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Experimental determinations of universal amplitude combination for binary fluids. II. Dynamics

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We have considered for binary fluids the universal dynamic amplitude ratio R which connects the typical frequency Γ of the order-parameter fluctuations to the viscosity $\bar{\eta}$ and to the correlation length ξ. We have analyzed the mode-coupling (MC) approach and the renormalization-group (RG) theory. The mode-coupling approach accounts for background terms in both $\bar{\eta}$ and Γ, whereas RG includes corrections to scaling in the transport coefficients with an effective exponent $\bar{\Delta}\simeq 0.7$. We emphasize that the two approaches are similar in formulation, the correction terms from MC showing a leading exponent $\nu=0.63$, close to $\bar{\Delta}$. The correction amplitudes a_Γ (linewidth) and $a_{\bar{\eta}}$ (viscosity) are essentially positive in the MC approach. Moreover, we claim that their ratio should be universal if we assume the Bhattacharjee-Ferrell crossover viscosity function: $a_{\bar{\eta}}/a_\Gamma=2x_{\bar{\eta}}$, with $x_{\bar{\eta}}\simeq 0.06$, the critical viscosity exponent. We also define an amplitude factor $\tilde{R}(q,t)$, the asymptotic value of which is R. It allows the corrections to scaling, in the framework of the RG theory, to be taken into account. New viscosity measurements have been made with the isobutyric acid-water (I-W) and triethylamine-water (T-W) systems. New Rayleigh linewidth measurements have been performed in the T-W mixture. Analyses of the viscosity data in I-W, T-W, nitrobenzene-n-hexane (N-H), nitroethane-3-methylpentane (N-M), and chlorex-n-dodecane (C-D) systems have led us to introduce correction terms for the I-W and T-W systems, with an experimental exponent $\simeq 0.7$. I-W corrections have been found negative. The linewidth data, analyzed in the N-H, I-W, C-D, N-M, and T-W systems, show that corrections are present in $\tilde{R}$ for the N-M and T-W mixtures, with exponent ~ 0.7. T-W corrections have been found to be negative, when using negative statics corrections. Finally, the asymptotic values of R were found in the range 1.00—1.14, with a mean uncertainty of 7%. They are in agreement with both the recent MC (1.027) and RG (1.038) expectations.

I. INTRODUCTION

Universal combinations among the amplitudes of the statics properties (order parameter, susceptibility, correlation length, specific heat, etc.) have already been investigated[1] for binary fluids. These are indeed good representatives of the class of fluids, characterized by the space dimensionality $d=3$ and the $n=1$ component of the order parameter, like the three-dimensional Ising model. Some mixtures have been seen to exhibit corrections to scaling in their static properties, which obviously had to be considered in the interpretation of the data.[2] We now consider in this work the dynamic properties of binary fluids, especially the ratio R which connects the decay rate of the order-parameter fluctuations (or the linewidth Γ of the Rayleigh spectrum) to the shear viscosity $\bar{\eta}$ and to the correlation length ξ: $R\propto\Gamma\bar{\eta}\xi$.

The experimental situation is somewhat puzzling considering the determination of R, as is the theoretical situation also. For the latter, two approaches have been used: the mode-coupling (MC) and the renormalization-group (RG) theories. The object of this work is to introduce and compare the two theories, to report linewidth and viscosity experiments on the nitrobenzene-n-hexane (N-H), isobutyric acid-water (I-W), and triethylamine-water (T-W) systems and to analyze in the framework of RG and MC theories these data as well as others already published, i.e., the nitroethane-3-Methylpentane (N-M) and chlorex-n-dodecane (C-D) mixtures. We will see that beyond the determination of R, corrections-to-scaling terms had to be considered to account for viscosity and linewidth data, as we have already emphasized in Ref. 3.

II. THEORETICAL

The critical dynamics of binary mixtures is well described by the so-called model $\mathscr{H}$ of Halperin and Hohenberg.[4] The relevant relaxing modes are the order parameter ψ (the relative concentration $c-c_c$ in binary fluids, where c is concentration and c_c is the critical concentration) and the transverse part of the local velocity, whose Onsager coefficients are, respectively, the mass conductivity Λ and the shear viscosity $\bar{\eta}$.

The MC theory assumes a Gaussian form of the static

Landau functional in order to solve the Langevin equations of model $\mathscr{H}$ and neglects the proper Feynman diagrams of perturbative expansion, as has often been done.[5] Moreover, the MC expansion is an uncontrolled approximation in three dimensions.

On the other hand, the RG approach takes into account the dissipative quartic term in the Landau functional and is able to expand in terms of the *small* parameter $\epsilon = d_c - d$.[4,6] Here d_c is the critical dimension above which the conventional Van Hove theory, neglecting the critical fluctuations, is valid ($d_c = 4$ in binary mixture dynamics). The MC approach leads to results in good agreement with those of the RG approach in computing the universal exponents and the scaling functions[4] because of the weak viscosity divergence.

A. The mode-coupling approach

In the transport coefficient (σ), the MC approach separates an anomalous part $\Delta\sigma_c$ determined by the long-wavelength critical fluctuations from a regular background σ_B. A simple additive law is assumed:

$$\sigma = \sigma_B + \Delta\sigma_C \ , \tag{1}$$

$$\Delta\sigma_C = \sigma_0 \xi^{x_\sigma} \ . \tag{2}$$

Here $\xi = \xi_0 t^{-\nu}$ is the correlation length, with ν the universal exponent;[7] $t = (T - T_c)/T_c$ is the reduced temperature, with $T = T_c$ the critical temperature. x_σ is a universal exponent, and σ_0 and ξ_0 are nonuniversal amplitudes. In the critical limit, $\xi \to \infty$, and the background becomes negligible. Then it is possible to identify the kinetic coefficient σ with its critical part $\Delta\sigma_c$. However, the background can be relatively important for temperatures far enough from the critical temperature, where ξ is not much larger than the intermolecular length scale.

Let us consider the local coefficients $\tilde{\sigma}(\vec{r})$ and their Fourier transforms:

$$\sigma(\vec{q}) = \int_{-\infty}^{\infty} d^d r \, e^{-i\vec{q}\cdot\vec{r}} \tilde{\sigma}(\vec{r}) \ . \tag{3}$$

Then one has to solve iteratively two coupled integrals for the viscosity $\Delta\bar{\eta}_c(q)$ and the conductivity $\Delta\Lambda_c(q)$ obtained from the equations of motion (see Sec. II A 1 below). Kawasaki[8] was able to give remarkable results assuming a constant viscosity, i.e., $\bar{\eta} = \bar{\eta}_B$. We will discuss the Kawasaki results, and will see that a clearer justification in the framework of the dynamic RG theory can be found. However, let us first briefly review the MC analysis for the viscosity and the Rayleigh linewidth.

1. The Kawasaki results

The characteristic frequency of the order-parameter fluctuations is measured by the linewidth Γ of the Rayleigh spectrum. In a Lorentzian approximation, Γ is defined from the linearized Fick equation of the concentration diffusion as

$$\Gamma(\vec{q}) = \frac{\Lambda(\vec{q})}{\chi(\vec{q})} q^2 = D(\vec{q}) q^2 \ , \tag{4}$$

where χ is the order-parameter static susceptibility, $\chi \propto \xi^{2-\eta}$ (η is the usual Fisher exponent[7]). In the full critical limit ($\vec{q} \to \vec{0}$, $\xi \to \infty$) an exact relation, known as the Kawasaki-Stokes relation, exists:[4,8]

$$D = R \frac{k_B T_c}{6\pi\bar{\eta}\xi} \ . \tag{5}$$

Here k_B is the Boltzmann constant and R is a universal amplitude ratio. If we assume $R = 1$, the relation (5) provides the same diffusion coefficient D as for a solid sphere of radius ξ moving in a fluid of viscosity $\bar{\eta}$. The correlation volumes move as Brownian particles in the medium.

