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Experimental evidence for the universality of the pseudospinodal

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There have been a number of experimental results[1-5] supporting the concept of a pseudospinodal for describing critical region data. Recently, Sorensen and Semon[6] have successfully used this concept to derive an equation of state for liquid–gas systems that fits PVT data as well as other phenomenological equations. In this note we have used available experimental evidence to test the existence of a *universal* pseudospinodal that describes all thermodynamic and transport properties of all liquid–gas and binary fluids systems with one curve.

The spinodal curve, first introduced by van der Waals, represents the limit of metastability of the one-phase state in the two-phase region. To describe critical region data off the critical isochore, Benedek[5] introduced the so-called *pseudospinodal assumption* that states that along any isochore, represented by density or concentration ρ, a given thermodynamic or transport property X diverges as the pseudospinodal temperature $T_s(\rho)$ is approached according to

$$X = X_0 \left[\frac{T - T_s(\rho)}{T_c} \right]^{-x} = X_0 [t + t_s(\rho)]^{-x} \qquad (1)$$

with $t = (T - T_c)/T_c$ and $t_s(\rho) = [T_c - T_s(\rho)]/T_c$. Here X_0 and x are the critical amplitude and exponent found along the critical isochore. Note that $T_s(\rho_c) = T_c$, where ρ_c is the critical density. Under the assumption of Eq. (1), the locus of $T_s(\rho)$, called the pseudospinodal curve, is found to have the form

$$|\rho - \rho_c| / \rho_c = \tfrac{1}{2}(\rho' - \rho'')/\rho_c = B_s \left[\frac{T_c - T_s(\rho)}{T_c} \right]^{\beta^\dagger} \qquad (2)$$

where B_s is the amplitude of the curve and ρ' and ρ'' are the densities or concentrations of the two phases. It is expected from homogeneity or scaling[7,8] that $\beta^\dagger = \beta$, the exponent describing the coexistence curve.[1,9]

To test the universality of the pseudospinodal, we have

attempted to use all available experimental results[1-4] specifically designed to test the pseudospinodal assumption. We have also analyzed experimental data not specifically designed for this problem but with ample off-critical isochore data to allow for our analysis. Such data are surprisingly rare. We have used specific heat data for He^4[10] and CO_2,[11] thermal diffusivity data for CO_2[12] and PVT data for He^4.[13] The PVT data were used to graphically obtain inverse isothermal compressibility data of He^4 along the off-critical isochores.

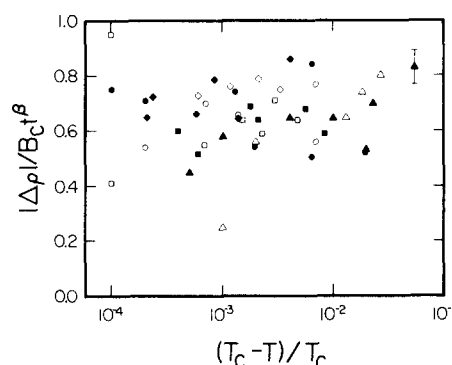In analyzing the data, a background term of the form

FIG. 1. Plot of pseudospinodal curve data $\Delta \rho_s$ normalized by the coexistence curve $B_c t^\beta$ versus the reduced temperature $t = (T_c - T)/T_c$. The symbols correspond to: ⧫ diffusivity and correlation length of isobutyric acid + water (Ref. 1), ◊ osmotic compressibility and correlation length of polystyrene + diethyl malonate (Ref. 4), ● viscosity of isobutyric acid + water (Ref. 3), ○ correlation length of polystyrene + cyclohexane (Ref. 2), ▲ isothermal compressibility of He^4 (Ref. 13), △ specific heat of CO_2 (Ref. 11), ■ specific heat of He^4 (Ref. 10), and □ thermal conductivity of CO_2 (Ref. 12). The value $|\Delta \rho|/B_c t^\beta = 1.0$ represents the coexistence curve. A typical error bar is also shown.

TABLE I. A list of pseudospinodal and coexistence curves obtained from either our data analysis or the analysis in the published work.

