YU ISSN 0015—3206
FZKAAA 14 (1) 29 (1982)

POSSIBLE UNIVERSAL EXISTENCE OF A MESOPHASE

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Received 24 November 1981

UDC 536.7

Original scientific paper

Examples of real and model fluids, and circumstantial experimental evidence are presented in support of two hypotheses: *A*) the P, ϱ, T surface of any real fluid exhibits at least two critical points, one of them possibly in the subcooled or solid state region; *B*) any substance may also exhibit an anisotropic phase of an intermediate order between the liquid and solid phases.

1. Introduction

Halperin and Nelson *(HN)*[1] proposed a theoretical model of melting in two dimension where the solid and fluid phases are separated by an intermediate liquid crystal phase with short range translational order and long range orientational order. Having performed molecular—dynamics calculations on a two dimensional Lennard—Jones (*LJ*) system, Frenkel and McTague [2] concluded that they indeed indicate the existence of such a liquid crystal hexatic phase at low temperatures. Their conclusions, however, have been opposed by the molecular-dynamic calculations of Toxvaerd[3] and van Swool and Woodcock[4]. In *HN*'s theory melting is a second order transition. Imry and Schwartz[5] evaluated this possibility qualitatively by considering a modified lattice-gas model for the gas-liquid-solid phase diagram. They found that it all *depends on the value of certain parameters, in a way that makes it probable in two but not in three dimensions.*

HN's results suggest that for a chemical substance to become an anisotropic liquid crystal it is not absolutely essential that its intermolecular forces are anisotropic. Thus *HN*'s results suggest the possibility that any chemical substance can be found in all four phases: gaseous, isotropic liquid, anisotropic liquid and crystal. Preceeding *HN*'s work, Hemmer and Stell$^{6)}$, Hecht and Lind$^{7)}$ and Hecht, Sapse and Shenkin$^{8)}$ have constructed models of isotropic fluids having more than one critical point by judiciously choosing the model inerparticle potential. Since nematic fluids do have two critical points, the question immediately arises whether all real fluids do exhibit more than one critical point.

2. *Evidence*

In what follows, we present evidence suggesting that the subcooled *LJ* fluid, in addition to the gas—liquid phase transition with the critical point at $T = T_c$ and $\varrho = \varrho_c$, also exhibits a first order phase transition having an additional critical point, say, $T_{ac} \approx 1/2\ T_c$ and $\varrho_{ac} \approx 2.8\ \varrho_c$. Namely, we observed that some empirical equations of state, which we used for reproducing calculated P, ϱ data of the *LJ* fluid, for isotherms $T \approx 1/2\ T_c$ start to exhibit an additional van der Waals—like loop (i. e. an additional non—monotonic P, ϱ, dependence) characteristic of the first order phase transition. For orientation we plotted Fig. 1, where using a dotted line we indicated on Fig. 6 of Nicolas et al.$^{9)}$ the possible coexistence curve between liquid and mesophase; the region of the experimental data used is above the dotted--dashed and gas—liquid coexistence lines, extending up to $T \approx 15\ T_c$. Since a phase transition into a phase of greater density increases order, these results that a sufficiently cooled *LJ* liquid on being compressed will change into a phase having an intermediary order between liquid and solid. Since the critical temperature and the critical density of this transition are deep in the region of the subcooled *LJ* fluid Fig. 1 indicates the possibility that it may actually be unobservable, or that its mesophase may at best be observable only coexisting with gas and/or liquid and/or solid phases.

As indicated on Fig. 1, our evidence for the existence of a *LJ* mesophase is based on an extrapolation of *experimental* P, ϱ, T data about the *LJ* fluid. Though many of the considered analogous analytic extrapolations of the *LJ* P, ϱ, T data do display behaviour analogous to that of Fig. 1, some of them do not. We will present therefore, additional corroborative experimental evidence that observed non—monotonic isothermal P, ϱ dependence along the density line $\varrho = 2.8\ \varrho_c$ in Fig. 1 does indeed indicate a possible phase transition, and is not incidental to the particular analytic form of the ansatz used for extrapolating P, ϱ, T data. This evidence is based on the fact that various considered analytic approximations to the P, ϱ, T surface of the *LJ* fluid all display along the density line $\varrho = 2.8\ \varrho_c$ certain analytic properties of the kind they display along the density line $\varrho = \varrho_c$ where we do have a gas—liquid phase transition. The observed symmetric properties are internal property of the P, ϱ T data used since the density line $\varrho = 2\ 8\ \varrho_c$ passes at higher temperatures through them as indicated by Fig. 1.

The ideas of Thom's theory of catastrophes have been used to obtain local characterization of possible phase diagrams$^{10)}$. However, it has escaped general