We should also note that (4) is equivalent to the relation among the exponents[9]

$$2 - \eta - x_\Lambda = 1 + x_{\bar{\eta}} \ . \tag{6}$$

The two coupled integrals to solve in MC theory are

$$\bar{\eta}(\vec{q}) = \bar{\eta}_B(\vec{q}) + \frac{k_B T}{2(d-1)q^2} \times \int_{-\infty}^{\infty} \frac{d^d k}{(2\pi)^d} \frac{\chi_{\vec{q}-\vec{k}} \chi_{\vec{k}} \left[\frac{1}{\chi_{\vec{k}}} - \frac{1}{\chi_{\vec{q}-\vec{k}}} \right]}{D(\vec{k})k^2 + (\vec{q}-\vec{k})^2 D(\vec{q}-\vec{k})} \ , \tag{7a}$$

$$D(q) = D_B(q) + k_B T \int_{-\infty}^{+\infty} \frac{d^d k}{(2\pi)^d} \frac{\chi_{\vec{q}-\vec{k}}}{\chi_{\vec{k}}} \times \frac{1}{\bar{\eta}(q)k^2 + (\vec{q}-\vec{k})^2 D(\vec{q}-\vec{k})} \ . \tag{7b}$$

We have to assume as a first approximation

$$\bar{\eta}(q) \simeq \Delta\bar{\eta}_c(q) = A_{\bar{\eta}} q^{x_{\bar{\eta}}}$$

and

$$D(q) \simeq \Delta D_c(q) = A_D q^{\bar{z}}$$

with $\bar{z} = 2 - \eta - x_\Lambda$ as trivial from relation (4). The first attempt to compute the integrals in (7) was made by Kawasaki,[8] who assumed a constant viscosity ($x_{\bar{\eta}} = 0$) and the Ornstein-Zernicke form ($\eta = 0$) for the susceptibility, i.e., $\chi_{\vec{q}} = \chi_0 \xi^2 X(q\xi)$. With $x = q\xi$, $X(x) = (x^2 + 1)^{-1}$.

Then one obtains, from (7b),

$$\Delta\Gamma_c = \frac{\Delta\Lambda_c}{\chi_q} q^2 = R \frac{k_B T}{6\pi\bar{\eta}\xi} \Omega(q\xi) q^2 \ , \tag{8}$$

where $R \equiv R_K = 1$ and

$$\Omega(x) = \Omega = \tfrac{3}{4} x^{-2} [1 + x^2 + (x^3 - x^{-1}) \tan^{-1}(x)] \ . \tag{9}$$

The Kawasaki assumption is not too arbitrary because of the weak viscosity divergence. It leads to a good representation of the critical dynamics. Using relations (7), Kawasaki and Lo[10] subsequently found a nonclosed form for Ω and a slightly different value of R, $R=1.027$.

On the other hand, Bhattacharjee and Ferrell, as cited in Refs. 11 and 12, proposed the following form for the scaling function Ω:

$$\Omega_B(x)=\Omega_K(p^2x^2+1)^{x_{\bar\eta}/2}C(x) \tag{10}$$

with $p=\frac{1}{2}$ and $C(x)\simeq 1$ a factor taking into account the difference between the Ornstein-Zernicke and the Fisher-Burford susceptibilities. The approximant (10) has the advantage of taking into account the viscosity divergence but it is based only on heuristical considerations (see Appendix A).

2. *Shear viscosity*

It is difficult to evaluate the viscosity integral (7a) which diverges if one tries to insert the first-order Kawasaki linewidth (8). Of course this problem does not occur in the RG perturbative expansion where there are no iterative integrals.

Perl and Ferrell[13(a)] imposed an arbitrary, adjustable, Debye cutoff q_D on the integral (7a), which must be extrapolated *a posteriori* by fitting the experimental data. Then it was possible to compute the critical exponent $x_{\bar\eta}$:

$$\begin{gathered}\frac{\Delta\bar\eta_c}{\bar\eta_B}=x_{\bar\eta}\ln(Q\xi)\ ,\\ x_{\bar\eta}=\frac{8}{15\pi^2}\simeq 0.054\ .\end{gathered} \tag{11}$$

$Q=q_D$ in this approximation. From (11) it follows that

$$\bar\eta=\bar\eta_B[1+x_{\bar\eta}\ln(Q\xi)]\simeq\bar\eta_B(Q\xi)^{x_{\bar\eta}}\ . \tag{12}$$

Kawasaki and Ohta[13(b)] were also able to give a value for $x_{\bar\eta}$ ($x_{\bar\eta}=0.067$) by mixing MC and ϵ-expansion methods. More recently, Bhattacharjee and Ferrell[13(c)] argued for the "old" value $8/(15\pi^2)$.

Oxtoby and Gelbart[14(a)] reached a remarkable result by considering a background Γ_B in the linewidth due to the conductivity background Λ_B, i.e., $\Lambda=\Delta\Lambda_{\text{cr}}+\Lambda_B$, leading to the relation

$$\Gamma_B=\frac{\Lambda_B}{\chi_q}q^2\ . \tag{13}$$

Then they estimated Q without any cutoff on the integral (7a) and obtained

$$Q_{\text{OG}}=\tfrac{3}{4}C\frac{k_BT}{6\pi\bar\eta\xi_0^2}q^2\left[\frac{\Lambda_B}{\chi_0}\right]^{-1}=\tfrac{3}{4}C\frac{\Lambda_0}{\Lambda_B}\frac{1}{\xi_0}\ , \tag{14a}$$

where $C\simeq 0.9$ and $\Lambda_0/\chi_0=k_BT/6\pi\bar\eta_0\xi_0$. Let us define q_c by the relation $\Lambda_B/\Lambda_0=1/q_c\xi_0$. The estimate (14a) becomes

$$Q=1/q_c\ ,\quad q_c=\tfrac{3}{4}C\frac{1}{Q_{\text{OG}}}\ . \tag{14b}$$

Besides, Bhattacharjee *et al.*[14(b)] and Burstyn *et al.*[14(c)] pointed out that the contribution to the MC integrals (7) from large wave vectors is not negligible. It is therefore necessary to impose a cutoff, supposed to have the same value q_D on the integrals (7a) and (7b). Indeed, the short-wavelength fluctuations are taken into account by the backgrounds.

In our notation their results can be written

$$\begin{gathered}Q^{-1}=\left[\frac{1}{q_c}+\frac{1}{q_D}\right]\ ,\\ \frac{1}{q_c}=\left[\frac{1}{\tilde q_c}-\frac{1}{2q_D}\right]\ ,\quad \frac{1}{\tilde q_C}=\tfrac{3}{4}C\frac{1}{Q_{\text{OG}}}\ ,\end{gathered} \tag{15}$$

which take the form of (14b) in the limit $q_D\to\infty$. The correction (15) to q_c does not seem to be important in binary mixtures owing to the small value of q_D^{-1} [$q_D^{-1}=(0.7\pm 0.1)$ Å as extrapolated in the N-M viscosity[11]] which does not essentially change the interpretation of the linewidth data.[14(b)] Nevertheless, the partition between the background and the critical part is not a trivial problem. While the asymptotic behaviors are well determined [$t\to 0$, $\bar\eta\sim(Q\xi)^{x_{\bar\eta}}$; $t\to\infty$, $\bar\eta\sim\bar\eta_B$], the intermediate region, precisely where the experimental data are available, is not simply represented by an analytic function. Bhattacharjee *et al.*[14(b)] proposed the crossover function $\bar\eta=\bar\eta_Be^{Hx_{\bar\eta}}$. We expanded it in powers of ξ^{-1} (see Appendix B), and found that the viscosity behavior can be described in a large region around T_c by the simple formula

$$\bar\eta=\bar\eta_B(Q\xi)^{x_{\bar\eta}}(1+\tilde a_{\bar\eta}\xi^{-1}+\cdots)\ , \tag{16}$$

with $\tilde a_{\bar\eta}=2x_{\bar\eta}/q_c$.

