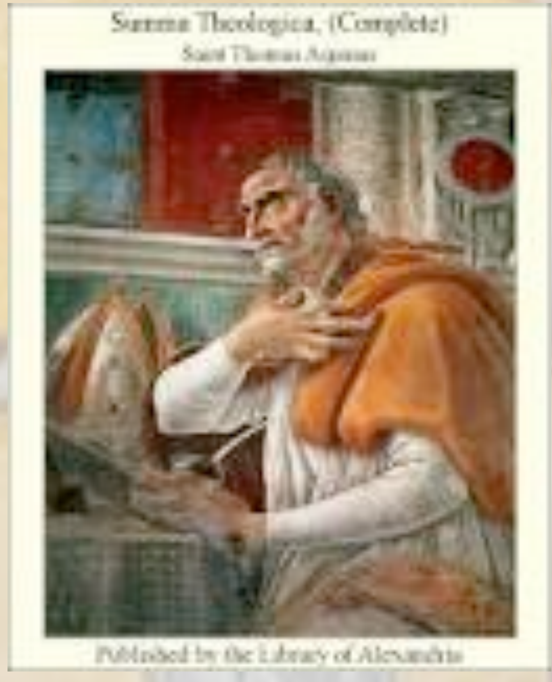
Angels Dancing on Pinheads

F. Sciortino, Sapienza Universita' di Roma

A little bit of background to the problem (Wikipedia):

Aquinas's Summa Theologica, written c. 1270, includes discussion of several questions regarding angels such as, "Can several angels be in the same place?”



The consensus:

Angels are pure intelligences, not material, but limited, so that they have location in space, but not extension.

How many Angels can Dance on a Pinhead ? Why was this question raised ?

The question of how many angels can dance on the point of a needle, or the head of a pin, is often attributed to 'late medieval writers'... In point of fact, the question has never been found in this form…

HS Lang, author of Aristotle's Physics and its Medieval Varieties (1992):

How many Angels can Dance on a Pinhead ? Why was this question raised ?

The question of how many angels can dance on the point of a needle, or the head of a pin, is often attributed to 'late medieval writers'... In point of fact, the question has never been found in this form…

HS Lang, author of Aristotle's Physics and its Medieval Varieties (1992):

One theory is that it is an early modern fabrication as used to discredit scholastic philosophy at a time when it still played a significant role in university education.

Is it still the case ?

Is it still the case ?
YES !!!!

" To my mind the question of whether there is or is not a reentrant spinodal is similar to the medieval debate concerning angels dancing on pinheads. "

(report of an unknown PRL Referee, January 2017, to the manuscript **Re-entrant limits of stability of the liquid phase and the Speedy scenario in colloidal model systems**)

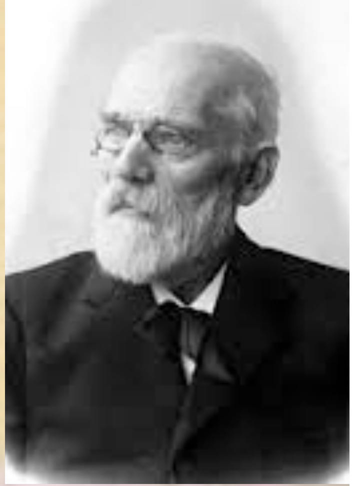
~~Angels Dancing on Pinheads~~

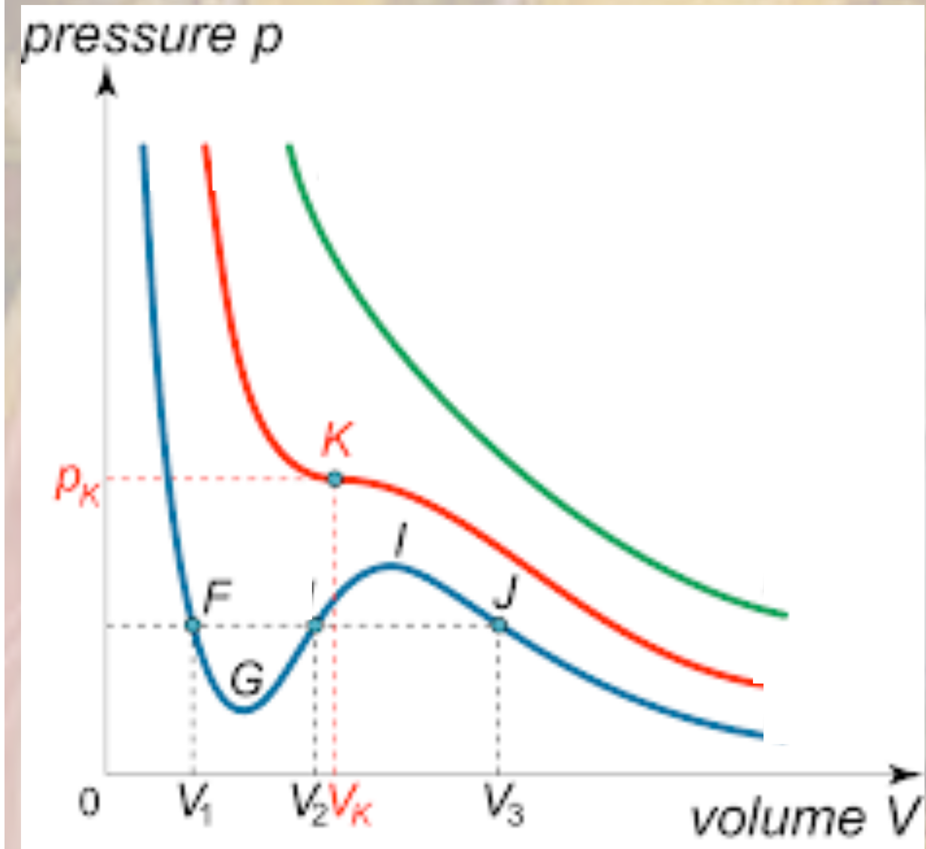
Re-entrant limits of stability of the liquid phase and the Speedy scenario in colloidal model systems

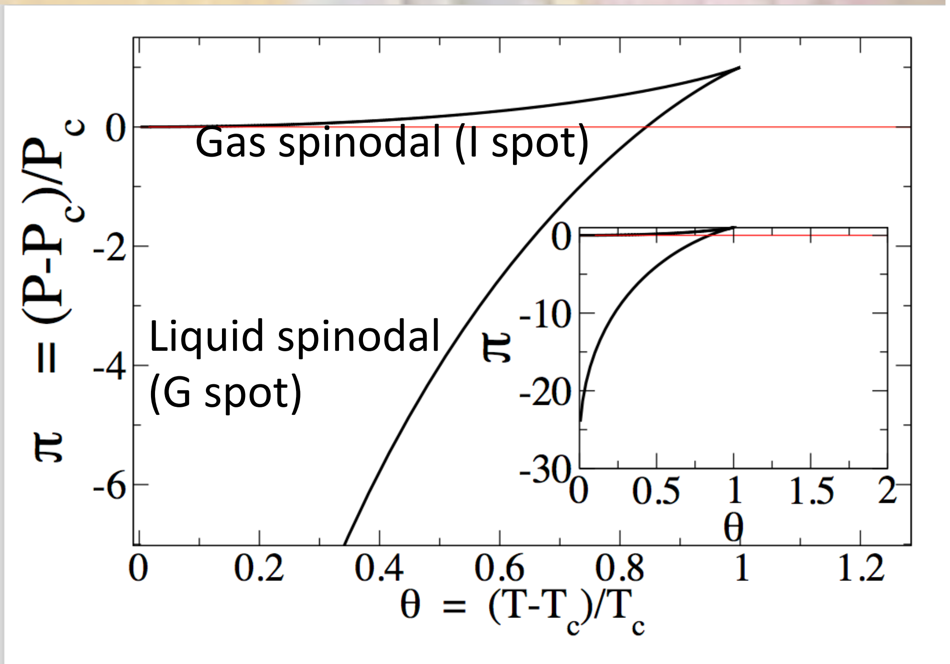
F. Sciortino, Sapienza Universita' di Roma

Spinodal: A mean-field concept.

VdW spinodals…….







Relevant to metastable states

Can spinodal be measured ?

