Critical Behavior of Viscosity at the Liquid–Gas Critical Point of Xe

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A brief survey is given of the theoretical calculation of the critical behavior of the shear viscosity at the liquid-gas critical point, as well as experimental attempts to measure the critical exponent.

1 Introduction

With regards to the subject of the title, the definition of shear viscosity seems a good place to start. Loosely, shear viscosity is the propensity of a system to sustain disturbances in transverse momentum ("shear"). Assuming isotropy and a classical system, it may calculate via the Kubo–Green relation[4], e.g.,

$$\eta = \frac{1}{k_B T V} \int_0^\infty \langle T_{xy}(t) T_{xy}(0) \rangle \, \mathrm{d}t. \tag{1}$$

In this equation η is the shear viscosity, k_B is the Boltzmann constant, T is the temperature, V is the system volume, T_{xy} is the flux density through areas normal to $\hat{x}$ of momentum pointing in direction $\hat{y}$ at a given time, and $\langle - \rangle$ denotes an ensemble average.

Along the critical isochore and near the liquid-gas critical point of a fluid, the shear viscosity exhibits power law behavior[2]

$$\eta \propto \xi^{z_\eta} \tag{2}$$

where ξ is the correlation length, which itself diverges as $t^{-\nu}$.

The critical behavior of viscosity and other transport coefficients is less straightforward than their thermodynamic counterparts, but the phenomenon is no less important. According to Das and Bhattacharjee (2003)[3], critical exponents come in two kinds: "large exponents", i.e., exponents that are of order unity; and "small exponents", quantities of fractional order. The latter kind provide opportunities for more sensitive tests of the theory of critical phenomena. In critical dynamics, the shear viscosity exponent z_η falls into the latter class. This is accordingly why the critical behavior of the shear viscosity at the liquid-gas critical point has received both theoretical and experimental attention well into the 21st century and decades past their heyday.

Viscosity at a liquid-gas transition might seem an overly tame topic for a term paper for a subject whose central theme is so (I regret the pun) universal. A great number of journal articles, both theoretical and experimental, claim critical or "fat-tailed" behaviour in a multitude of unsual and exotic systems. However, when searching for a suitable topic, I found that a large number of theoretical papers lacked the data to justify the conclusions; conversely, a large number of experimental papers lacked the phenomenology to gird their claims. I thus elected to focus on a more traditional condensed matter system. I like transport phenomena, so I wanted to study a transport coefficient, but I was tired of studying electron transport, so I went with a classical liquid–gas transition and viscosity instead.

In spite of the amenability to contemporary theoretical and experimental techniques, however, it appears that the study of this particular phenomenon has reached a mature phase, or at the very least research is stalled. On the theoretical side, one paper[6] appears to have estimated the contributions to z_η from all higher orders in the loop expansion. I couldn't find any information on the supposed successor experiment to the one I described, which was supposed to have been analysed circa 2008, according to a 2007 review article concerning critical phenomena in microgravity[1]. Use of a search engine quickly clears up the matter, and, as it turns out, the reason is dramatically macabre: CVX-2 was performed aboard the final mission of the space shuttle *Columbia*. The data was recovered from the debris[1] in 2008, but judging from a search on *arXiv* for a follow-through with this data, it does not appear to have been touched since.

That absence of recent progress aside, I will summarize field-theoretic renormalization group approach to calculating the critical behavior of the shear viscosity. I will explain the demand for an experiment in microgravity, and detail the setup of the one experiment of this kind, CVX-1. I will compare the theoretical and experimental values for z_η, and speculate as to the underlying reasons for the discrepancy.

2 Theory

The first order of business is to characterise the problem. The liquid-gas critical point falls into the $O(1)$ universality class of "Model H"[7], one of several heavily studied dynamic analogues to the static $O(1)$ ϕ^4 theory[8]. At the current time there appears to exist a well-understood theoretical prediction for z_η, accurate to 2 significant figures and estimating the effects of fluctuations to all orders in the loop expansion[6]. This value is

$$z_\eta = 0.0679(7). \tag{3}$$

The paper in which this value appears[6] briefly recounts the history of this value, starting from the first raw estimates from nearly four decades ago and demonstrating the various corrections that must be added to yield a reasonable value. My discussion starts with an earlier paper[3].

