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Critical Transport Properties of Fluids

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An analysis of earlier data on the shear viscosity of pure and binary fluids leads to the expected universal description of the critical transport properties.

It is customary to assume that any physical property F ($F > 0$) of a system near a critical point can be written as the sum of a critical part F^{crit} due to the critical behavior of the system and a regular part F^{reg} present in the absence of criticality.[1] Thus F^{reg} is a positive analytic function of both the temperature T and the other parameter N. This assumption has been used to explain dynamic properties of critical systems such as the thermal conductivity[1] and diffusivity[2] of pure fluids and the shear viscosity of both pure and binary fluids.[3,4] However, this partition does not always give a convincing description of these properties.[4,5] In particular the critical viscosity η^{crit} cannot scale as do the other critical properties.[4] The purpose of this Letter is to show how this apparent difficulty can be solved in agreement with the current theoretical expectations.

First, renormalization-group theory predicts that any anomalous kinetic coefficient $K(T, N)$ can be approximated in the form[6,7]

$$K = K_0 t^{-y_K}\Big[f_0(x) + \sum_{i=1} K_i t^{\omega_i} f_i(x)\Big] + K_B, \tag{1}$$

where the exponents y_K and ω_i are universal. The leading amplitude K_0, the amplitudes K_i of the nonanalytic corrections, and K_B the background part of K are analytic functions of T and N. $f_i(x)$ (with $i = 0, 1\ldots.$) are functions of the scaling parameter $x = t^{\beta}/|n|$, where $t = (T - T_c)/T_c$, $n = (N - N_c)N_c$, and β is the exponent of the coexistence curve $|n| \simeq B(-t)^{\beta}$. The functions $f_i(x)$ have universal asymptotic behaviors. In particular

$$\lim_{x\to\infty} f_i(x) \equiv 1 \text{ and } \lim_{x\to 0} f_0(x) \propto x^{y_K/\beta}.$$

Secondly, in the particular case for the thermal or mass conductivity Λ of pure or binary fluids and for the shear viscosity η of both systems a recent renormalization-group treatment of the dynamics of critical fluids predicted that[7]

$$y_\Lambda + y_\eta = \gamma - \nu \quad \text{with} \quad y_\eta \simeq 0.04, \tag{2}$$

$$\Lambda_0 \eta_0 = R k_{\mathrm{B}} T_c \chi_0 \xi_0^{-1} \quad \text{with} \quad R \simeq (5\pi)^{-1}, \tag{3}$$

where k_{B} is the Boltzmann's constant, $\chi = \chi_0 t^{-\gamma}$ with $\gamma \simeq 1.24$ is the static susceptibility of the order parameter and $\xi = \xi_0 t^{-\gamma}$ with $\nu \simeq 0.63$ is the correlation length.

Finally it is worth noticing that Ref. 7 can be regarded as a more accurate statement of the mode-coupling theory[8] in which the approximations $\gamma = 2\nu$ and $y_\eta \equiv 0$ were made. Thus $\eta_0 \equiv \eta^{\mathrm{reg}}$ in this theory. Since more precisely $y_\eta \ll y_\Lambda$ it could be expected that $\eta_0 \simeq \eta^{\mathrm{reg}} \gg \eta_B$ in a sizable range of temperatures near T_c,[9] but $\lambda_B \simeq \lambda^{\mathrm{reg}}$. On the other hand, the nonanalytic corrections are also implicit in the mode-coupling theory where they are generated by the regular coefficients.[7]

A careful analysis of the shear viscosity data for critical fluids will provide a crucial test of the above predictions. To this end I have selected the numerical data reported in literature for ethane and xenon,[10] and for the mixtures of isobutyric acid-water,[11,12] 2,6 lutidine-water,[13] and 3-methylpentane-nitroethane.[4,14] I have estimated, following Oxtoby,[15] the temperature ranges R in which the viscosity data are not affected by shear by more than 1% and I have neglected the data which are not in R. R is given in Table I.

I have paid particular attention to the very care-

TABLE I. Experimental and theoretical values for the critical exponent of the viscosity y_η and the corresponding universal parameter y_η' of decoupled-mode theory. R is the temperature range in which viscosity data are not affected by shear by more than 1%.