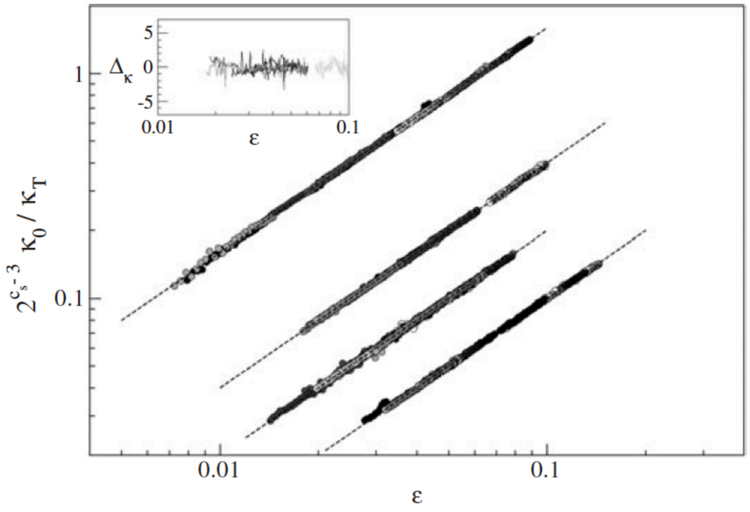


Figure 1. Scaling of the isothermal compressibility κ_T at different protein and salt concentrations. Solid lines are linear fits to data. NaCl concentration (from top to bottom): 7, 5, 4, 3% w/v. The factor $f = 2^{c_s - 3}$, where c_s is the salt concentration in % w/v, has been used to visually separate the salt concentrations. Protein volume fractions at NaCl 7% w/v: $\phi = 0.039$, 0.040, 0.051, 0.065, 0.076, 0.079, 0.091, 0.097, 0.118, 0.096, 0.097, 0.119; at NaCl 5% w/v: $\phi = 0.032$, 0.056, 0.075, 0.087, 0.109, 0.110, 0.119, 0.138; at NaCl 4% w/v: $\phi = 0.027$, 0.038, 0.036, 0.036, 0.048, 0.049, 0.050, 0.079, 0.064, 0.085, 0.097, 0.108, 0.109, 0.113, 0.127; at NaCl 3% w/v: $\phi = 0.042$, 0.049, 0.085, 0.99, 0.126, 0.115. Inset: the percentual error of data at 5% NaCl, $\Delta_\kappa = 100(\kappa_T/\kappa_0 - \epsilon)/\epsilon$.

M Manno, D Bulone, V Martorana and P L San Biagio
Journal of Physics: Condensed Matter, 16, 42

Self-Assembly of Bioelastomeric Structures from Solutions: Mean-Field Critical Behavior and Flory–Huggins Free Energy of Interactions

F. SCIORTINO,[1,*] K. U. PRASAD,[2] D. W. URRY,[2] and M. U. PALMA[3]

[1]Graduate School of Physics, University of Palermo, Via Archirafi 36, I-90123 Palermo, Italy; [2]Laboratory of Molecular Biophysics, The University of Alabama at Birmingham, P. O. Box 300, University Station, Birmingham, Alabama 35294; and [3]Institute for Interdisciplinary Applications of Physics, National Research Council, and Department of Physics, University of Palermo, Via Archirafi, 36, I-90123 Palermo, Italy

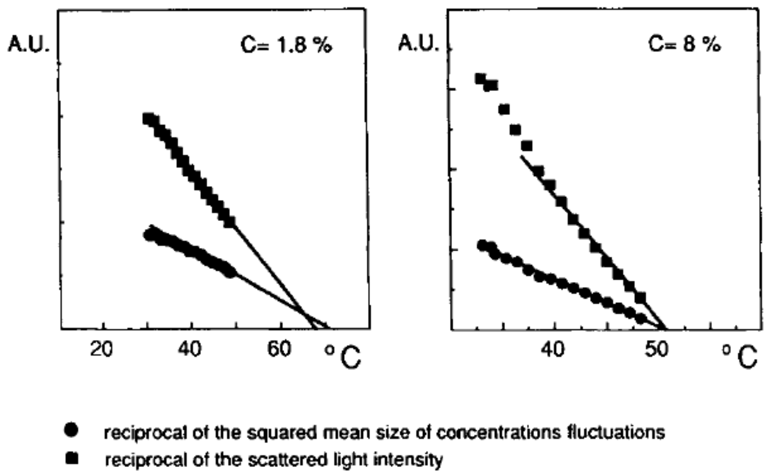


Figure 3. Reciprocal of scattered light intensity and reciprocal of the squared mean size of concentration fluctuations for two selected concentrations of poly(Val-Pro-Gly-Gly). Note the close fit in terms of mean-field critical exponents and the coincidence (within the stated accuracy) of T_{SP}. Also note that only one of the two concentrations is close to the critical point.

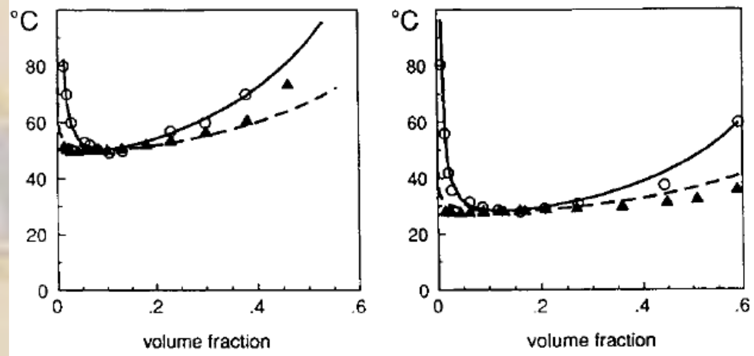


Figure 4. Complete phase diagram, including spinodal (solid) and coexistence (broken) lines for poly(Val-Pro-Gly-Val-Gly)–water (right) and poly(Val-Pro-Gly-Gly)–water (left) solutions. Full lines have been generated using

Spinodals of liquid water

Stability-Limit Conjecture. An Interpretation of the Properties of Water

Robin J. Speedy

Chemistry Department, Victoria University of Wellington, Wellington, New Zealand *(Received: April 8, 1981; In Final Form: October 20, 1981)*

It is assumed that liquid water cannot be superheated
rather than the free energy surface terminates at a line of
Extrapolations of available data suggest a continuous l
metastable superheated, stretched, and supercooled sta
significance, one can deduce the thermodynamic anomalie
and a heat capacity divergence in supercooled water, f
are shown to be in accord with the several implication

Vaporizing liquid water on cooling !!!!

Stability-Limit Conjecture

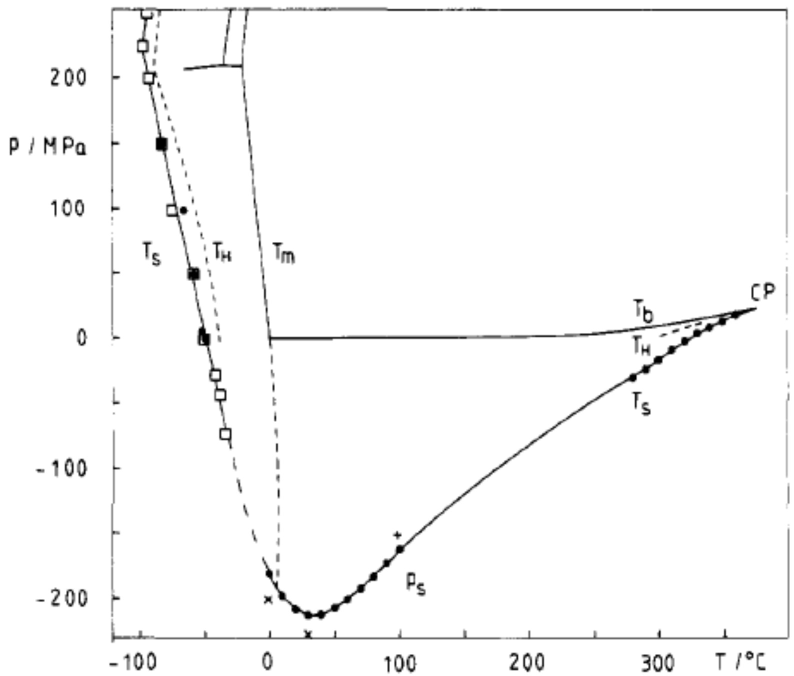


Figure 5. Estimated locus of the limit of stability for water T_s or p_s, shown in relation to the equilibrium phase diagram (T_m = melting line, T_b = boiling line, CP = critical point) and the experimental kinetic limits of stability T_H: (●) values of T_s and p_s for H_2O from Tables I–III (column 2); (□) values of T_s – 7 °C for D_2O from Table III (column 2) and Figure 4; (+) p_s(100 °C) calculated from ref 20; (×) p_s(0 °C) and p_s(25 °C) estimated by Yayanos;[21] (T_H) values from Table I for superheated H_2O and Table III for supercooled water; (T_m) is extrapolated to terminate at p_s(5 °C) = –190 MPa as discussed in section

Debenedetti's criticism

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **15** (2003) R1669–R1726 PII: S0953-8984(03)21725-2