[1]See, for instance, http://www.foxnews.com/story/0,2933,354799,00.html

The authors start with Langevin equations for the time evolution of the coarse-grained order parameter and velocity. These equations are stochastic nonlinear equations that depend on the Onsager coefficient Γ and the shear velocity η. Propagation of the order parameter is determined by the susceptibility $\chi = (k^2 + \kappa^2)^{-1}$, whose static part diverges as $\kappa \to 0$. These Langevin equations can be solved self-consistently in terms of the noise term. Doing so amounts to a loop expansion of the coefficients Γ and η in terms of Wyld diagrams (see Figure). Γ and η are assumed to have scaling behavior in k as $\kappa \to 0$. Appling this hypothesis to the expressions for Γ and η, expanding in small powers of z_η, and keeping terms up to fixed loop order amounts to a self-consistent solution for z_η. The leading and next-to-leading order expressions for z_η are

$$z_\eta^{(1)} = \frac{8}{15\pi^2} \approx 0.0540 \tag{4a}$$

$$z_\eta^{(2)} = \frac{8}{15\pi^2}\left(1 + \frac{8}{3\pi^2}\right) \approx 0.0685. \tag{4b}$$

The authors argue that, because of the small z_η expansion, the contributions from higher-loop terms are suppressed by a factor of z_η for each additional order.

The sequel to this paper[6] evaluates the Wyld diagrammatic method to three-loop order, introduces self-interactions of the order parameter, and then compares the result with the ϵ-expansion method (about $d = 4$). As it turns out, the ϵ expansion leads to gross overestimation of z_η, leading to a result $\tilde{z}_\eta \approx 0.071$. The authors extrapolate the 1-, 2, and 3-loop results using an "enhancement factor" to lead to the final result described above.

3 Experiment

Because the critical exponent for the viscosity z_η that is expected for a real liquid is so small, it is very difficult measure in a pure fluid. Far from the critical point, not much is known about the deviation from critical behavior, and the analytic background dominates the signal[2]. Close the the critical point, the effects of gravity become important[1]. The latter flaw is more serious. In a fluid at hydrostatic equilibrium in a a gravitational field, a pressure gradient develops[1]:

$$\frac{\mathrm{d}P}{\mathrm{d}z} = -\rho g \tag{5}$$

where P is the pressure gradient, ρ is the mass density of the fluid, and $g(z)$ is the gravitational accleration. Therefore, a sample subject to gravity does not have uniform pressure throughout, but instead has some "rounding" in the pressure proportional to its height.

This problem is magnified further near the critical point. Near the critical point, theisothermal compressibility of a fluid (essentially the susceptibility) diverges as t^{γ}. This means that it becomes much more difficult to maintain an isochoric approach to the critical point. In addition to this, the candidate for the measurement of the critical exponent, xenon, has a high compressibility to begin with[2].

There are several potential solutions to this problem. First, one might make a smaller viscometer. However, even the use of a high-Q oscillator only 0.7 mm in size leads to a minimum t of 3×10^{-5}. One might also choose to use a smaller sample, but then the critical region becomes limited by finite-size effects. In absence of finite-size effects, it has been shown that the lower limit of the critical region may be estimated by[1]

$$t_{\min} = \left(\frac{mgh}{2k_B T_c} \right)^{(\beta\delta)^{-1}} . \tag{6}$$

Here h is the height of the sample and m is the mass of a single particle. A similar figure of merit is the length scale associated with gravity near the critical point[1]:

$$H_0 = \frac{P_c}{\rho_c g}. \tag{7}$$

For Xe at the Earth's surface, $H_0 = 0.525$ mm < 0.7 mm[1], and other candidates have similar values for H_0. Thus, there is little choice but to perform experiments in conditions with much smaller gravitational acceleration.

These and other considerations were addressed in the "Critical Viscosity of Xenon" (CVX) experiment[1, 2]. CVX was performed on Space Shuttle mission STS-85 in 1997. Through technological innovation and the use of microgravity, CVX was able to increase the extent of the critical region by two decades, to $t_{\min} \simeq 10^{-7}$.

I now briefly describe the experimental setup, as detailed in the 1999 paper on CVX[2]. Basically, the experiment consisted of a viscometer made of a nickel screen—a torsion oscillator—driven by ac electric fields while immersed in xenon near the liquid-gas critical point, held at constant temperature via a sensitive thermostat. The viscosity was found by measuring the the response of the oscillator to the applied electric field, given knowledge of its Q-factor and resonant frequency.