3. *Linewidth*

The Oxtoby and Gelbart result implies that the linewidth background may be computed using the viscosity critical part $\Delta\bar\eta_c$. We do not consider the problem of determining the regular viscosity, which is not trivial and somewhat arbitrary, as noted above. The relations (14) correspond to the assumption[14(a)]

$$\Gamma=\Delta\Gamma_c[1+\tilde a_\Gamma\xi^{-1+x_\eta}\tilde L^{-1}(q\xi)]\ , \tag{17}$$

where the amplitude $\tilde a_\Gamma$ is

$$\tilde a_\Gamma=\frac{(Q\xi)^{x_{\bar\eta}}}{q_c}\simeq\frac{1}{q_c}\ . \tag{18}$$

In fact (assuming $x_\Lambda=1$ and $x_{\bar\eta}=0$) we have

$$\frac{\Gamma_B}{\Delta\Gamma_c}=\frac{\Lambda_B}{\Lambda_0t^{-\nu}}\frac{\Omega(q\xi)}{(1+q^2\xi^2)}=\frac{1}{q_c\xi}\tilde L^{-1}(q\xi)\ .$$

The scaling function $\tilde L(x)=\Omega(x)/(x^2+1)$ ensures that the background continues to exist up to the critical point but only when $q\xi\gg 1$ (i.e., $q\neq 0$, $T\simeq T_c$). In this limit $\tilde L(x)$ compensates exactly the ξ vanishing power of the ratio $\Gamma_B/\Delta\Gamma_{\text{cr}}$. On the other hand, the value of $\tilde L$ is very close to unity for $q\xi<1$.

We note that the ratio $\tilde a_\Gamma/\tilde a_{\bar\eta}$ should be universal if one admits that the crossover behavior of the viscosity is well described by the function H. Namely, we obtain, from (16) and (18),

$$\frac{\tilde{a}_\eta}{\tilde{a}_\Gamma} = 2x_{\bar{\eta}} \simeq \tfrac{1}{8} \; . \tag{19}$$

B. The renormalization approach

1. Corrections to scaling

The RG approach analyzes both statics and dynamics in a quite similar manner. The corrections to the asymptotic behavior are governed by universal transient exponents ω related to the Wilson functions derivatives whose zeros give the fixed point of RG transformations.[15]

The situation is more complicated in dynamics than in statics because the perturbative expansion involves many parameters depending on the couplings between the slow modes and not just the quartic coefficient g of the Landau functional.

a. Statics. The binary mixtures belong to the universality class of the three-dimensional Ising model. Then the Wegner exponent has the value[7] $\omega_g = 0.78$. In the following we will be interested in the correlation length:

$$\xi = \xi_0 t^{-\nu}[1 + a_\xi t^{\omega\nu} + O(t)] \; . \tag{20}$$

The exponent ν has the value $\nu = 0.630$ according to the RG estimation.[7]

b. Dynamics. From the equations of model $\mathscr{H}$ it is possible to write the parameters of the bare perturbative expansion[15] of the viscosity and of the order-parameter correlation functions as

$$f_0 = \frac{k_B T}{\Lambda_0 \eta_0} \; , \quad w_0 = \frac{\Lambda_0}{\bar{\eta}_0} \; . \tag{21}$$

w_0 is an irrelevant parameter vanishing at the fixed point. It is often neglected since it does not enter in the computation of the asymptotic behavior. However, we have to take it into account in order to analyze the dynamical corrections to scaling. There are, in fact, two transient exponents, ω_f and ω_w, and the transport coefficient σ (e.g., Λ or $\bar{\eta}$) takes the form

$$\begin{aligned}\sigma(q,\xi) = \sigma_0 \xi^{x_\sigma} S_0(x)[1 + a_{f,\sigma} S_f(x) \xi^{-\omega_f} \\ + a_{w,\sigma} S_w(x) \xi^{-\omega_w} + \cdots] \; .\end{aligned} \tag{22}$$

The $S(x)$ are universal scaling functions which have to satisfy the requirements[4]

$$\begin{aligned} &S_0(x) \sim x^{-x_\sigma} \quad \text{as } x \rightarrow \infty \\ &S_{f,w}(x) \sim x^{\omega_{f,w}} \quad \text{as } x \rightarrow \infty \end{aligned} \tag{23}$$

and the normalization condition

$$S(x=0) = 1 \; . \tag{24}$$

Let us note that, as a consequence of (23), the corrections to scaling can be not negligible near the critical point for $x \gg 1$.

2. Dynamical exponents

The fixed point of the scale transformation in the space of the renormalized dimensionless parameters is[6,16,17]

$$\begin{aligned} &w^* = 0 \; , \\ &f^* = \tfrac{24}{19}\epsilon[1 - 0.1\epsilon^2 + O(\epsilon^3)] \; . \end{aligned} \tag{25}$$

Here we use, instead of (21), the more convenient definition $f_0 = K_d g_0^2 / \Lambda_0 \bar{\eta}_0$ where $K_d = 2^{1-d}\pi^{-d/2}/\Gamma(d/2)$ is a suitable factor, $d = 4 - \epsilon$ is the dimension of interest, Γ is the Euler function, and g_0 measures the coupling strength. $g_0 \neq 1$ in units where $k_B T_c = 1$. Then it is possible to compute the critical exponent values from (25):[6,17]

$$x_\Lambda = \tfrac{18}{19}\epsilon[1 - 0.033\epsilon^2 + O(\epsilon^3)] + O(f^{*3}) \simeq 0.916 \; , \tag{26}$$

$$x_{\bar{\eta}} = \tfrac{1}{19}\epsilon[1 + 0.238\epsilon + O(\epsilon^3)] + O(f^{*3}) \simeq 0.065 \; , \tag{27}$$

while the transient exponents are[16,18]

$$\begin{aligned} &\omega_f = \epsilon + 0.121\epsilon^2 + O(\epsilon^3, f^{*3}) \simeq 1.121 \; , \\ &\omega_w = 2 - \tfrac{17}{19}\epsilon + 0.136\epsilon^2 + O(\epsilon^3, f^{*3}) \simeq 1.241 \; . \end{aligned} \tag{28}$$

The values in (25) and (28) are obtained from a second-order ϵ expansion. In principle it is possible to compute all the scaling functions $S_0(x)$ in (22), but up to now only the function $L_0(x)$ for the mass conductivity has been calculated.