TOPICAL REVIEW

Supercooled and glassy water

Pablo G Debenedetti

Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, USA

Topical Review

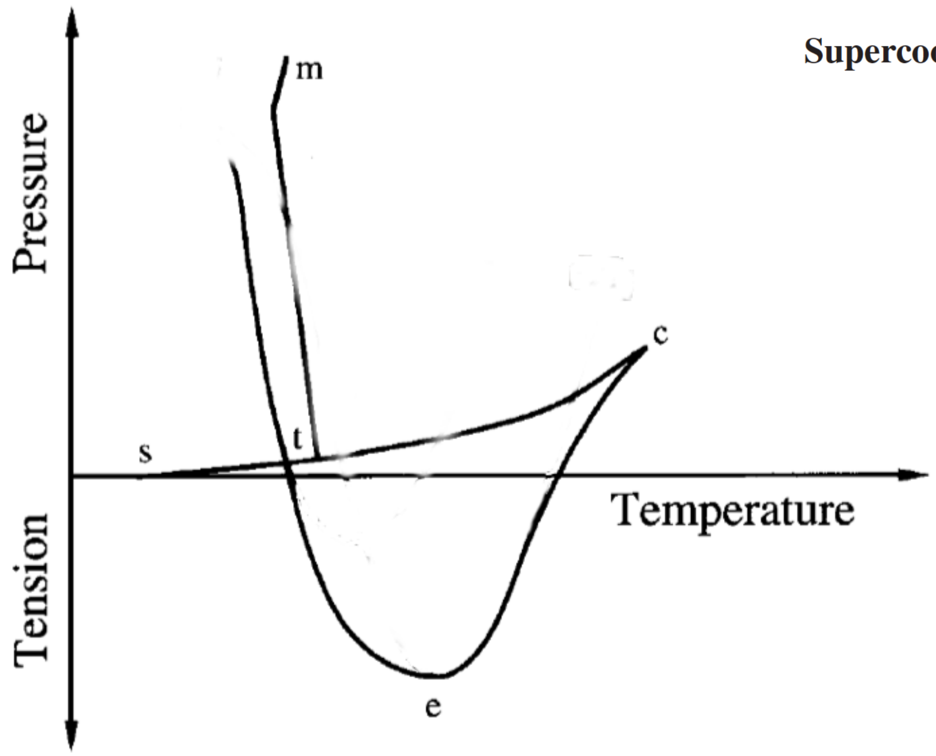


Figure 21. A schematic representation of Speedy's stability limit conjecture. 'st' is the sublimation curve, 'tc' is the boiling curve and 'tm' is the melting curve. 'g' and 'h' are isochores ($\rho_g > \rho_h$), 'c' and 't' are the critical and triple points, respectively. 'fae' is the locus of density maxima and 'cef' is the continuous spinodal bounding the superheated, supercooled and simultaneously superheated–supercooled states. Reprinted, with permission, from [24], Debenedetti P G, *Metastable Liquids, Concepts and Principles* copyright (1996) Princeton University Press.

Mean Field Models with Reentrant Spinodal

(but no divergence of compressibility at positive pressures)

Volume 207, number 2,3 CHEMICAL PHYSICS LETTERS 21 May 1993

Density anomalies and reentrant spinodal behavior ☆

Srikanth Sastry [a], Francesco Sciortino [a,b] and H. Eugene Stanley [a]

[a] Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215, USA

[b] CRS4, Centro di Ricerca, Sviluppo e Studi Superiori in Sardegna, P.O. Box 488, 09100 Cagliari, Italy

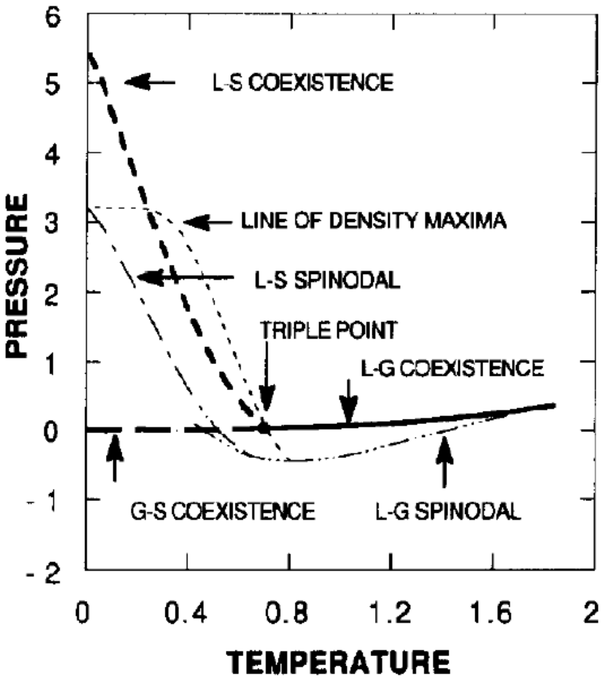


Fig. 2. Coexistence lines, spinodal boundaries of the liquid and the line of density maxima in the liquid phase. Note that the line of density maxima meets the liquid–gas spinodal at the point of reentrance and the liquid–solid spinodal at zero temperature. Both temperature and pressure are expressed in units of J, i.e. by fixing $k_B = 1$ and the value of the volume to 1.

J. Phys. Chem. 1995, 99, 3781–3792 3781

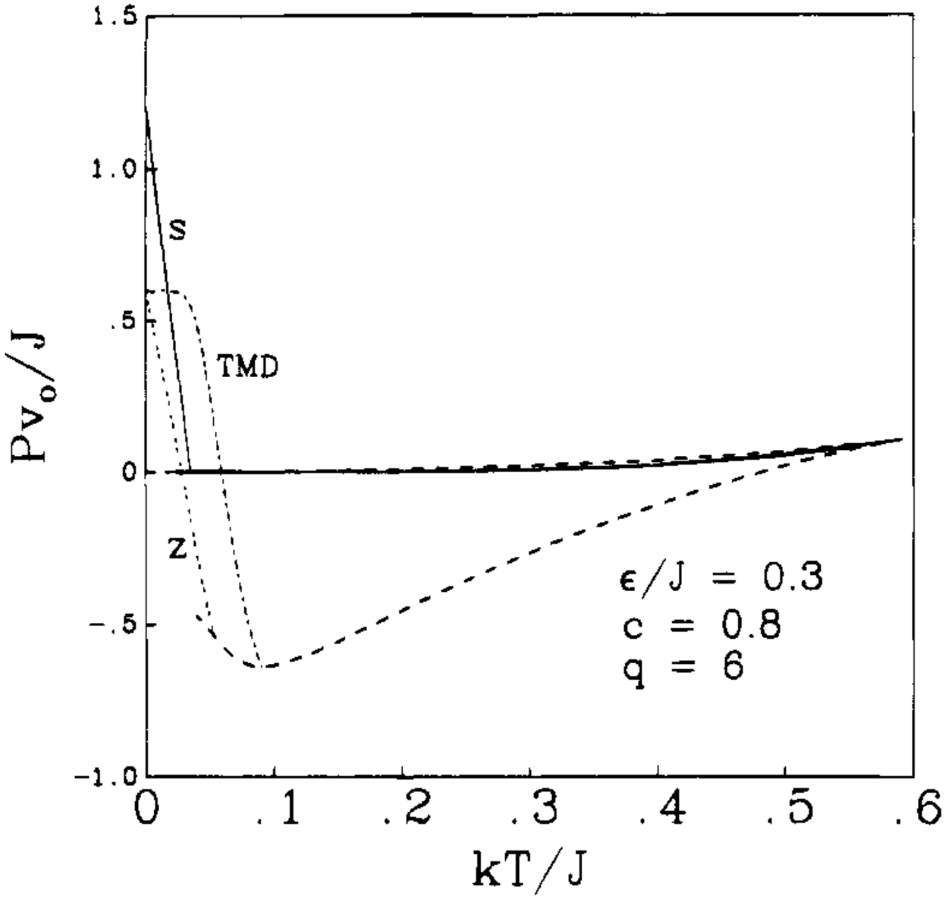
A Lattice Model of Network-Forming Fluids with Orientation-Dependent Bonding: Equilibrium, Stability, and Implications for the Phase Behavior of Supercooled Water

Steven S. Borick and Pablo G. Debenedetti*

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544-5263

Srikanth Sastry

Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland 20892



Sasai M 1993 Bull. Chem. Soc. Japan 66 3362

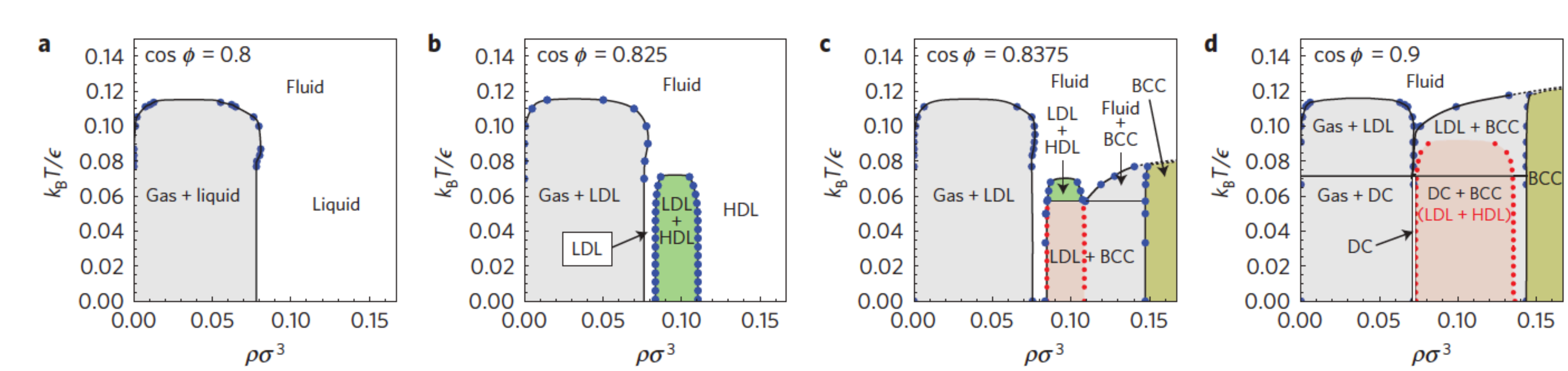
Colloids and water…..

nature physics
LETTERS
PUBLISHED ONLINE: 27 JULY 2014 | DOI: 10.1038/NPHYS3030

Erasing no-man's land by thermodynamically stabilizing the liquid–liquid transition in tetrahedral particles