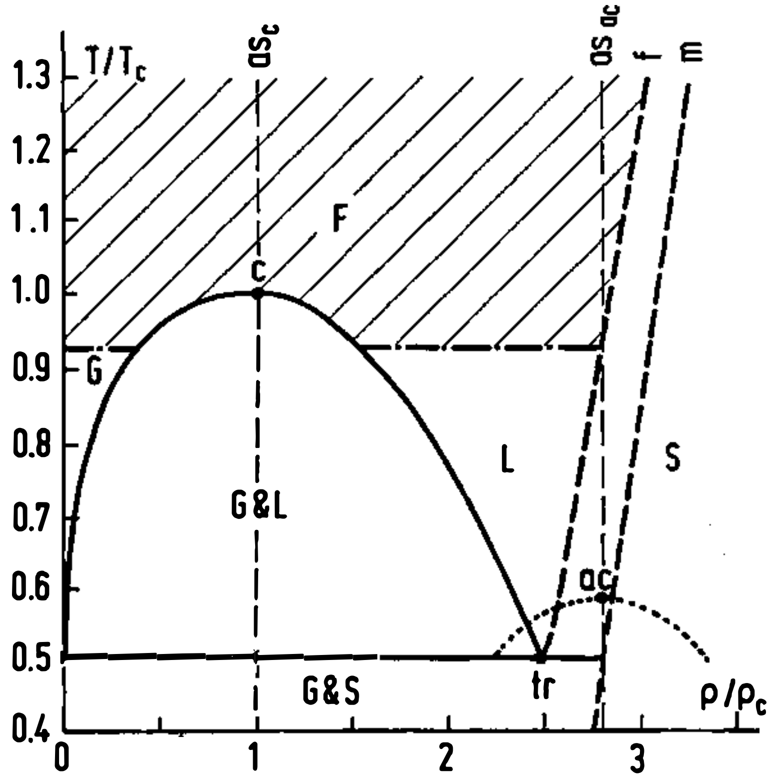

Fig. 1. Phase diagram of the *LJ* fluid, *f, m, as$_c$, as$_{ac}$* being freezing, melting, and antisymmetry lines; *c, ac,* and *tr* being critical, additional critical and triple points; *G. F, L, S* indicating gas, fluid, liquid and solid state regions.

attention that the results of Thom's theory suggest the existence of peculiar global analytic relations between observable physical quantities such that certain powers of (ϱ — ϱ_c) are absent everywhere, not only in the vicinity of the critical point. As pointed out by Ribarič and Žekš[11] any such relation, if universally experimentally verified, would imply a global physical law of a hitherto possibly unknown type. The simplest example of such an analytic relation is provided by van der Waals' equation, expressing the pressure, say P_w of the van der Waals gas in terms of density ϱ and temperature T; it satisfies the relation $\partial(\varrho^{-1}\, \partial P_w/\partial\varrho)/\partial\varrho = 0$ at $\varrho = \varrho_c$ for any temperature T, which tells us that the chemical potential μ_w of the van der Waals gas is locally antisymmetric along the density line $\varrho = \varrho_c$. Results of Thom's theory of catastrophes thus suggest for any critical density ϱ_{cr} the possibility that $\varrho = \varrho_{cr}$ is the line of some kind of symmetry. The first observed symmetry of the P, ϱ, T surface of real fluids has been the apparent local antisymmetry of the chemical potential μ, where experimental data suggest $\partial^2\mu/\partial\varrho^2 = 0$ and possibly also $\partial^4\mu/\partial\varrho^4 = 0$ along the line of the gas—liquid critical density ϱ . This fact was discovered by Tisza and Chase[12] in the vicinity of the critical point $T = T_c$, $\varrho = \varrho_c$, and shown by Vicentini—Missoni, Levelt Sengers and Green[13] to be also true for temperatures above critical, and brought into relation with Thom's theory of catastrophes by Ribarič and Žekš[14]. Recently Ribarič and Žekš[15] collected experimental evidence suggesting that for many different real fluids the logarithm of the compressibility factor $z = P/\varrho\ RT$ may be antisymmetric along the density line $\varrho = \varrho_{ac} \in (2\varrho_c, 3.4\ \varrho_c)$. Subsequent investigations suggest that for an LJ fluid $\varrho_{ac} \in (2.6\ \varrho_c, 2.9\ \varrho_c)$[16]. In addition, for the LJ and some real fluids we found experimental evidence that for any temperature (i) $\partial^6 P/\partial \varrho^6 = 0$ at $\varrho = (1 \pm 0.1)\varrho_c$ and $\varrho = (2.7 \pm 0.3)\varrho_c$, and (ii) $\partial^4 \mu/\partial \varrho^4 = 0$ at $\varrho = (2.7 \pm 0.3)\varrho_c$ [16]. These results by themselves suggest for the LJ fluid the existence of a symmetry line $\varrho = \varrho_{ac} = (2.7 \pm \pm 0.3)\varrho_c$ associated with a certain kind of phase transition whose critical density equals ϱ_{ac}. They represent circumstantial evidence that the observed van der Waals—like loops of the extrapolated approximate P, ϱ, T equations of the LJ fluid in the vicinity of the density $\varrho \approx 2.8\ \varrho_c$ are not incidental, but a physical property of the LJ fluid associated with an additional phase transition.

3. *Conclusion*

We have presented evidence that the subcooled LJ fluid exhibis a first order transition into a mesophase of an intermediary order between liquid and solid. It is also reasonable to expect that a variety of real fluids whose effective intermolecular potential is well approximated by the LJ potential will exhibit similar behaviour in their metastable subcooled regions. Moreover, nematic fluids whose long molecules interact with highly anisotropic forces, do exhibit an observable phase transition into a stable, liquid crystal mesophase, and the same goes for fluids with planar or disc—like molecules[17]. Since both spherical as well as strongly anisotropic molecules give indications of having two critical points associated with first order phase transitions, speculating about the properties of intermediate molecules, we propose the following two hypotheses: *A*) The P, ϱ, T surface of any real fluid has at least two critical points associated with first order phase transitions, one of them possibly in the subcooled or solid state region, and *B*) When occuring, this additional phase transition turns fluids into an anisotropic mesophase.

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O MOŽNOSTI VSESPLOŠNEGA NASTOPA MEZOFAZE

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UDK 536.7

Originalno znanstveno delo

Primeri modelne in realnih tekočin, ter posredni eksperimetalni dokazi so navedeni v podporo dveh hipotez: *A*) P, ϱ, T ploskev vsake realne tekočine ima vsaj dve kritični točki, eno od njih morebiti v območju podhlajene tekočine ali trdne snovi; *B*) vsaka snov more imeti tudi anizotropno fazo vmesne urejenosti med trdno in tekočo fazo.