Angels Dancing on Pinheads

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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...

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

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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 $\kappa_T$ 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 $f = 2^{(n-1)}$, where $c_i$ 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, 0.100, 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, 0.078, 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, 0.099, 0.126, 0.115. Inset: the percentile error of data at 5% NaCl, $\Delta \kappa_T = 100(\kappa_T / \kappa_0 - 1)/\kappa_T$.

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) and poly (Val-Pro-Gly-Gly)-water systems. 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.

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


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

M Manno, D Bulone, V Martorana and P L San Biagio
Journal of Physics: Condensed Matter, 16, 42
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 6, 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 I metastable superheated, stretched, and supercooled sta significance, one can deduce the thermodynamic anomali and a heat capacity divergence in supercooled water, are shown to be in accord with the several implication

Vaporizing liquid water on cooling !!!!

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 $T_{st}$: (○) values of $T_s$ and $p_s$ for H$_2$O from Tables I-III (column 2); (●) values of $T_s$ for H$_2$O from Table III (column 2) and Figure 4; (+) $p_s$ at 100 °C calculated from ref 20; (X) $p_s$ (100 °C) and $p_s$ (25 °C) estimated by Yayanos; (×) $T_m$ values from Table I for superheated H$_2$O and Table III for supercooled water; ($T_n$) is extrapolated to terminate at $p_n$ (5 °C) = -190 MPa as discussed in section 8.
Debenedetti’s criticism

Topical Review

Supercooled and glassy water

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Figure 21. A schematic representation of Speedy’s stability limit conjecture. ‘st’ is the sublimation curve, ‘te’ 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. ‘fac’ 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.
Density anomalies and reentrant spinodal behavior

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.
Colloids and water.....
Getting closer to the real colloidal world

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

Simone Ciarella, Oleg Gang, and Francesco Sciortino

Diamond family of nanoparticle superlattices

Wenyuan Liu, Miho Tagawa, Huolin L. Xin, Tong Wang, Hamed Emamy, Huilin Li, Kevin G. Yager, Francis W. Starr, Alexei V. Tkachenko, Oleg Gang
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

(a)  
(b)  

(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

(a) LG critical point
Liquid-gas
coexistence region
Liquid phase
Gas phase

(b) LG critical point
Liquid-gas
coexistence region
Liquid phase
Gas phase

Density
Temperature

PRL 103, 237801 (2009)

PHYSICAL REVIEW LETTERS

Phase Diagram of Janus Particles
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PHYSICAL REVIEW LETTERS

Self-Assembly in Chains, Rings, and Branches: A Single Component System with Two Critical Points
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(Received 2 July 2013; published 14 October 2013)
The raw data... (Janus)
The Re-entrant Spinodal in the Janus system
The patchy model...
Conclusions:

• **One component** systems can exhibit close-loops phase diagrams.

• Re-entrant Speedy spinodals at positive pressures can exist (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
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

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Density anomalies and reentrant spinodal behavior

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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.