Frank Smallenburg[1]*, Laura Filion[2] and Francesco Sciortino[1,3]

NATURE PHYSICS DOI: 10.1038/NPHYS3030 LETTERS



Getting closer to the real colloidal world

Eur. Phys. J. E (2016) **39**: 131
DOI 10.1140/epje/i2016-16131-5

THE EUROPEAN PHYSICAL JOURNAL E

Regular Article

Toward the observation of a liquid-liquid phase transition in patchy origami tetrahedra: a numerical study

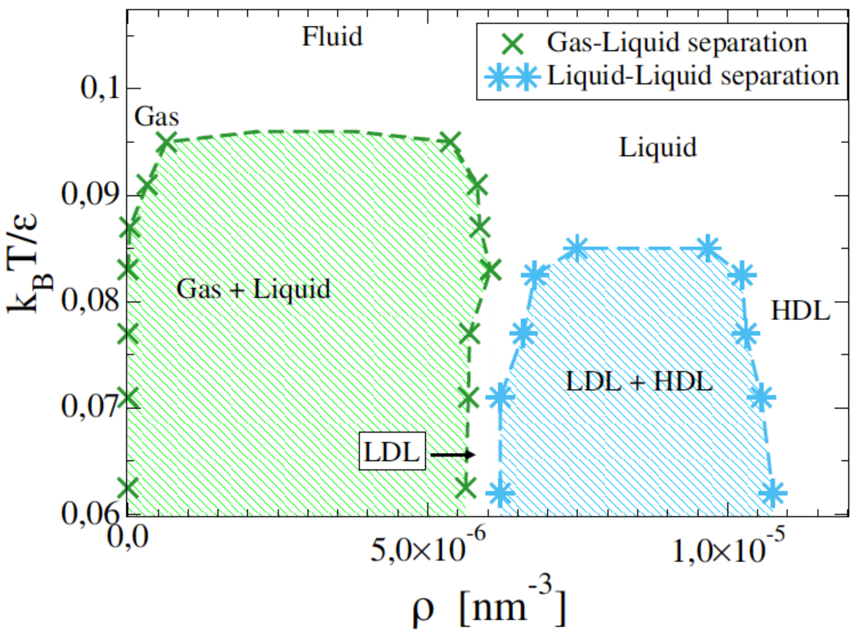
Simone Ciarella[1,a], Oleg Gang[2], and Francesco Sciortino[1]

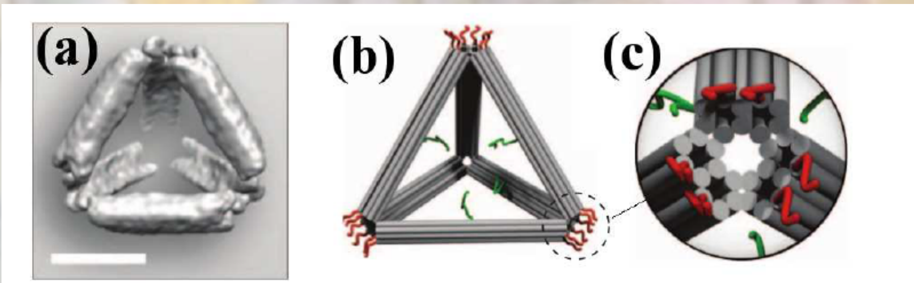
Diamond family of nanoparticle superlattices

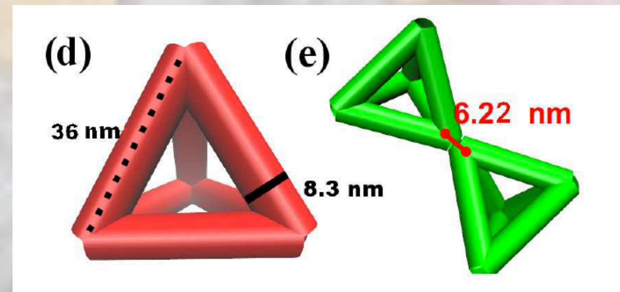
Wenyan Liu,[1] Miho Tagawa,[2] Huolin L. Xin,[1] Tong Wang,[3] Hamed Emamy,[4] Huilin Li,[3,5] Kevin G. Yager,[1] Francis W. Starr,[4] Alexei V. Tkachenko,[1] Oleg Gang[1]*

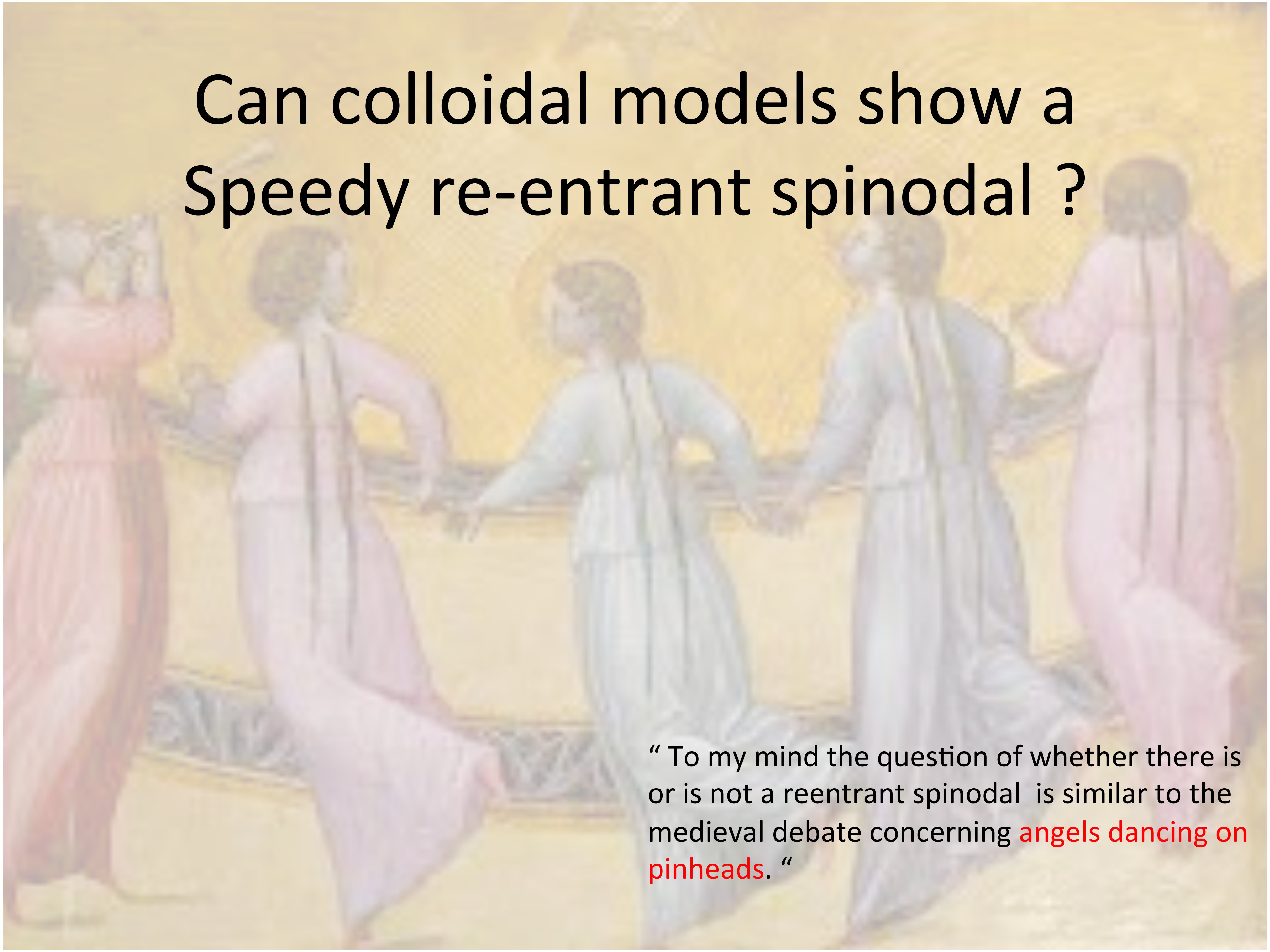
Science Vol. 351, pp. 582-586 2016:

Eur. Phys. J. E (2016) **39**: 131







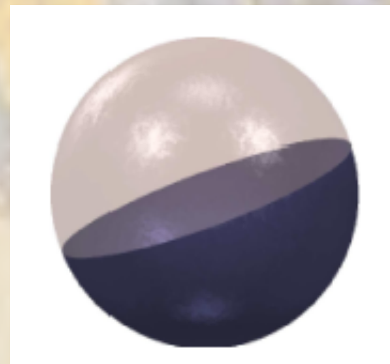


Can colloidal models show a Speedy re-entrant spinodal ?