The RG theory justifies the scaling assumption for the order-parameter decay rate Γ:[4]

$$\Gamma(q,\xi) \propto q^z \bar{\Omega}(q\xi) \; . \tag{29}$$

$\bar{\Omega}$, as Ω, shows a universal form, z is the characteristic dynamical exponent[4,6]

$$z = 3 + x_{\bar{\eta}} \; . \tag{30}$$

A relation such as (29) is not valid for the decay rate of the two other modes of the transverse velocity: we should speak of "restricted (to the order parameter) scaling" in model $\mathscr{H}$.[4,16]

3. The scaling function Ω

The universal scaling function Ω can be defined from (4) as the ratio of the scaling functions of Λ and X:

$$\Omega(x) = L(x) X^{-1}(x) \tag{31}$$

and Ref. 17 gives the first-order result

$$\Omega \equiv \Omega_P = \left[\frac{\Omega_K(x)}{x^2 + 1} \right]^{x_\Lambda} (x^2 + 1)^{1 - \eta/2} \tag{32}$$

with $x_\Lambda = 0.96$, $\eta = 0$. We will use the value of $x_{\bar{\eta}}$ found in the viscosity fit and the fixed dimensional computation $\eta = 0.0315$ (Ref. 7) [instead of the ϵ-expansion value $\eta = \frac{1}{54}\epsilon^2$ (Ref. 15)] in applying the relation (32) to the analysis of the linewidth data. Then we obtain, using relation (6),

$$\Omega_P = \Omega_K^{1 - x_{\bar{\eta}} - \eta} (x^2 + 1)^{x_{\bar{\eta}} + \eta/2} \; . \tag{33}$$

Relation (33), as well as the Bhattacharjee expression of Eq. (10), satisfies the scaling requirements of Eq. (23):

$$\Omega(x) \sim x^{1 + x_{\bar{\eta}}} \quad \text{as } x \rightarrow \infty \; . \tag{34}$$

4. *The universal amplitude ratio R*

There is some disagreement between different theoretical previsions concerning the value of R defined by (5). Siggia *et al.* found[6]

$$R=6\pi K_d \tfrac{19}{24}\epsilon[1+0.06\epsilon+O(\epsilon^2)]\simeq 0.79\ , \tag{35}$$

setting directly $\epsilon=1$ and $d=3$. This value does not seem believable compared to the experimental results. Perhaps the amplitude ratio and the scaling functions show an ϵ dependence which is stronger than the ϵ dependence of the exponents.

In fact, Ref. 6 does not provide an explicit form for $\Omega(x)$. Another R estimate is obtained in a rather artificial manner, mixing RG and MC calculations at $d=4$:[6]

$$R=1.2R_K+O(\epsilon^3)\simeq 1.2\ . \tag{36}$$

Let us note that (36) corresponds to the Stokes law for a spherical droplet of viscosity $\bar{\eta}$ moving in a medium of the same viscosity. Finally, a fixed dimensional computation has given,[17] to first order:

$$R=6\pi K_d \frac{\pi}{3}\frac{83}{80}+O(f^{*2})\simeq 1.0375\ , \tag{37}$$

and we think that the second-order correction should be less than 8%. Then the most reliable prevision of R lies in the range 1—1.12.

On the other hand, from an experimental point of view, the most important problem to solve is to infer the right asymptotic R value from linewidth measurements carried out in a wide region of temperatures. The results (35) and (37) are inferred with an amplitude ratio R defined as the inverse of the fixed point value f^* of the renormalized parameter f.[4,6,16]

One obtains, with a convenient normalization condition,

$$R=K_d f^{*-1}\ . \tag{38}$$

*Therefore we see that R has the same correction-to-scaling terms as f**, at least to a first-order approximation. In other words, we can treat R just as the other dynamical parameters $\Lambda,\bar{\eta}$. Let us generalize the relation (5) at $q\neq 0$ by defining two scaling functions, $E_0(x)$ for the viscosity $\bar{\eta}$ and $\tilde{R}_0(x)$ for the amplitude ratio R, according to the relation (22):

$$D(q)=\frac{R}{\xi}\tilde{R}_0(q\xi)\frac{k_B T}{\bar{\eta}E_0(q\xi)}\ . \tag{39}$$

Then we can identify, from (8), $\Omega(x)=\tilde{R}_0(x)/E_0(x)$, where $\tilde{R}_0(x)\,|_{x\to\infty}\propto x$ and $\tilde{R}_0(0)=1$ following the boundary conditions (23) and (24).

Now we can consider the correction-to-scaling terms by defining a parameter $\tilde{R}(q\xi)$,

$$\tilde{R}(q\xi)=R\tilde{R}_0(q\xi)[1+a_{R,f}\xi^{-\omega_f}\tilde{R}_f(q\xi)+a_{R,w}\xi^{-\omega_w}\tilde{R}_w(q\xi)+\cdots]\ , \tag{40}$$

where the amplitudes $a_{R,f},a_{R,w}$ and the functions $\tilde{R}_{f,w}$ are defined using the general notations of formula (22).

5. *Shear viscosity*

Considering the corrections-to-scaling terms in (22), the shear viscosity takes the form[19]

$$\bar{\eta}(q,\xi)=\bar{\eta}_0\xi^{x_{\bar{\eta}}}E_0(x)[1+a_{f,\bar{\eta}}E_f(x)\xi^{-\omega_f}+a_{w,\bar{\eta}}E_w(x)\xi^{-\omega_w}+\cdots]\ . \tag{41}$$

It is nearly impossible to distinguish between the values of the transient exponents [see Eq. (28)]. We thus have to define an effective exponent ω_{eff} which should be experimentally determined. Since $q\simeq 0$ in usual shear flow viscosimeters, $x\simeq 0$ and $E(x)\simeq 1$ in (41). Therefore the Eq. (41) becomes, in terms of the reduced temperature t,

$$\bar{\eta}=\bar{\eta}_0 t^{-Y_{\bar{\eta}}}(1+a_{\bar{\eta}}t^{\bar{\Delta}}+\cdots)\ , \tag{42}$$

with $Y_{\bar{\eta}}\equiv x_{\bar{\eta}}\nu$, $\bar{\Delta}\equiv\omega_{\text{eff}}\nu$, and $a_{\bar{\eta}}$ an effective amplitude. It is important to consider the temperature dependence of $\bar{\eta}_0$ because the critical exponent is very small; one usually assumes an Arrhenius behavior, valid far from T_c, or simply a polynomial expansion in power of t:

$$\bar{\eta}_0(T)=\eta_0\exp[E/(1+t)]\ , \tag{43a}$$

$$\bar{\eta}_0(T)=\eta'_0+At+Bt^2+\cdots\ , \tag{43b}$$

as well as for the MC background in (16).

6. *The linewidth*

The considerations concerning the amplitude ratios developed above allow us to modify the Kawasaki-Stokes relation (5) as

$$\Gamma(q,\xi)=R\frac{k_B T}{6\pi\bar{\eta}_0(T)}\xi^{-1+x_{\bar{\eta}}}\frac{\tilde{R}_0(x)}{E_0(x)}\times\left[\frac{1+a_{Rf}\tilde{R}_f(x)\xi^{-\omega_f}+a_{Rw}\tilde{R}_w(x)\xi^{-\omega_w}}{1+a_{\bar{\eta}f}E_f(x)\xi^{-\omega_f}+a_{\bar{\eta}w}E_w(x)\xi^{-\omega_w}}\right]q^2\ . \tag{44}$$

Note that $\Omega\equiv\tilde{R}_0/E_0$.

The scaling functions $\tilde{R}_{f,w},E_{f,w}$ exhibit a value close to unity in the hydrodynamical region $x<1$, precisely where the corrections have some importance. Then we shall apply the same approximation used to obtain the form (42) of the shear viscosity,

$$\Gamma(q,\xi)=R\frac{k_B T}{6\pi\bar{\eta}\xi}\Omega_P(x)(1+a_R t^{\bar{\Delta}})q^2\ , \tag{45}$$

with a_R the effective amplitude of the linewidth corrections to scaling and $\bar{\eta}$ given by (42).