Thermodynamic or transport property and system	Coexistence curve	Pseudospinodal curve
Diffusivity and correlation length of isobutyric acid in H_2O[a]	$\dfrac{\rho' - \rho''}{\rho_c} = 5.82\, t^{1/3}$	$\dfrac{\rho' - \rho''}{\rho_c} = 4.42\, t_s^{1/3}$
Viscosity of isobutyric acid in H_2O[b]	$\dfrac{\rho' - \rho''}{\rho_c} = 6.78\, t^{0.36}$	$\dfrac{\rho' - \rho''}{\rho_c} = 4.69\, t_s^{0.37}$
Correlation length of polystyrene–cyclohexane[c]	$\dfrac{\rho' - \rho''}{\rho_c} = 14.68\, t^{0.37}$	$\dfrac{\rho' - \rho''}{\rho_c} = 10.24\, t_s^{0.38}$
Osmotic compressibility and correlation length of polystyrene in diethyl malonate[d]	$\dfrac{|\rho - \rho_c|}{\rho_c} = 0.295\, t^{1/3}$	$\dfrac{|\rho - \rho_c|}{\rho_c} = 0.25\, t_s^{0.35}$
Specific heat of He^4[e]	$\dfrac{|\rho - \rho_c|}{\rho_c} = 1.57\, t^{0.3724}$	$\dfrac{\rho' - \rho''}{\rho_c} = 2.63\, t_s^{0.41}$
Specific heat of CO_2[f]	$\dfrac{|\rho - \rho_c|}{\rho_c} = 1.54\, t^{0.3486}$[g]	$\dfrac{|\rho - \rho_c|}{\rho_c} = 2.07\, t_s^{0.495}$
Thermal conductivity of CO_2[h]	$\dfrac{|\rho - \rho_c|}{\rho_c} = 1.54\, t^{0.3486}$[g]	$\dfrac{\rho' - \rho''}{\rho_c} = 1.9\, t_s^{0.34}$
Inverse isothermal compressibility of He^4[i]	$\dfrac{\rho' - \rho''}{\rho_c} = 2.77\, t^{0.35}$	$\dfrac{\rho' - \rho''}{\rho_c} = 1.84\, t_s^{0.37}$

[a] Reference 1.
[b] Reference 3.
[c] Reference 2.
[d] Reference 4.
[e] Reference 10.
[f] Reference 11.
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[h] Reference 12.
[i] Reference 13.

$B + D\Delta\rho + Et$, where B, D, and E are constants and t and $\Delta\rho$ are the reduced temperature and density, was used to correct for nonsingular behavior. The backgrounds were found both graphically and using a fitting procedure; both methods were consistent. The data were then fit with a linear least-squares method to the pseudospinodal assumption form Eq. (1) by varying t_s to obtain the best fit. Fits to all isochores yielded, within error, the same values of X_0 and x obtained on the critical isochore. Thus, it is important to stress, the consistency of the pseudospinodal was well verified. To determine the amplitude B_s and the exponent $\beta^\dagger$, the values of t_s so obtained were then fit to either form of Eq. (2), the latter form was used when the pseudospinodal curve was not symmetric. Our results along with earlier published pseudospinodal curves are displayed in Table I.

Inspection of Table I shows that there is a small but persistent tendency for $\beta^\dagger \geq \beta$ in nearly all cases. This is especially true for both sets of specific heat data, the data for CO_2 having an essentially mean field value of $\beta^\dagger \simeq \frac{1}{2}$.

To compare these various pseudospinodals, we normalized relative to the coexistence curve of the fluid. Some ambiguity in coexistence curves arises. When possible we used the coexistence curve that was presented with, or could be obtained from, the data used to find the pseudospinodal. Otherwise the best literature value was used. In any event, the ambiguity is usually only a few percent. Thus, along any given isotherm t, we divide a given data value $\Delta\rho_s = (\rho_s - \rho_c)/\rho_c$ on the pseudospinodal by $\Delta\rho = (\rho - \rho_c)/\rho_c = B_c t^\beta$, the coexistence curve. This method of normalization is preferable to simply dividing the pseudospinodal by B_c because of statistical correlations between B_c and β.