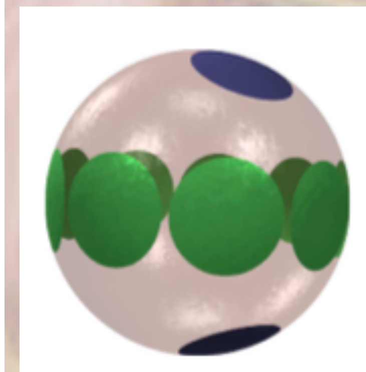
“ To my mind the question of whether there is or is not a reentrant spinodal is similar to the medieval debate concerning angels dancing on pinheads. “

Two pair-wise additive particle models

(one component system with close loops and a structured gas phase)

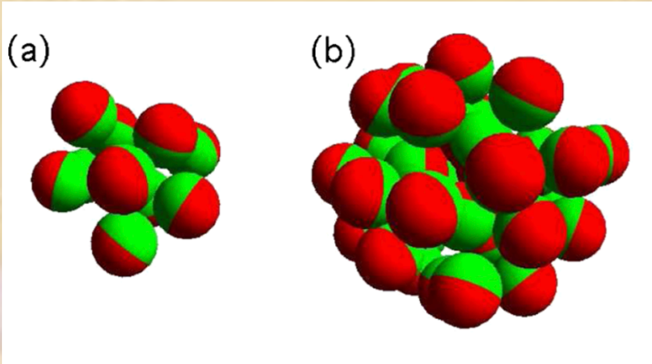


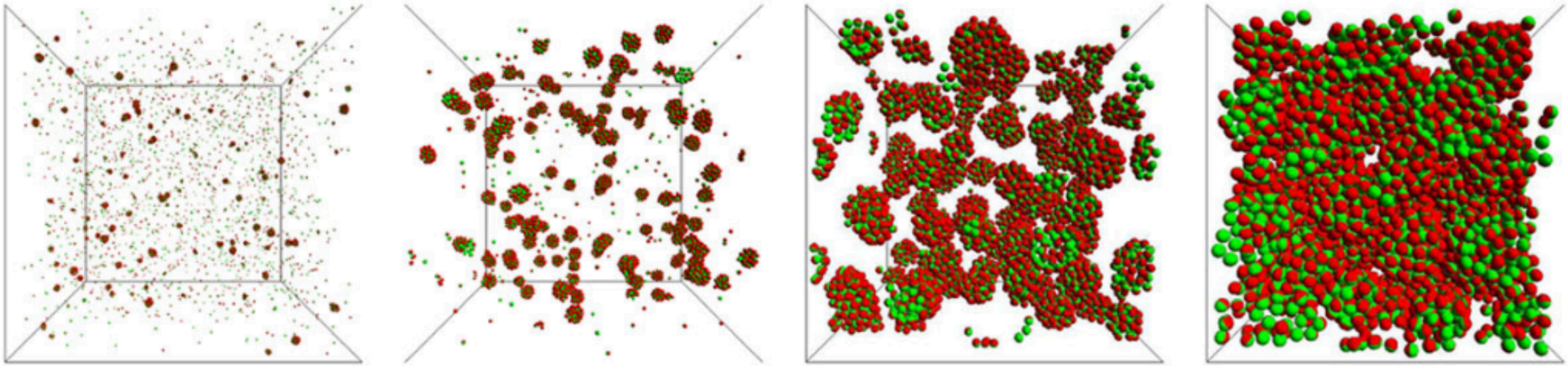
1) Janus Particles
   gas of micelles



2) Multiple-patches Particles
   gas of rings and chains

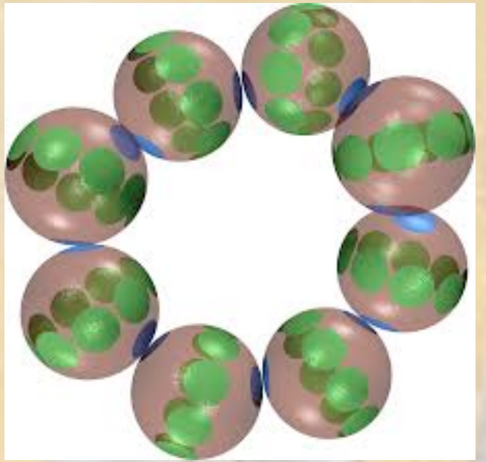
Janus Particles



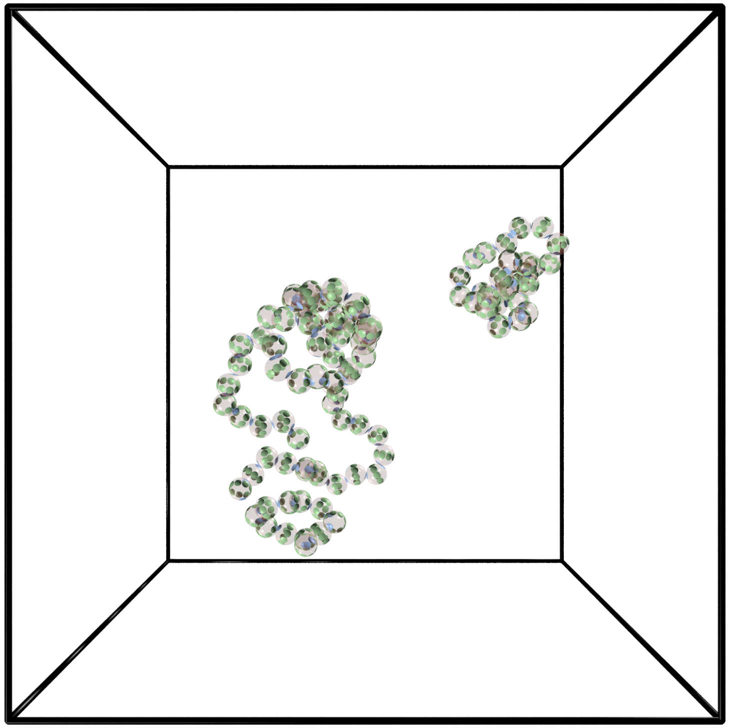


(f) $\rho\sigma^3 = 0.001$ (g) $\rho\sigma^3 = 0.01$ (h) $\rho\sigma^3 = 0.1$ (i) $\rho\sigma^3 = 0.4$

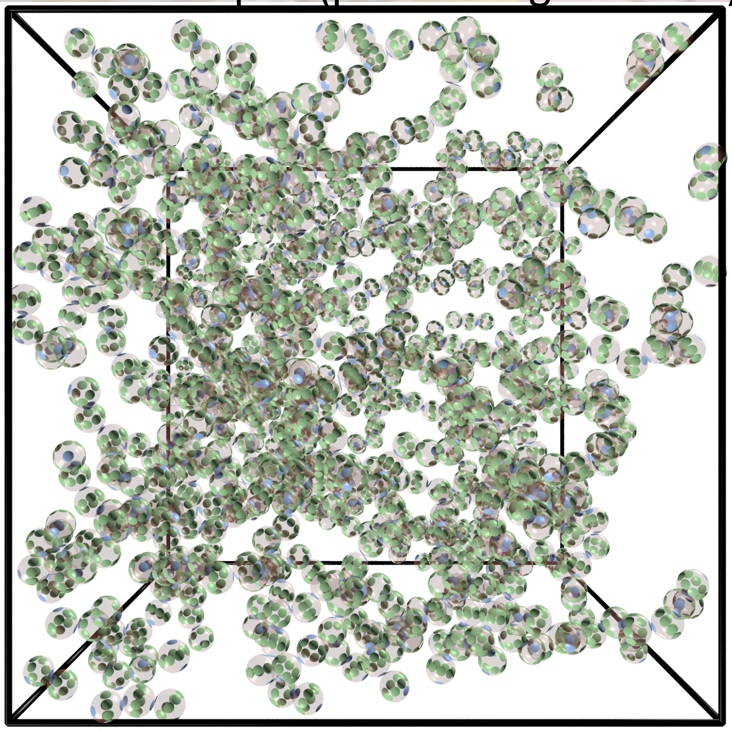
Multiple patches colloids



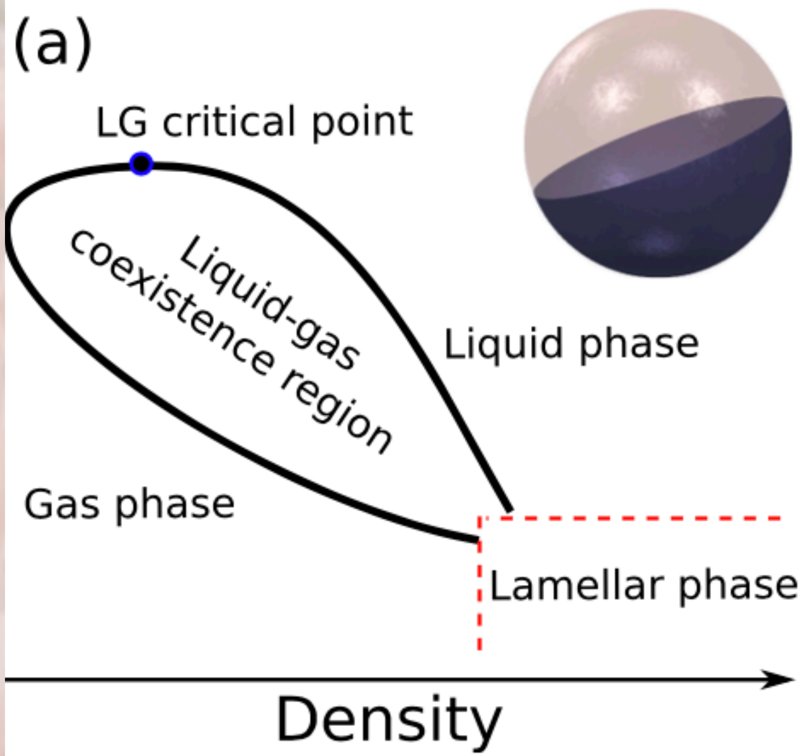
Gas of rings and chains



Liquid (percolating network)