An accurate measurement of the critical behavior of the viscosity required sensitive control of the thermodynamic parameters of the system to avoid inhomogeneities and deviations from criticality that might have spoiled measurements. The density ρ was controlled by filling and sealing the tank with xenon at a temperature just below T_c. The average density inferred from this process was $\rho/\rho_c = 0.9985(17)$. In the most sensitive region, the corresponding relative shift in viscosity was approximately 10^{-3}. The homogeneity of the temperature of the sample was maintained using a very sensitive thermostat, one capable of acheiving homogeneity to a threshold of less than 0.2 μK.

The limiting element to critical behavior was not the thermostat, but viscoelasticity (as described in a review article on microgravity[1]; see figure). The liquid-gas critical point is characterised by a divergent timescale $\tau \propto \xi^z$, where $z = z_\eta + 3$ is the dynamical critical exponent. When this timescale becomes comparable to the period of the oscillations, there is a change from the $\omega = 0$-type viscous behavior to the strongly ω-dependent viscoelastic behavior: the fluid "remembers" previous oscillations and is able to stretch. As a result of this behavior, the function used to model the data required a viscoelastic contribution[2].

Altogether, about two decades of reliable data were taken (see figure), leading to the experimental value for z_η:

$$z_\eta = 0.0690(6). \tag{8}$$

4 Discussion

To the precision available, the theoretical and experimental values are consistent. If the CVX-2 data were analysed, it might be the case that a more precise theoretical calculation would be called for. In lieu of this, other measurements of viscosity have taken place, e.g., of the frequency-dependent bulk viscosity[5], which require further theoretical analysis.

References

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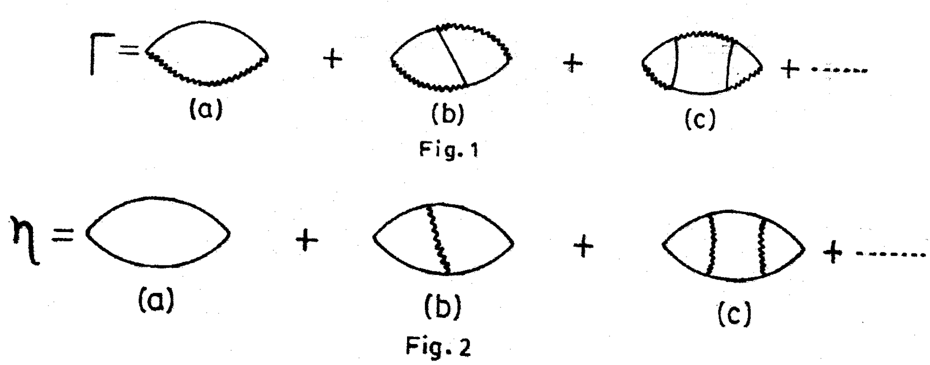

Figure 1: First few terms in the Wyld diagrammatic expansions of Γ and η[3]. The straight lines are order parameter fluctuations and the wavy lines are velocity fluctuations.

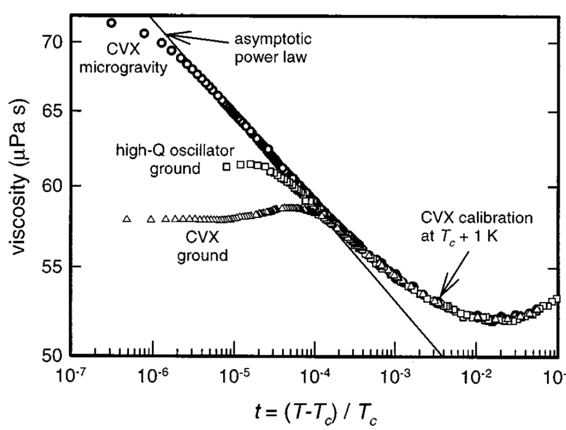

Figure 2: η v. t: static limit, along the critical isochore. The deviation from power law behavior near the critical point is becuase of viscoelastic effects.

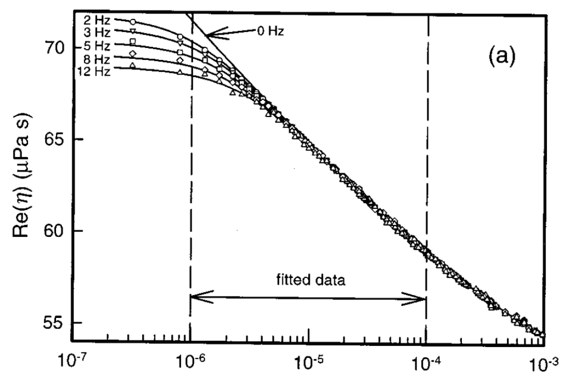

Figure 3: η v. t for several frequencies. Two decaades of data in the scaling region were taken.