	R	y_η	y_η'
3-methylpentane–nitroethane	$t \geq 1.4 \times 10^{-5}$ [a]	0.0398 ± 0.0003 [a]	0.0573 ± 0.0005 [a]
	$t \geq 3.0 \times 10^{-5}$ [b]	0.0398 ± 0.0002 [b]	0.0593 ± 0.0006 [b]
	$t \geq 4.0 \times 10^{-5}$ [c]	0.0387 ± 0.0018 [c]	0.0589 ± 0.0031 [c]
Isobutyric acid–water [d]	$t \geq 9.3 \times 10^{-5}$	0.0394 ± 0.0032	0.0629 ± 0.0043
2.6 lutidine–water [e]	$t \geq 9.3 \times 10^{-5}$	0.0390 ± 0.0027	0.0659 ± 0.0041
Xenon [f]	$t \geq 2.4 \times 10^{-4}$	0.0348 ± 0.0066	0.0392 ± 0.0043
Theories			
(assuming $\nu = 0.6 \pm 0.01$)		0.04 [g]	0.0340 ± 0.0006 [h]

[a] Ref. 4, $\gamma = 170\ \mathrm{s}^{-1}$.
[b] Ref. 4, $\gamma = 700\ \mathrm{s}^{-1}$.
[c] Ref. 13.
[d] Ref. 10.
[e] Ref. 12.
[f] Ref. 9.
[g] Ref. 7
[h] Ref. 16.

ful work of Tsai and McIntyre for the mixture of nitroethane and 3-methylpentane.[4] This mixture has an interesting property: The viscosities η_N of nitroethane and η_T of 3-methylpentane have nearly the same temperature dependence. Consequently the regular viscosity η^{reg} of the mixture must be proportional to η_N or η_T. In order to reduce the small difference between the temperature dependences of η_N and η_T I have calculated the quantities $2\eta/(\eta_N+\eta_T)$ and $\eta(\eta_N^{-1}+\eta_T^{-1})/2$ using the values obtained for the shear rate $\sigma = 170\ \mathrm{s}^{-1}$. In Fig. 1, a log-log plot of these two quantities versus temperature shows that each of them is proportional to t^{-y_η} with $y_\eta \simeq 0.040$. The deviations from this power law are always very much smaller than the experimental uncertainties ($\simeq \pm 1.3\%$), even for the farthest point from T_c. Therefore, this simple analysis shows that the leading amplitude η_0 of the viscosity is proportional and approximately equal to the reqular viscosity η^{reg} while the sum of the nonanalytic corrections and of η_B is lower than $10^{-2}\eta_0$. This agrees perfectly with the above theoretical results.

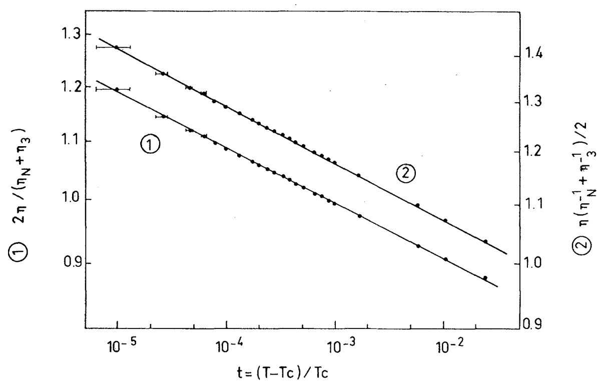

FIG. 1. Reduced viscosities at a 170 s^{-1} shear rate as a function of the reduced temperature $t = (T-T_c)/T_c$ for the critical mixture of 3-methylpentane and nitroethane (see text).

To verify this result and to test its generality I have first fitted expression (1) with $x = 1$ to all the available viscosity data at $N = N_c$. I have used the statistical refining method of Tournarie[16] in which the adjustable parameters are varied together. Therefore the "standard deviations" obtained for a parameter reflects the deviations in the other ones. Furthermore, it also reflects the systematic deviations.[16] As a first result I have found that nonanalytic corrections are not necessary to account for the temperature dependence of the viscosity, except for ethane. Consequently the expression $\eta = \eta_0 t^{-y_\eta} + \eta_B$ with $\eta_0(T, N_c) = \eta_0(T_c, N_c)(1 + \eta_1 t + \eta_2 t^2 + \ldots)$ has been fitted to the data using $y_\eta, \eta_0, \eta_B, \eta_1, \eta_2, \ldots$ as adjustable parameters. Thus we find that y_η, η_0, and η_B are not well defined. This means that either η_B or y_η is a redundant parameter. Assuming first that $\eta_B > 0$ this term remains undetermined but it is always nearly zero (typically $\eta_B \approx 10^{-4}\eta_0$) so that the additional constraint $\eta_B \equiv 0$ does not change the quality[16] of the fits but somewhat reduces the errors. The values of y_η given in Table I have been obtained in this way. On the other hand, with $\eta_B < 0$, y_η, η_0, and η_B are still undetermined but the results ($y_\eta \to 0$ and $\eta_0 \simeq -\eta_B \to \infty$) indicate that the data can be described by $\eta = \eta_0'(1 - y_\eta' \times \ln t)$. Fits to this expression with $\eta_0'(T, N_c)$ expanded in power of t give for y_η' the values listed in Table I.