Figure 1 is a plot of normalized pseudospinodal curve data, $\Delta\rho_s / B_c t^\beta$, versus reduced temperature t. To within the rather large scatter of the data, the pseudospinodal curves for the various substances and properties do display universal behavior. This possible universality implies that the pseudospinodal may have more physical significance than is usually recognized. If $\beta = \beta^\dagger$, then these results suggest the ratio B_s/B_c, equal to 0.66 ± 0.13 for these data, is a universal quantity. For comparison, theoretical spinodals predict $B_s/B_c = 0.58$ for the mean field model ($\beta = \beta^\dagger = \frac{1}{2}$, however), $B_s/B_c = 0.82 \pm 0.1$ for the Ising model,[14] and $B_s/B_c = 0.63$ from, not surprisingly, the pseudospinodal equation of state.[8]

We also mention that recent experiments on spinodal decomposition have indicated that temporal evolution characteristics differ for critical and off-critical quenches.[15] Inspection of this data suggests that most

of the off-critical quenches were not deep enough to go below the spinodal implied above, suggesting deeper quenches could be interesting.

In conclusion, we have shown that pseudospinodal data for both a variety of properties and systems lie in the same general area of the phase diagram when normalized relative to the coexistence curve, providing evidence for the concept of a universal pseudospinodal curve, the ratio B_s/B_c being a universal amplitude ratio. There is some tendency, however, for $\beta\dagger \geq \beta$.

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Effect of viscosity on fluorescence of anthracenes in solution

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Recently, there have been considerable interests in the effects of temperature,[1-7] pressure,[8-10] nature and position of substituents,[1-4] and solvents,[1,7] on the fluorescence of anthracene derivative, but there has not been a systematic investigation on the effect of solvent viscosity since the original report by Bowen and Sahu.[1] We investigated the fluorescence of anthracene, 9,10-dimethylanthracene and several 9-alkylated anthracenes in several pure hydrocarbons, and found that the fluorescence quantum yields, Φ_f, of 9-alkylated anthracenes increase in a more viscous solvent. By the application of kinetic spectrophotometry, we found that the increase is due to the decrease in the rate of nonradiative decay. Since the solvent viscosity varies with both the temperature and pressure, we also analyzed the relationship between the effect of solvent viscosity on the fluorescence relative to those of temperature and pressure.

Reagents. All solvents used in this investigation were the "Gold Label" spectrophotometric grade of the Aldrich Chemical Company or its equivalent. Anthracene was the "Gold Label" grade from Aldrich and sublimed at 0.1 Torr before use, 9-methylanthracene, 9,10-dimethylanthracene and 9,10-diphenylanthracene were the 99% grade from Aldrich and further purified by re-

crystallization, chromatography over silica gel and sublimation. 9-Ethylanthracene[11] and 9-(3-phenyl-1-propyl)-anthracene[12] were prepared in this laboratory. Quinine sulfate was purchased from Aldrich and recrystallized twice from water before use.

Instrumentation. All absorption spectra were measured at 22.0 ± 0.5 °C on a Cary 219 Spectrophotometer. All fluorescence spectra were measured at 22.0 ± 0.5° on a Perkin-Elmer MPF-4 Spectrofluorimeter with an integrated electronic corrected spectra unit and a thermostatic sample compartment. Fluorescence lifetimes were measured by a time correlated photon counting technique described in detail elsewhere.[13,14] The resolution in lifetime measurements was estimated to be better than 0.2 nsec.

Fluorescence Quantum Yield Determination. Φ_f's where determined by the aid of two secondary standards, quinine sulfate and 9,10-diphenylanthracene.[15] All sample solutions were deaerated by multiple freeze-thaw degassings and sealed under purified argon. The excitation slit of the spectrometer was arbitrarily set at 1 nm and the emission slit at 2 nm. The results presented in the Tables are those of duplicate runs. The reproducibility under these conditions was found to be