Int J Thermophys (2010) 31:1220–1222
DOI 10.1007/s10765-010-0812-y

BOOK REVIEW

D. Yu. Ivanov: Critical Behavior of Non-Ideal Systems

Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2008, English Edition, 271 pp

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Published online: 31 August 2010

The words "non-ideal systems" in the title of Dmitry Yu. Ivanov's book (translated from Russian by Jürn Schmelzer, University of Rostock), refer to "Ising-like systems (pure liquids, binary mixtures, and magnets)" subjected to disturbing fields such as: "gravity, Coulomb and surface forces, shear stresses, boundaries, etc." In fact, the first half of the book is devoted almost entirely to reviewing the experimental literature for measurements of the coexisting densities and isothermal compressibility near liquid–vapor critical points and the second half of the book is devoted primarily to the theory of critical opalescence and measurements of quasi-elastic light scattering. The second half includes shorter discussions of measurements of the thermal conductivity near liquid–vapor critical points.

In the Introduction (p. 3), Ivanov reports that his review of published data reached "the seemingly unexpected conclusion that on approaching the critical point there is continuous growth in the system's susceptibility to external influences which eventually leads to a point where fluctuations are first deformed and then completely suppressed by some of these factors. As a result, the system is found to have mean-field, classical behavior with corresponding critical indices." Ivanov's conclusion goes beyond the current, quantitative, understanding of critical phenomena and, unfortunately, it is not convincingly supported by the data cited.

As one takes a system towards its critical point, well-verified theory predicts a broad crossover from "classical" or "mean field" thermodynamic behavior to fluctuation-dominated critical behavior. In effect, Ivanov argues that still closer to critical

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points, there is *always* a second crossover to classical behavior at a location that depends upon non-idealities of the system under study.

To illustrate Ivanov's thinking we consider two examples of non-ideality: (1) that caused by gravity, and (2) that caused by impurities. Consider thermodynamic measurements very near a liquid–vapor critical point where ideal critical behavior is three-dimensional, Ising-like, and the earth's gravity is the dominant external field causing "non-ideal" behavior. Ivanov identifies two effects of gravity. The first, which he calls "primitive," is the gravitational stratification of the density of near-critical fluids in equilibrium. He calls the second gravitational effect "intrinsic" and Ivanov asserts that this intrinsic effect generates a second crossover to classical critical behavior; however, he does not quantify this assertion. There is a plausible alternative to Ivanov's second crossover to classical behavior. The literature from the 1970s argues that critical fluctuations in a liquid–vapor system larger than a system-dependent size will be suppressed by gravity [1]. This size was estimated using the criterion that the gravitational contribution to the potential energy of a fluctuation is equal to $k_B T_c$. For xenon, this criterion is satisfied at the reduced temperature $(T - T_c)/T_c \approx 10^{-6}$ where the correlation length is on the order of 10^{-6} m. For $(T - T_c)/T_c < 10^{-6}$, a plausible, quantitative alternative to Ivanov's speculation is an approximate calculation that predicts the fluctuations become anisotropic with a larger, finite bound in the horizontal plane than in the vertical direction [2]. Which speculation is correct? No definitive experiment has been published.

As a second example, consider a critical point with impurities. Ivanov ignores the phenomenological framework that has been developed during the past 50 years to deal with this situation. He does not discuss the essential distinction between thermodynamic "density" and "field" variables and the assumption that the field variables are linear functions of the physical field variables: temperature, pressure, and chemical potential. Ivanov does not distinguish frozen impurities (typical in solids) from mobile, equilibrating impurities (typical in liquid–vapor systems). Conventional theory and experiments agree that measurements made on a path with a fixed concentration of mobile impurities result in predictable changes ("renormalized") in the asymptotic critical exponents; there is no second crossover at an impurity-dependent temperature to classical behavior [3,4].

Remarkably, this book contains 601 references. However, Ivanov's discussion of these references appears to be driven by his conclusion. For example, Ivanov discusses at length the failed attempt by Straub's group to measure the heat capacity of SF_6 in microgravity (the "D1 mission"). However, he does not discuss Straub's follow-up measurements during the D2 mission [5,6]. Between the D1 and the D2 missions, the experimenters greatly improved their understanding of the thermal equilibration of their macroscopic near-critical fluid sample. Using the improved understanding, Straub adopted a temperature-vs-time profile that resulted in heat-capacity data taken in microgravity that are consistent with the accepted divergence of the heat capacity and provide no evidence of a second crossover.

Similar selectivity occurs when Ivanov discusses equation-of-state measurements. He highlights data from Wagner's group as evidence of a second crossover to classical behavior [7]. Wagner's group measured height-averaged pressure differences between 1 cm tall sulfur hexafluoride (SF_6) samples near T_c. A proper analysis of these data would require a very tedious accounting for the “primitive” gravitational effect. The accounting requires a calculation of the response of the vertical pressure transducers to gravitationally stratified samples. The pressure calculated from a suitable scaling equation of state must be integrated over the height of the transducers. The integral must be weighted by the position-dependent, non-vanishing compliance of the transducers. Neither Wagner’s group nor Ivanov published such an analysis. (Indeed, Ivanov’s book contains neither a scaling equation of state nor definitions of the parametric variables that are usually used to write scaling equations of state.) Instead, Ivanov (and Wagner) simply assert that the data support a second crossover to classical critical behavior. In doing this, they either reject or ignore evidence that contradicts their assertion. The ignored evidence includes optical measurements of the densities of the coexisting phases and optical measurements of the fluid density as a function of height that are consistent with Ising-like behavior for the same fluid (SF_6) in the same temperature regime [8,9]. Futhermore, they ignore Ising-like behavior demonstrated by measurements of the heat capacity, quasi-elastic light scattering, and the speed-of-sound in stirred near-critical samples [10–12]. (Stirring reduces the density stratification by replacing an isothermal density-vs-height profile with an adiabatic density-vs-height profile.)

To summarize, Ivanov’s book ignores much of what has been learned about critical phenomena during the past 50 years, including the accepted phenomenology, many thoughtful experiments, and calculations based on well-defined models; therefore, this book is not an up-to-date review of the field. An up-to-date review of the Ising-like behavior of near-critical fluids can be found in [13].

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