C. Conclusion of the theoretical part

According to the above analysis, we can make the following remarks.

(1) The critical exponent $x_{\bar{\eta}}$ is poorly determined by both MC and RG theories. Indeed $x_{\bar{\eta}}$ is very small (~ 0.06) and it is $2+x_{\bar{\eta}}$ rather than $x_{\bar{\eta}}$ which is effec-

tively computed. We will use the RG value 0.063,[19] close to the MC value calculated by Ohta-Kawasaki.[13(b)] This is slightly different from the Bhattacharjee-Ferrell estimate 0.053.[13(c)]

(2) The values of the amplitude R from the MC and RG approaches agree within some percent; R is expected to lie in the range 1.00—1.12.

(3) The corrections to the asymptotic behaviors are not too large in binary mixtures and in fact they are often neglected in determining the value of the amplitude ratio R and of the exponent $Y_{\overline{\eta}}$. Nevertheless they may contribute up to 10% at $t=10^{-2}$ to the linewidths of some systems.

An attempt to take into account these contributions has been made by subtracting the Oxtoby-Gelbart background related to the critical viscosity.[11,14,20] On the other hand, up to now, there have been no attempts to verify the RG corrections in binary fluids (except our work[3]).

(4) The viscosity and linewidth corrections to scaling, compared to the MC corrections, show a similar temperature dependence [$\nu=0.63$ in (16) and (17), while the first transient exponent is $\omega_f \nu \simeq 0.7$], and the scaling functions $R_{f,w}$ play the same role as $\widetilde{L}$ in (17).

No simple relations exist in RG between the amplitude of the linewidth corrections a_R and the amplitude of the critical viscosity $\overline{\eta}_0$. Then we have to consider a_R and $a_{\overline{\eta}}$ as free parameters. To compute them, one has to integrate the Wilson functions (coupled differential equations) for the renormalized parameters f and w. Thus it is possible to show that $(a_R)_{f,w}$ and $(a_{\overline{\eta}})_{f,w}$ depend on the initial conditions (see, e.g., the analysis made in Refs. 22 and 23 for the ^{4}He thermal conductivity), i.e., depend on both the critical amplitudes $\overline{\eta}_0$ and Λ_0.

(5) The predictions of MC are precise and restrictive: the corrections induced by backgrounds are essentially positive and we have estimated their ratio: $\widetilde{a}_{\overline{\eta}}/\widetilde{a}_{\Gamma}=a_{\overline{\eta}}/a_{\Gamma}=2x_{\overline{\eta}}\simeq\frac{1}{8}$. Here $a_{\Gamma}=\widetilde{a}_{\Gamma}\xi_0^{-1}$ and corresponds to the RG correction a_R.

III. EXPERIMENTAL

This part is devoted to the viscosity and linewidth measurements. The correlation length, which is the third parameter entering in the $\widetilde{R}$ determination, has been already examined in detail in Refs. 1 and 7, together with other static properties.

A. Sample preparation

It is of prime importance to accurately know the critical composition whenever data very close to T_c are needed. Roughly speaking, a deviation $\Delta\phi$ with respect to the critical composition ϕ_c will lead to some deviations for data obtained in the temperature region $\Delta T_0 \simeq T_c(\Delta\phi/B)^{1/\beta}$, where B is the coexistence curve amplitude.

(i) N-H system. Components were of spectroscopic grade and filtered through 0.2-μm Teflon filters. The binary mixture has been thought to exhibit the critical concentration of 0.510 mass fraction of nitrobenzene according to Ref. 24. However, recent experimental determinations and analyses[1,25] have shown that the critical composition was 0.525.

The experimental concentration that we used was 0.509 ± 0.002 for the linewidth measurements, and 0.509 ± 0.007 for the viscosity measurements reported in Ref. 26. Data have been obtained in a temperature range further from T_c than 0.1 K (linewidth) or 0.03 K (viscosity), which is much larger than $\Delta T_0 \simeq 2$ mK, deduced by using $B=0.77$ and $T_c=293$ K.[1,25] Note that the correlation length determination, which needs data much closer to T_c, has been performed in a sample with the critical mass fraction 0.525.[25] All samples were frozen in liquid nitrogen and then sealed under vacuum.

(ii) I-W system. Isobutyric acid was of quality better than 99.5% purity, and the water comes from a sophisticated industrial purification setup, giving an Ohmic resistance of 18 MΩ cm. The experimental mass fraction of the acid was 0.3889 ± 0.005 (linewidth) and 0.3882 ± 0.0003 (viscosity), to be compared with the value 0.3885.[27] Deviations to criticality seem negligible here. The same sample has been used to determine both the linewidth and the correlation length.[1] Due to the presence of water, we could not freeze the sample without breaking the cell; so we sealed all samples at atmospheric pressure and at 0 °C where the vapor pressures of the components are low.

(iii) T-W system. Purity of the triethylamine was better than 99.5%. Water was from the same origin as above. The experimental mass fraction of triethylamine used in the samples was 0.321 ± 0.001 (linewidth) and 0.3211 ± 0.0001 (viscosity). The generally admitted value is 0.321 according to Ref. 28 and our determination of Ref. 2; therefore, the samples that we used did not show appreciable deviations to criticality. As above, the sample used for linewidth measurements is the same as that already used for the correlation length determination.[1,7,29] As explained above, we sealed the samples at 0 °C at atmospheric pressure.

All the cells used in the linewidth measurements were made of fused quartz; they were of cylindrical shape, with an inner radius of 1.0 cm and inner length of 2.000 ± 0.001 cm (N-H) or 5.000 ± 0.0002 cm (I-W, T-W). The viscosimeter was made of Pyrex (see below).

B. Thermal regulation

The cells for the linewidth measurements were placed into a thermally stabilized copper oven, enclosed inside an air regulated box. Over time intervals of some hours, the stability was within ±0.1 mK. The viscosimeter was immersed in a large water bath giving a stability of ±0.5 mK. Temperature was measured with a quartz thermometer that we calibrated with the triple point of water (+0.01 °C).

C. Linewidth measurements

We have applied a conventional light beating spectroscopy method,[30] in a homodyne arrangement. As a light source, we used a He-Ne laser with power up to 80 mW. Particular attention was given to spurious heating by the laser beam near T_c, which was seen to reach in some cases

0.5 mK per mW incident power. Fortunately, it is precisely near T_c that the signal-to-noise ratio is the highest, so that low exciting power can be used.

The scattering angle was nearly equal to 90°, where the spurious contributions from stray light and multiple scattering are minimized. This angle was measured with a goniometer allowing an accuracy of some minutes of angle to be obtained. In fact it was rather the incident beam convergence and the solid angle of collection which contributed to the mean uncertainty of 0.5% to the transfer wave vector q.

The signal was analyzed with a single clipped correlator, whose calibration was checked. The correlation function that we obtained fitted well to a single exponential function whose characteristic time τ could be related of the typical frequency Γ by $\Gamma = 1/2\tau$.

Multiple scattering had negligible effects here, owing to the weak turbidity of the I-W and T-W systems and/or the temperature range of interest (N-H). Gravity effects were negligible since the laser beam was located nearly in the middle of the sample.[31] Moreover, these effects take a very long time to settle close to T_c, and show negligible amplitudes far from T_c.

D. Viscosity measurements

We use a calibrated capillary flow viscosimeter from Allen's group (the same as in Ref. 26). It was filled with the mixture and sealed as indicated above. It was placed on a special rotary mount immersed in a large water bath.