The “gas-liquid” phase diagrams



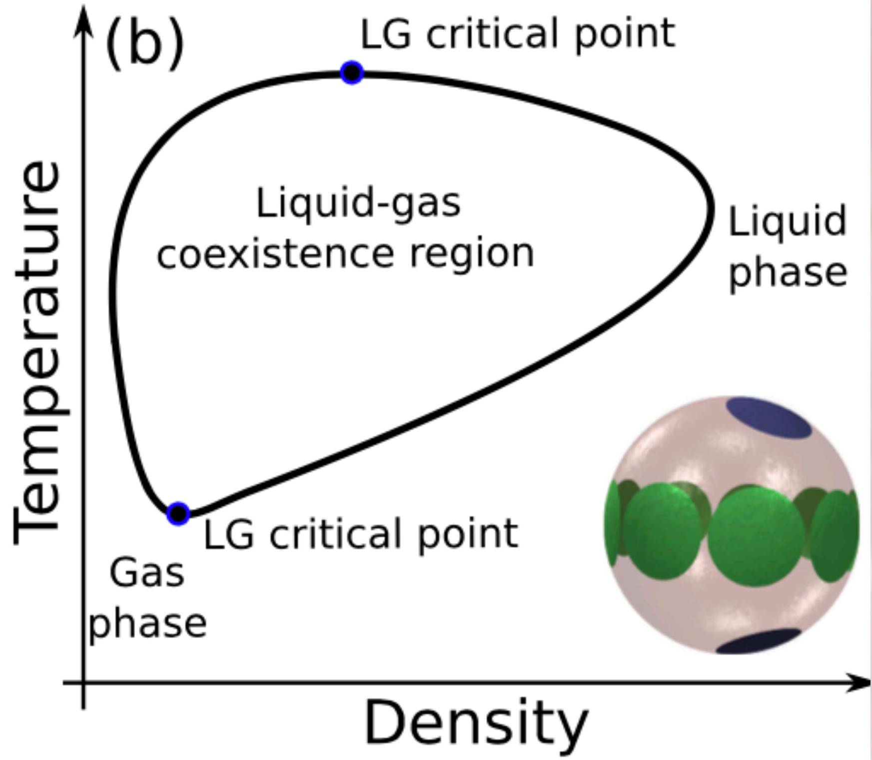
PRL 103, 237801 (2009) PHYSICAL REVIEW LETTERS week endin
4 DECEMBER

Phase Diagram of Janus Particles

Francesco Sciortino,[1] Achille Giacometti,[2] and Giorgio Pastore[3]

[1]*Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale A. Moro 2, 00185 Roma, Italy*
[2]*Dipartimento di Chimica Fisica, Università di Venezia, Calle Larga S. Marta DD2137, I-30123 Venezia, Italy*
[3]*INFM-CNR Democritos and Dipartimento di Fisica dell' Università, Strada Costiera 11, 34014 Trieste, Italy*

(Received 7 August 2009; published 30 November 2009)



PRL 111, 168302 (2013) PHYSICAL REVIEW LETTERS week ending
18 OCTOBER 2013

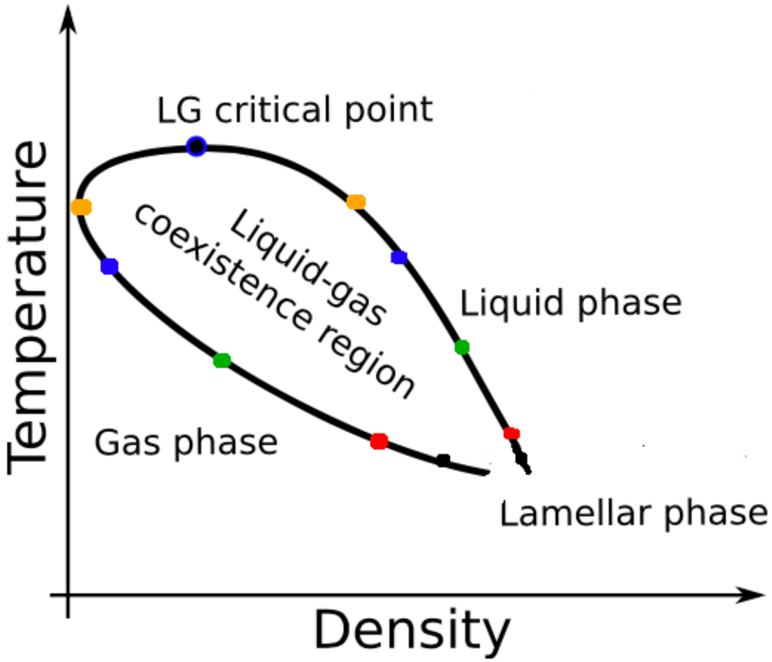
Self-Assembly in Chains, Rings, and Branches: A Single Component System with Two Critical Points

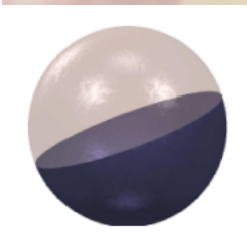
Lorenzo Rovigatti,[1] José Maria Tavares,[2] and Francesco Sciortino[3]

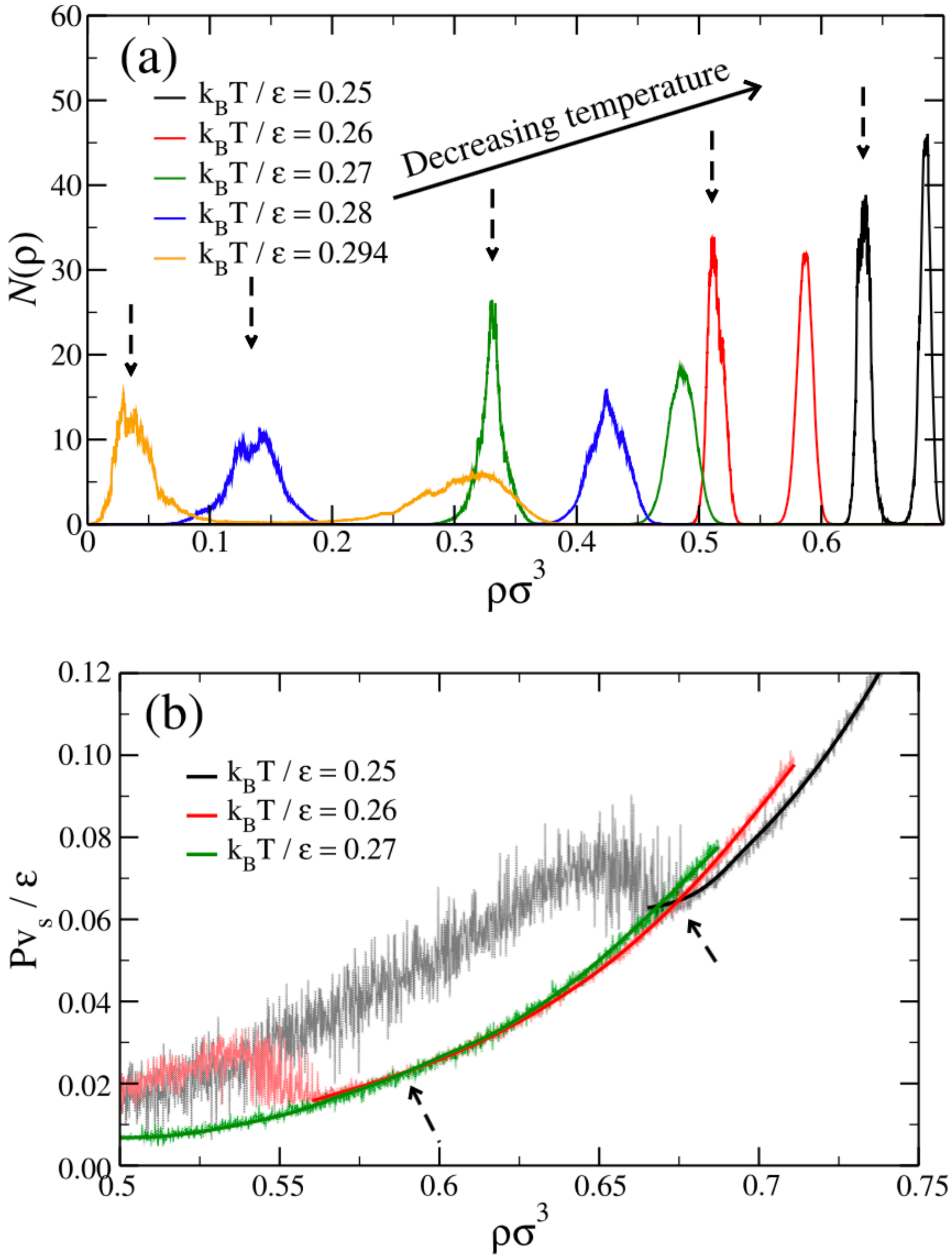
[1]*Dipartimento di Fisica, Sapienza Università di Roma, Piazzale Aldo Moro 2, 00185 Roma, Italy*
[2]*Instituto Superior de Engenharia de Lisboa–ISEL, Rua Conselheiro Emídio Navarro 1, P-1950-062 Lisbon, Portugal and Centro de Física Teórica e Computacional, Avenida Professor Gama Pinto 2, P-1649-003 Lisbon, Portugal*
[3]*Dipartimento di Fisica and CNR-ISC, Sapienza Università di Roma, Piazzale Aldo Moro 2, 00185 Roma, Italy*