This statistical analysis shows that both a power-law divergence with $\eta_B \simeq 0$ or a logarithmic divergence can describe the data in the investigated temperature ranges. However, the scatter of y_η' values is greater than for y_η. Furthermore, y_η is found to have nearly the value expected from the theory[7] while y_η' disagrees with the result of decoupled-mode approximation[17]: $y_\eta' = 8\nu/15\pi^2 \simeq 0.034$. Therefore the shear viscosity can be regarded as better described by a power law. For binary solutions this fact has been noticed as early as 1963,[18] assuming an Arrhenius-like behavior for $\eta_0(T, N_c)$.

An important additional point is the comparison of the viscosity data at $N \neq N_c$ with the scaling expression (1). Because of the particular property previously noticed for the 3-methylpentane–nitroethane mixture $\eta_0(T, N)$ can be written as $\eta_0(T, N) = \eta_0(T, N_c)\varphi(N)$, where $\varphi(N)$ is a function of N only. An inspection of the data[19] shows that $\varphi(N)$ can be well approximated by $\varphi^{-1}(N) = (1 - an)(1 - bn)^{-1}$, where a and b are constants.

Figure 2 shows the experimental function $f_0(x)$ which is obtained for $a = 0.39$ and $b = 0.12$, using[20] $\beta = 0.34$ and the results inferred from the data at $N = N_c$: $\eta_0(T_c, N_c) = 0.3381 \pm 0.0006$ cP, $\eta_1 = -2.7 \pm 0.3$, $\eta_2 = -49 \pm 18$, $\eta_3 = 1140 \pm 310$, and $y_\eta = 0.0398$. All the data for[4] $\sigma = 700$ s^{-1} are represented even for pure 3-methylpentane and nitroethane. Of course, I obtain quite similar results for the data at $\sigma = 170$ s^{-1}. For sake of clarity, they are not shown in Fig. 2.

As quoted in Ref. 4 the average error of a sample viscosity measurement is within ± 0.005 cP. This corresponds to relative errors varying from ± 1% to ± 2%. Although these errors are certainly greater for measurements on the many different samples they are consistent with the scatter of data points in Fig. 2. Furthermore, the parameters a and b have not been adjusted to give minimum scatter.

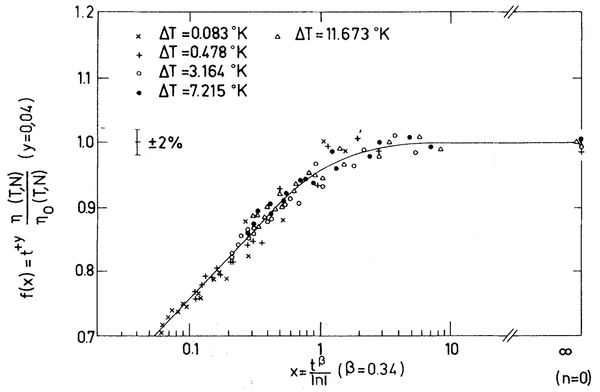

FIG. 2. Scaled reduced viscosity $f(x) = t^{y_\eta}\,\eta(T, N)/\eta_0(T, N)$ as a function of the scaling parameter $x = t^\beta/|n|$, for the mixture of 3-methylpentane and nitroethane.

Therefore, well within the experimental errors $f_0(x)$ is a single-valued function of $x = t^\beta/|n|$ which has the expected properties:

$$\lim_{x\to\infty} f_0(x) = 1 \quad \text{and} \quad \lim_{x\to 0} f_0(x) \propto x^{y_\eta/\beta}$$

with $0.109 \leq y_\eta/\beta \leq 0.121$, in good agreement with the value 0.117 ± 0.004 obtained using $\beta = 0.34 \pm 0.01$ and $y_\eta \simeq 0.04$.