The inner diameter of the capillary was $\phi = 0.02$ cm. With ρ the density, the mean shear rate S can be easily deduced, $g \simeq 10^3$ cm^2/s being the gravitational acceleration: $S = g\phi/16(\bar{\eta}/\rho)$. To prevent deformations of the critical fluctuations by shear (see Ref. 32), leading to a leveling[33] off of the viscosity behavior, we had to consider temperature regions such that the lifetime of fluctuations $\tau \simeq (16\bar{\eta}/k_B T)\xi^3$ is lower than the typical shear time S^{-1}.

The conditions $S\tau < 1$ means that data are considered only in the region $\Delta T_S > \xi^{3/2}(\rho g \phi T_c/k_B)^{1/2}$. Taking ξ_0 from Ref. 1, one finds, for N-H, studied in Ref. 26 with the same viscosimeter,

$$\Delta T_s \simeq 0.03 \text{ K} ,$$

for I-W

$$\Delta T_s \simeq 0.05 \text{ K} ,$$

and for T-W

$$\Delta T_s \simeq 0.01 \text{ K} .$$

In such a viscosimeter, we measured a flow time related to the kinematic viscosity $(\bar{\eta}/\rho)$, and we needed density data to obtain the shear viscosity $\bar{\eta}$. Care had to be taken since ρ exhibits some anomaly near T_c, related to the (weak) divergence of the specific heat. For I-W the density is taken from Refs. 27, 34(a), and 34(b):

$$\rho = 0.9930 - [6.15 \times 10^{-4}(T - T_c)] .$$

For T-W the critical density is deduced from Ref. 35. This system exhibits a relatively large anomaly near T_c. Since refractive index data have been shown[1,36] to behave as the density, we have used the relative data from Ref. 36:

$$\rho_{\text{T-W}} = \rho_c + (\partial\rho/\partial n)(n - n_c) ,$$

where

$$\rho_c = 0.9242 , \quad (\partial\rho/\partial n) = 2.3 ,$$

$$n - n_c = 2.34 \times 10^{-4}(T_c - T) + 16.2 \times 10^{-6}(T_c - T)^2$$
$$- 1.93 \times 10^{-7}(T_c - T)^3 + 6.14 \times 10^{-4}(T_c - T)^{0.89}[1 - 0.278(T_c - T)^{0.491}] .$$

Finally, we checked the viscosimeter calibration with pure water. By varying temperature, it was possible to vary η from $0.6 \times 10^{-2} P_0$ to $1.5 \times 10^{-2} P_0$. Figure 1 shows that the previous calibration given with the viscosimeter did not take into account all the kinetic energy corrections. We have therefore determined another calibration formula, and have consequently recalibrated the data of Ref. 26 obtained in a region where a simple proportionality constant is not sufficient.

E. Determination of T_c

Two striking phenomena are associated with the phase-separation process; the transmission goes practically to zero, and intense speckles appear at low scattering angles. By performing temperature steps of about 0.2 mK (linewidth), or 1 mK (viscosity), it is possible to determine T_c to within the same accuracy.

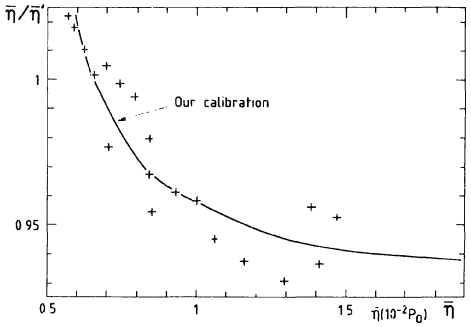

FIG. 1. Calibration of the viscosimeter. The ratio of the viscosity of water $(\bar{\eta})$ to the measured viscosity $(\bar{\eta}')$, using the calibration given with the viscosimeter, is plotted vs $\bar{\eta}$. The curve represents our calibration, which has been used for binary fluids.

IV. RESULTS AND DISCUSSION

Three quantities ξ, $\bar{\eta}$, and Γ enter in the determination of R, and they will be successively analyzed below. Since R is defined only in the critical limit $q \rightarrow 0$, $t \rightarrow 0$, we must extrapolate its asymptotic value according to the scheme developed above, which includes corrections to scaling.

Static corrections (a_ξ) were found only in the mixture T-W. In the other systems we will simply use the correlation length with $a_\xi = 0$, i.e., $\xi = \xi_0 t^{-\nu}$, the theoretical exponent $\nu = 0.630$ being imposed. But before analyzing in detail the results on the five systems N-H, I-W, C-D, N-M, and T-W, we will describe the fitting procedure.

A. Fitting procedure

We have used the Tournarie statistical refining method.[37] Among other qualities, it has the advantage of giving, for each fit, the contribution of the experimental information to the determination of a given parameter. It also enables an estimate to be made of the systematical distortion by means of a statistical quality coefficient Q:

$$Q = 1 - \frac{\sum \frac{\Delta Y_i \Delta Y_{i+1}}{\sigma_i \sigma_{i+1}}}{\left[\sum \frac{\Delta Y_i^2}{\sigma_i^2} \sum \frac{\Delta Y_{i+1}}{\sigma_{i+1}^2} \right]^{1/2}} ,$$

where ΔY_i is the deviation of the data Y_i with respect to the function of fit and σ_i is the corresponding statistical error. We also have an access to the correlation coefficients between the parameters to be determined. The *viscosity data* have been fitted to Eq. (42) as follows:

(i) all parameters free;
(ii) $Y_{\bar{\eta}}$ imposed to 0.04;
(iii) $Y_{\bar{\eta}} = 0.04$ and $\bar{\Delta} = 0.7$ imposed.

The *linewidth data* have been fitted in nearly the same way:

(i) all parameters free, except $\nu = 0.63$ and $Y_{\bar{\eta}} = 0.04$;
(ii) all parameters free, except $\nu = 0.63$, $Y_{\bar{\eta}} = 0.04$, and $\bar{\Delta} = 0.7$.

We used formula (42) as the fitting function for the viscosity, and for the linewidth, formula (45). The t dependence of q has been taken into account, through the coefficient $(1/q)dq/dT = (1/n)dn/dT$, which can be inferred from refractive index data. The weak anomaly of the refractive index near T_c has been accounted only for the T-W system, where it was found to be important.[36]

When determining $\bar{\Delta}$ by the viscosity analysis, we have fixed $Y_{\bar{\eta}}$ to 0.04, the value we considered the most probable. Finally, we have always fixed in the linewidth fitting function (45) $Y_{\bar{\eta}}$ to the same values as those used in the viscosity fit in order to preserve the Γ limiting behavior. We have also made visible the temperature variation of $\tilde{R}$. From formula (45)

$$\tilde{R}(t) = [\Gamma / k_B T \Omega_P(x)] 6\pi \bar{\eta} \xi \ . \tag{46}$$

B. Nitrobenzene and *n*-hexane

The correlation length is taken from Refs. 1 and 25, where it was found to be $\xi_0 = (2.65 \pm 0.07)$ Å.

The *viscosity data*, obtained in the range 10 mK–45 K, using the viscosimeter we described in Sec. III, has been already analyzed in Ref. 26. We have reported in Table I the values corresponding to the new calibration of the viscosimeter. We have reported in Table II the parameter values of the best fit. The exponent $Y_{\bar{\eta}}$ is found to be close to the expected theoretical value, so corrections to scaling are indeed very small in this system. We note the nearly identical result obtained on $Y_{\bar{\eta}}$ assuming for $\eta_0(T)$ either an Arrhenius or a polynomial function.