(Received 2 July 2013; published 14 October 2013)

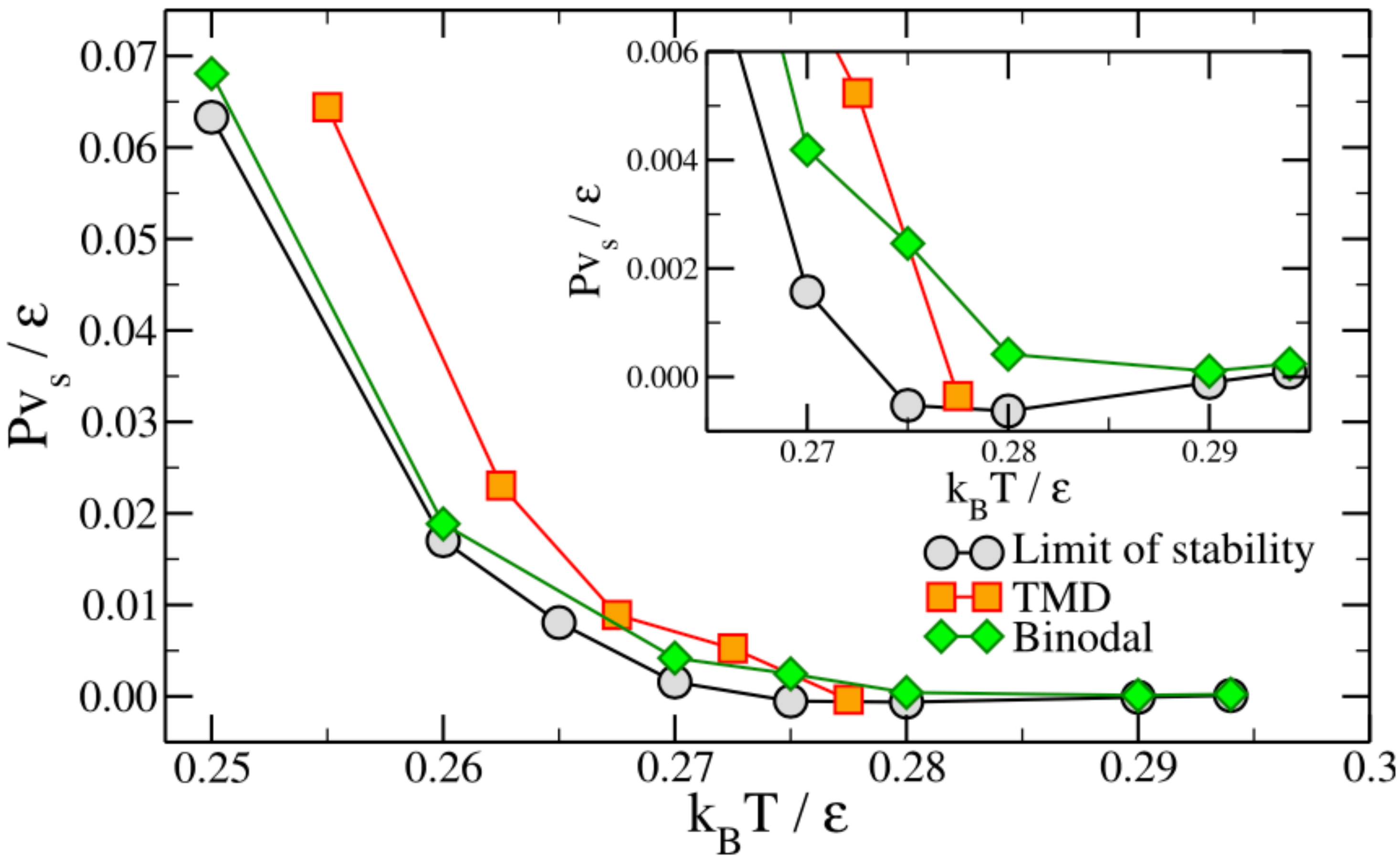
The raw data…. (Janus)

