FETOPEN-RIA-2019-01 grant PathoGelTrap No. 899616. The computer resources were supported by the PL-GRID infrastructure. This project is also a part of the European COST Action EUTOPIA.
- Discussions with P. R. F. de Carvalho and his technical help are appreciated. We are grateful for comments of Piotr Szymczak about the manuscript.

Authors' contacts

- D.Q.H. Pham: quochuy@ifpan.edu.pl
- Mateusz Chwastyk: chwastyk@ifpan.edu.pl
- Marek Cieplak: passed away

References

[1] Pham, D.Q.H., Chwastyk, M. and Cieplak, M. (2022), The coexistence region in the van der Waals fluid and the liquid-liquid phase transitions. Frontiers in Chemistry, 10, p.1646.

[2] Stephan, S. *et al.*, (2019). Thermophysical properties of the Lennard-Jones fluid: Database and data assessment. J. Chem. Info. Model. 59, 4248–4265. doi:10.1021/acs.jcim.9b00620

[3] Silmore K. S. *et al.* (2017), Vapour-liquid phase equilibrium and surface tension of fully flexible Lennard-Jones chains. Molec. Phys. 115, 320–327.