Linewidth data are reported[25] in the range 0.1–5 K or $q\xi = 1$–0.08; most of the data lie therefore in the hydrodynamic region, leading to a difference between the functions Ω_K and Ω_P lower than 1.5%. $\tilde{R}(t)$, as obtained from (46), has been plotted in Fig. 2 where no clear variations appear, indicating the smallness of corrections to scaling. The results of the fit are given in Table III, and corroborate the absence of corrections. We think that the more reliable result is the first one ($Q = 0.818$). Accounting for the different experimental sources of uncertainties, we obtain

$$R = 1.03 \pm 0.06 \ .$$

These results are not in agreement with others[20] obtained in the same mixture. However, the concentration was not the same, leading to discrepancies in both Γ and ξ_0. Also, the R value is now changed compared to the value one of us reported in Refs. 7, because the ξ_0 value has been changed according to Refs. 1 and 25 (see above Sec. III A). The 4% discrepancy with the analysis made in Ref. 25 is due to the new calibration of the viscosimeter.

C. Isobutyric acid-water

The correlation length amplitude has been determined by two groups[1,38] and leads to the same value $\xi_0 = (3.625 \pm 0.065)$ Å.

The *viscosity data* are reported in Table IV and Fig. 3. They cover the range 0.1–15 K and agree well with the Ref. 34 data. Although the data from Ref. 34 are in

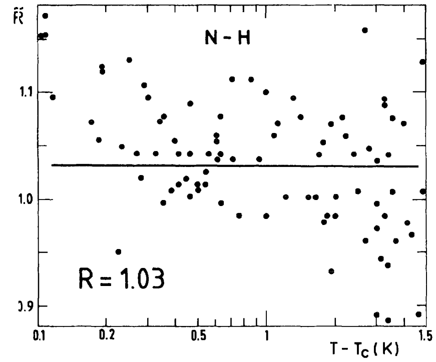

FIG. 2. Temperature variation of $\tilde{R}$ for the N-H system.

TABLE I. Shear viscosity of the N-H system. $T_c = 20.00\,^{\circ}\mathrm{C}$. Shear rate is about 150 sec^{-1}. Typical relative uncertainty is 0.5%.

$L_N\left[\frac{T-T_c}{T_c}\right]$	$\bar{\eta}(10^{-3}P_0)$	$L_N\left[\frac{T-T_c}{T_c}\right]$	$\bar{\eta}(10^{-3}P_0)$	$L_N\left[\frac{T-T_c}{T_c}\right]$	$\bar{\eta}(10^{-3}P_0)$
−1.836	3.667	−5.115	6.130	−6.700	6.657
−2.053	3.953	−5.210	6.246	−6.759	6.677
−2.344	4.348	−5.228	6.187	−6.840	6.698
−2.508	4.514	−5.255	6.179	−6.936	6.758
−2.618	4.657	−5.351	6.236	−6.990	6.718
−2.867	4.883	−5.373	6.261	−7.027	6.718
−2.984	5.003	−5.494	6.274	−7.341	6.839
−3.169	5.138	−5.515	6.270	−7.368	6.839
−3.290	5.269	−5.604	6.303	−7.512	6.859
−3.443	5.361	−5.621	6.350	−7.577	6.879
−3.458	5.350	−5.652	6.278	−7.610	6.920
−3.458	5.322	−5.786	6.343	−7.647	6.904
−3.542	5.386	−5.809	6.400	−7.721	6.920
−3.542	5.386	−5.903	6.416	−7.761	6.952
−3.604	5.449	−5.918	6.425	−7.801	6.940
−3.603	5.429	−5.967	6.434	−7.888	6.992
−3.603	5.429	−6.074	6.466	−7.983	6.980
−3.662	5.471	−6.209	6.478	−7.983	7.013
−3.662	5.471	−6.250	6.535	−8.088	7.049
−3.770	5.594	−6.287	6.519	−8.145	7.101
−3.766	5.555	−6.502	6.616	−8.206	7.061
−3.766	5.555	−6.550	6.600	−8.206	7.101
−3.796	5.576	−6.759	6.677	−8.170	7.061
−3.796	5.596	−6.868	6.685	−8.368	7.161
−3.843	5.598	−6.990	6.750	−8.386	7.141
−3.843	5.598	−7.106	6.738	−8.412	7.154
−3.909	5.601	−7.293	6.839	−8.412	7.129
−3.981	5.682	−7.505	6.879	−8.412	7.162
−4.079	5.716	−5.663	6.331	−8.492	7.202
−4.194	5.800	−5.663	6.331	−8.492	7.161
−4.194	5.761	−5.663	6.307	−8.492	7.141
−4.194	5.828	−5.663	6.318	−8.673	7.181
−4.260	5.803	−5.722	6.331	−8.673	7.162
−4.284	5.799	−5.726	6.331	−8.673	7.154
−4.284	5.799	−5.839	6.400	−8.721	7.262
−4.342	5.857	−5.853	6.372	−8.902	7.275
−4.345	5.872	−5.863	6.372	−8.902	7.262
−4.345	5.852	−5.956	6.413	−9.190	7.323
−4.431	5.934	−5.956	6.413	−9.190	7.323
−4.511	5.928	−5.956	6.393	−9.190	7.283
−4.543	5.917	−5.983	6.394	−9.256	7.371
−4.566	5.878	−5.983	6.413	−9.593	7.444
−4.570	5.878	−6.224	6.543	−9.593	7.484
−4.674	5.980	−6.287	6.515	−9.593	7.484
−4.709	5.968	−6.336	6.535		
−4.740	6.012				
−4.813	6.041				
−4.874	6.062				
−4.938	6.068				
−5.002	6.084				

TABLE II. Fit of the viscosity data to $\bar{\eta}(t)=\bar{\eta}_0(t)t^{-Y_{\bar{\eta}}}(1+a_{\bar{\eta}}t^{\bar{\Delta}})$, where $\bar{\eta}_0(t)$ is either a polynomial function $\bar{\eta}_0(t)=\bar{\eta}'_0+At+Bt^2+Ct^3$ or an Arrhenius function $\bar{\eta}_0(t)=\bar{\eta}_0\exp[E/(1+t)]$. Values in parentheses have been imposed in the fit. Q measures the quality of the fit (see text). PF stands for a polynomial function for $\bar{\eta}_0(t)$, AF denotes an Arrhenius function for $\bar{\eta}_0(t)$.

System		$Y_{\bar{\eta}}$	$a_{\bar{\eta}}$	$\bar{\Delta}$	η_0 ($10^{-4}P_0$)	E	η'_0 ($10^{-3}P_0$)	A ($10^{-3}P_0$)	B ($10^{-3}P_0$)	C ($10^{-3}P_0$)	Q
N-H	PF	0.0397	(0)				5.111	−15.3	41	−78	0.814
		±0.0004					±0.015	±0.6	±10	±47	
	AF	0.0398	(0)		2.696	2.941					0.810
		±0.0003			±0.040	±0.03					
I-W	PF	0.0454	(0)				18.70	−146	925	−31	0.976
		±0.0018					±0.25	±12	±210	±1000	
	AF	0.0484	(0)		27.4	6.50					0.808
		±0.0015			±4.7	±0.18					
		(0.04)	−1.5	0.65	16.9	2.45					0.935
			±4.8	±0.42	±190	±11.2					
		(0.04)	−2.13	(0.7)	72	0.99					0.920
			±0.46		±113	±1.6					
N-M[a]	PF	0.0398[a]	(0)				?	?	?	?	?
		±0.0003[b]									
	AF	0.0399	(0)		2.208	2.76					0.518
		±0.0002			±0.086	±0.04					
T-W	PF	0.0306	(0)				31.51	474	5380	5430	0.468
		±0.0020					±0.52	±30	±970	±9900	
	AF	0.032	(0)		$\begin{bmatrix}0.536\pm\\0.093\end{bmatrix}\times10^{-4}$	15.6					0.785
		±0.001				±0.1					
		(0.04)	1.4	0.75	$\begin{bmatrix}3.57\pm\\0.12\end{bmatrix}\times10^{-4}$	13.6					0.669
			±3	±0.32		±3.1					
		(0.04)	1.45	(0.7)	$\begin{bmatrix}5.79\pm\\3.3\end{bmatrix}\times10^{-4}$	13.1					0.730
			±0.2			±0.5					

[a]Data from Ref. 43, with the calibration of Ref. 11.