These results are not uniquely related to this particular mixture. In the same way I obtain quite similar results for the other systems. Nonanalytic corrections can be estimated for ethane for which a single term, $t^{\omega_1} f_1(x)$ with $\omega_1 = 0.5 \pm 0.1$, is a good approximation. Within the experimental errors each function $f_0(x)$ has the same form but is shifted by different amounts along the x axis. If we use $Bt^\beta/|n|$ as the scaling parameter I obtain for $f_0(x)$ an universal function which describes the viscosities of all the studied critical systems.

Finally it is interesting to test relations (2) and (3). For binary solutions there is no measurements of the mass conductivity so that Eqs. (2) and (3) cannot be directly tested. However, the mass diffusivity $D_M = \Lambda/\chi$ is found to behave as t^{y_D} with $0.66 \lesssim y_D \lesssim 0.68$,[3] in good agreement with the value $y_D = \nu + y_\eta \simeq 0.67$ deduced from (2). On the other hand, the "Kawasaki-Stokes" result[8] $D_M = Rk_B T/\eta\xi$ with $R = (6\pi)^{-1}$ has been already shown to agree with experiment[21] but $R \simeq (5\pi)^{-1}$ is probably also consistent with the data because of the experimental errors, mainly in ξ.

On the contrary, for pure fluids the exponents describing the thermal diffusivity is found to have apparent values ranging from 0.73 to 0.78,[3,5] but in this case corrections to the leading behavior cannot be neglected.[2] On the other hand, near the critical point, viscosity and thermal conductivity data are not available together, except for carbon dioxide. However, the data[22,23] do not allow the interesting parameters to be obtained with a sufficient accuracy. Therefore I assume that $\eta \simeq \eta_0(T_c, N_c)t^{-y_\eta}$ with $y_\eta = 0.04$ for the value $\eta = 345.9$ μP at $t = 1.15 \times 10^{-3}$.[23] This gives $\eta_0(T_c, N_c) \simeq 265$ μP. Furthermore, according to the scaling law (2) we assume that $y_\Lambda = 0.57$ and fit expression (1), with $\Lambda_i = 0$ as a first approximation, to the data corresponding to the two nearer critical isotherms.[22] Thus I obtain $\Lambda_0(T_c, N_c) = 0.0904 \pm 0.0008$ and $\Lambda_B = 1.04 \pm 0.03$ [$1 + (0.9$

$\pm 0.3)t]$ in units of 10^{-4} cal/cm s K. With these results and the values quoted in Ref. 2 for the other quantities, expression (3) leads to $R \simeq (5.1\pi)^{-1}$, in agreement with the theoretical value. Furthermore, the result for Λ_B is very near the value $\Lambda^{\text{reg}}(T,N_c) = 1.042(1+0.58t)10^{-4}$ cal/cm s K inferred from the Sengers-Keyes *Ansatz*.[1,3]

To conclude, this analysis solves the main remaining difficulties concerning the interpretation of experimental data for the critical-transport properties of fluids, in particular for shear viscosity. It also shows that, at least for pure fluids, the nonanalytic corrections expected from theory cannot be always neglected.

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Relaxing Specific Heat in the Superionic Conductor $RbAg_4I_5$

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An analysis is presented of data on sound absorption, specific heat, and ionic conductivity that demonstrates the existence, in the superionic conductor $RbAg_4I_5$, of internal degrees of freedom associated with the diffusing silver ions which may be characterized thermodynamically by a relaxing specific heat. It is pointed out that this simple analysis should provide useful information on ionic diffusive modes in other superionic conductors, particularly in regard to their coupling to lattice modes.

In the past few years, the class of solid electrolytes known as *superionic conductors* has attracted a great deal of interest.[1] What distinguishes superionic conductors from ordinary solid electrolytes is the fact that whereas the latter exhibit ionic conductivities of the order of $10^{-6}/\Omega\cdot$cm or less, superionic conductors have ionic conductivities comparable to those typical of liquid electrolytes ($0.5/\Omega\cdot$cm). This property makes superionic conductors likely candidates for potential use in solid-state batteries. One of the most thoroughly studied superionic conductors is $RbAg_4I_5$ (rubidium tetrasilver pentaiodide), which at 20°C has an ionic conductivity of $0.21/\Omega\cdot$cm,[2] the charge carriers being the silver ions.[3] Experimental work has also yielded information on its (cubic) crystallographic structure,[4] specific heat,[5,6] diffusion coefficient[7] and Hall effect[8] of the silver ions, elastic constants,[9] thermal expansion coefficient,[9] ultrasonic attenuation (15–45 MHz)[9,10] and optical birefringence.[11] In the present Letter, the simultaneous analysis of data on ultrasound