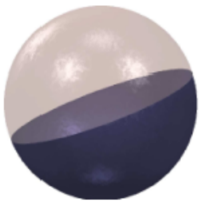




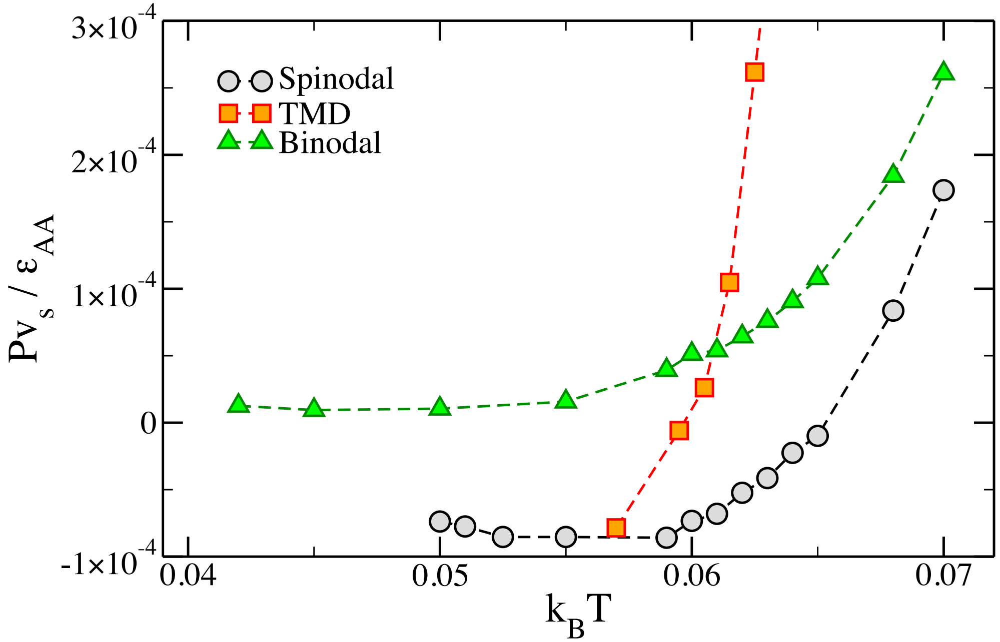


The Re-entrant Spinodal in the Janus system

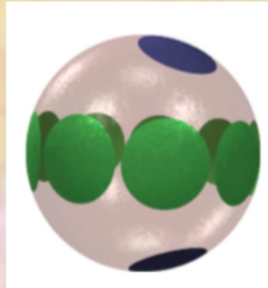




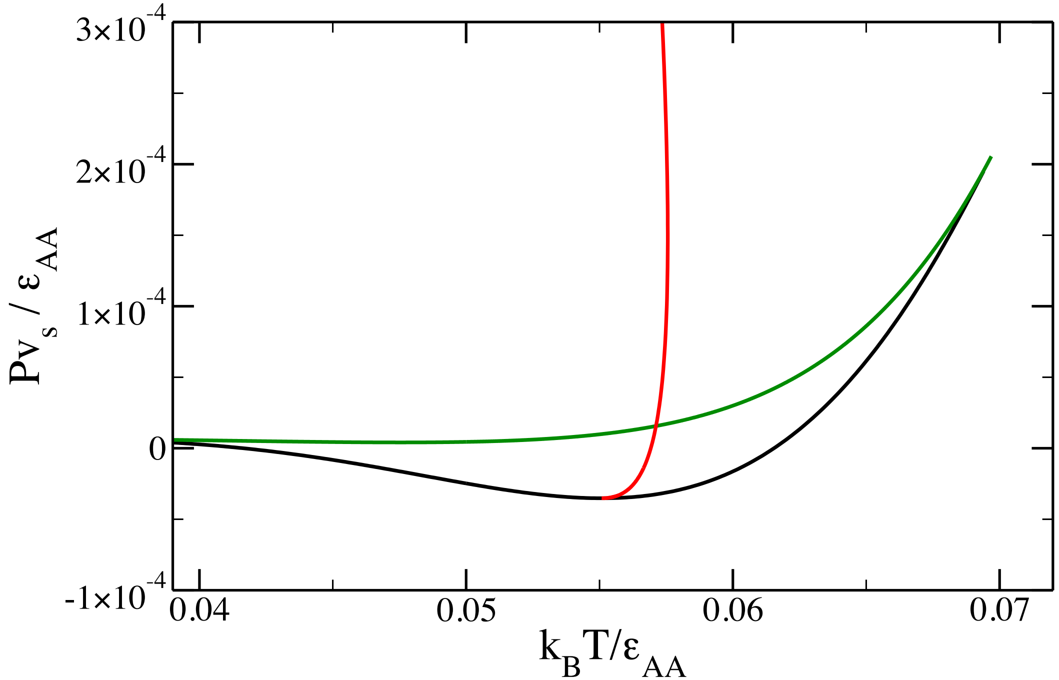
The patchy model…



← Simulation

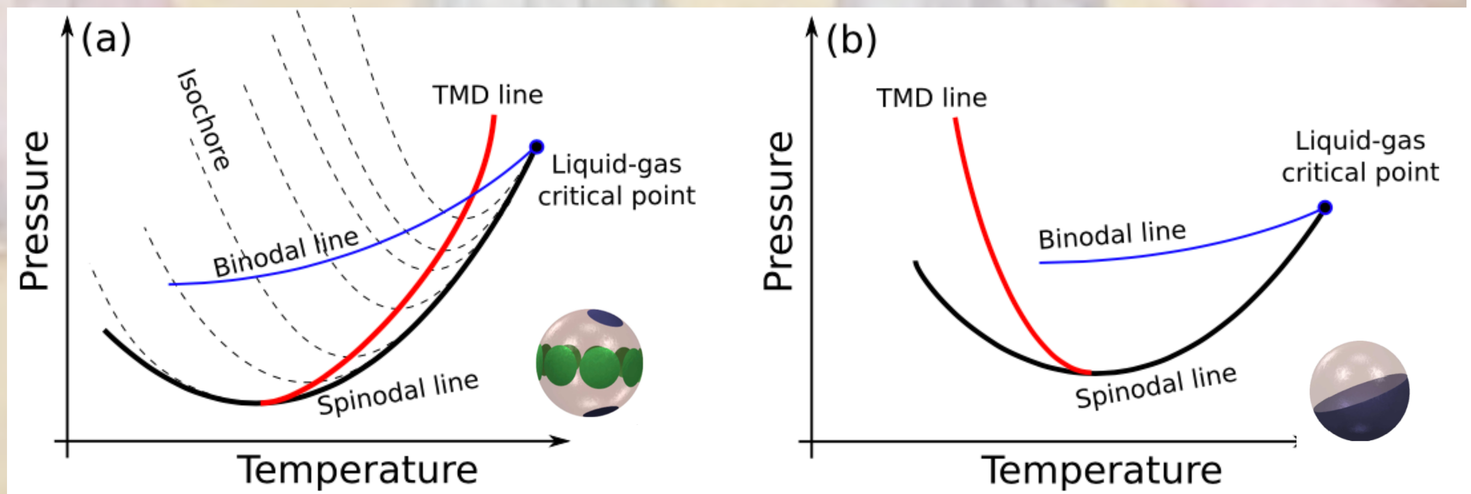


(Mean-field) Theory →



Conclusions:

- One component systems can exhibit close-loops phase diagrams.
- Re-entrant Speedy spinodals at positive pressures can exists (if the gas-liquid coexistence also retraces) (their presence can be detected by the increasing compressibility on cooling)
- “Patchy” colloidal systems offer the possibility to realize these thermodynamic scenarios and perhaps even a colloidal water



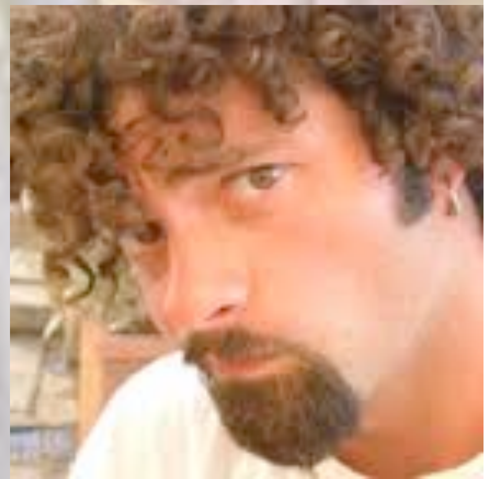
Auguri Piero !

Thanks for listening !

Collaborators

Lorenzo Rovigatti

Valentino Bianco



José Maria Tavares

Communication: Re-entrant limits of stability of the liquid phase and the Speedy scenario in colloidal model systems

Lorenzo Rovigatti, Valentino Bianco, José Maria Tavares, and Francesco Sciortino

Citation: The Journal of Chemical Physics **146**, 041103 (2017); doi: 10.1063/1.4974830

On lattice and analytic models

Volume 207, number 2,3 CHEMICAL PHYSICS LETTERS 21 May 1993

Density anomalies and reentrant spinodal behavior ☆

Srikanth Sastry [a], Francesco Sciortino [a,b] and H. Eugene Stanley [a]
[a] Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215, USA
[b] CRS4, Centro di Ricerca, Sviluppo e Studi Superiori in Sardegna, P.O. Box 488, 09100 Cagliari, Italy

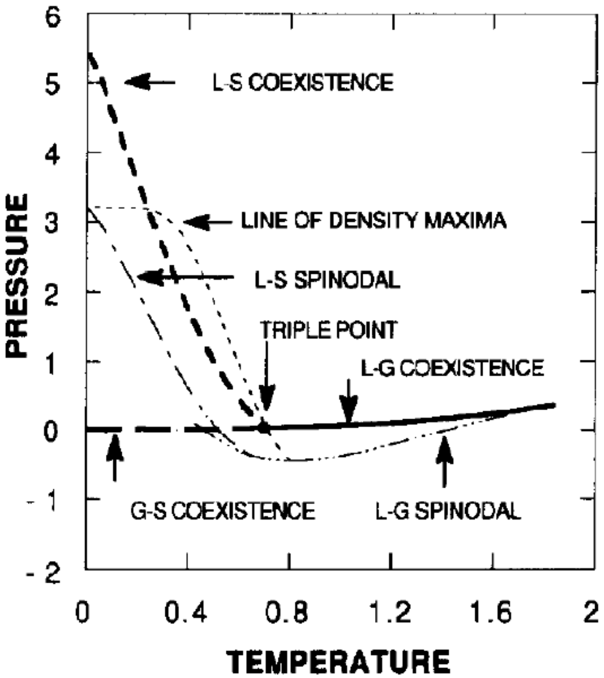
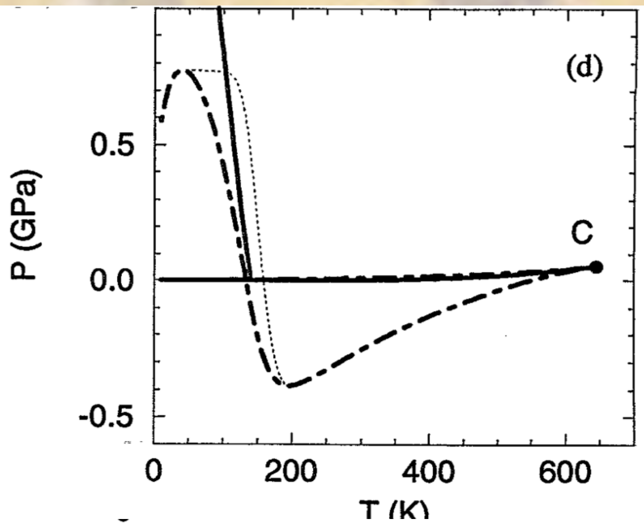


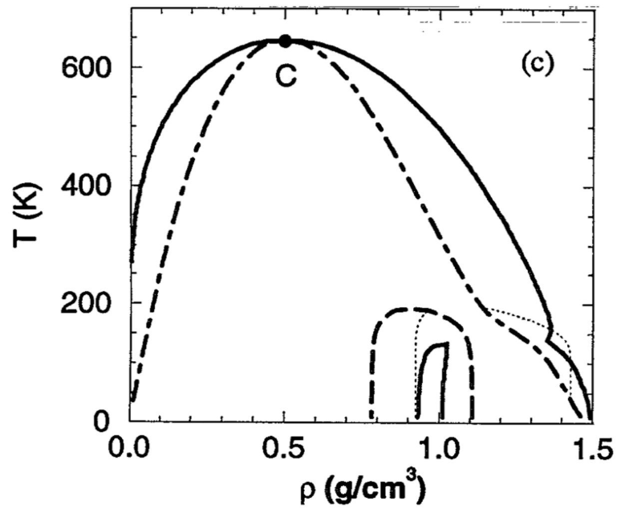
Fig. 2. Coexistence lines, spinodal boundaries of the liquid and the line of density maxima in the liquid phase. Note that the line of density maxima meets the liquid–gas spinodal at the point of reentrance and the liquid–solid spinodal at zero temperature. Both temperature and pressure are expressed in units of J, i.e. by fixing $k_B = 1$ and the value of the volume to 1.

VOLUME 73, NUMBER 12 PHYSICAL REVIEW LETTERS 19 SEPTEMBER 1994

Effect of Hydrogen Bonds on the Thermodynamic Behavior of Liquid Water

Peter H. Poole,[1] Francesco Sciortino,[2] Tor Grande,[1,3] H. Eugene Stanley,[4] and C. Austen Angell[1]
[1] Department of Chemistry, Arizona State University, Tempe, Arizona 85287
[2] Dipartimento di Fisica, Università "La Sapienza," Piazzale Aldo Moro, 00185 Roma, Italy
[3] Department of Inorganic Chemistry, Norwegian Institute of Technology, N-7034 Trondheim, Norway
[4] Center for Polymer Studies and Physics Department, Boston University, Boston, Massachusetts 02215





Sasai M 1993 Bull. Chem. Soc. Japan 66 3362
Borick S S, Debenedetti P G and Sastry S 1995 J. Phys. Chem. 99 3781