[b]From Ref. 19.

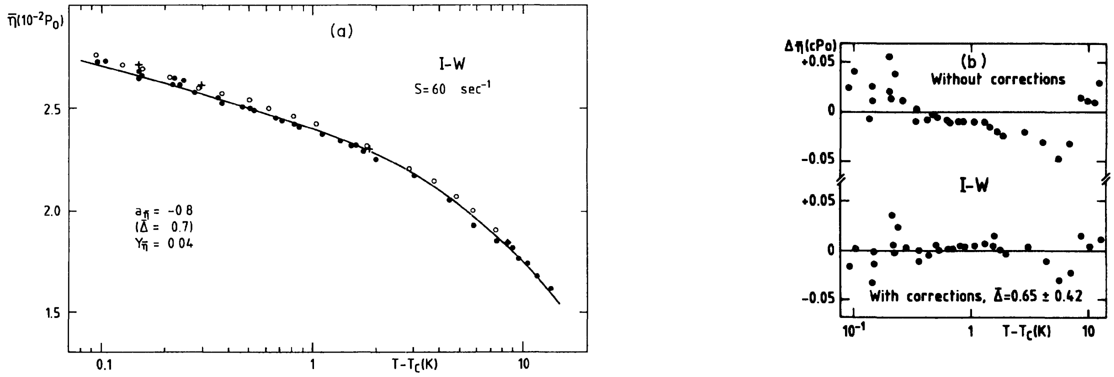

FIG. 3. (a) Temperature variation of the shear viscosity $\bar{\eta}$ in the I-W system at the shear rate $S=60\ \mathrm{sec}^{-1}$. Data affected by shear ($T-T_c<0.1$ K) have been discarded. ●, our data; +, data from Ref. 34(a); ○, data from Ref. 34(b). Full line is the fit to our data with $\bar{\Delta}=0.7$ and $Y_{\bar{\eta}}=0.04$ imposed. (b) Deviation $\Delta\bar{\eta}$ between our shear viscosity data and formula (42), imposing $Y_{\bar{\eta}}=0.04$. Without correction to scaling, systematic distortions appear.

TABLE III. The values in parentheses are imposed.

System		R	a_R	$\bar{\Delta}$	Q
N-H		1.033 ±0.006	(0)		0.893
($Y_{\bar{\eta}}=0.043$)		1.10 ±0.16	−0.3 ±0.5	0.27 ±0.70	0.980
I-W					
($Y_{\bar{\eta}}=0.04$)		1.062 ±0.008	(0)		0.601
($a_{\bar{\eta}}=-1.50$)		1.066 ±0.02	−0.06±0.2	0.5 ±10	0.632
N-M	q_1[a]	1.006 ±0.001	(0)		0.197
($Y_{\bar{\eta}}=0.0399$)		0.998 ±0.001	0.76±0.08	0.527±0.015[d]	0.636
		1.0005±0.0007	1.97±0.12	(0.7)	0.451
	q_1,q_2[b]	1.007 ±0.001	(0)		0.211
		0.994 ±0.003	0.28±0.09	0.35 ±0.1	0.458
		1.0001±0.0007	1.9 ±0.1	(0.7)	0.339
	q_3[c]	1.166 ±0.009	(0)		0.696
		1.138 ±0.012	2.74±0.86	0.70 ±0.10	0.919
		1.136 ±0.009	2.85±0.50	(0.7)	0.920
T-W		1.00 ±0.01	(0)		0.212
($Y_{\bar{\eta}}=0.04$)	$a_\xi=-3.5$	1.065 ±0.006	−7.3 ±1.4	0.683±0.044	0.962
($a_{\bar{\eta}}=1.45$)		1.057 ±0.004	−7.78±0.25	(0.7)	0.989
	$a_\xi=0$	1.090 ±0.005	(0)		0.571

[a] From Ref. 11, $q_1=1.92\times10^5$ cm^{-1}. Typical uncertainty is 0.3%.

[b] From Ref. 11, both q_1 and $q_2=7.04\times10^5$ cm^{-1}, with a typical uncertainty of 1.6%.

[c] From Ref. 44, $q_3=3065$ cm^{-1}.

[d] We imposed the $\bar{\Delta}$ range to be 0.5—0.9. When $\bar{\Delta}$ was set completely free, the value $\bar{\Delta}=0.11\pm0.04$ was found. This is why in Ref. 3 we estimated $\bar{\Delta}\simeq0.5\pm0.4$.

agreement with ours, we have not considered them in our analysis because they have been obtained in mixtures with a somewhat different concentration. The results of the fits are reported in Table II, where weak corrections to scaling have been detected. The value of the exponent found here ($\bar{\Delta}=0.65\pm0.42$) is slightly different from the value (0.45±0.4) cited in our Ref. 3. This is due to the fact that in Ref. 3 we simply recalibrated the rough viscosity data by a constant value (0.94). Considering Fig. 1, the calibration error is small, but this changes the $\bar{\Delta}$ central value. We have retained the best fit ($Q=0.935$) to analyze the linewidth data.

Linewidth data are from Ref. 39 ($q=1.90\times10^5$ cm^{-1}) and from Ref. 40 where the data have been extrapolated at $q=0$ from experiments performed in the range $q=(1-2.5)\times10^5$ cm^{-1}. In order to remove this source of error, we have considered only the data in the range $T-T_c=1.39-15$ K ($q\xi<1$), where $\Omega_K\simeq\Omega_B\simeq\Omega_P\simeq1$ within 1%.

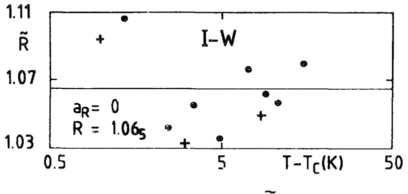

FIG. 4. Temperature variation of $\tilde{R}$ for the I-W system. No corrections are visible. Points correspond to Ref. 41 and crosses to Ref. 40. Both are strictly in the hydrodynamic region.

The results of the fits are given in Table III. No available information, as shown in Fig. 4, could be extracted concerning corrections to scaling. The more reliable value is thus

$$R=1.06\pm0.07$$

taking into acount all the experimental uncertainties.

D. Chlorex-*n*-dodecane

We only report here the main results obtained with this system. Details can be found elsewhere.[41]

The *viscosity data*, obtained in the range 0.1—15 K, have been obtained in the same viscosimeter we used for the N-H, I-W, and T-W systems. The exponent found, $Y_{\bar{\eta}}=0.0415\pm0.0005$, is close to the expected theoretical value, so corrections to scaling should be very small in this system. The *linewidth data*, obtained in the range 6×10^{-4} to 6 K or $q\xi=2\times10^{-2}$ to 20 at the wave vector

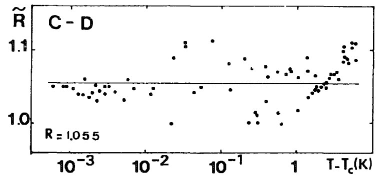

FIG. 5. Temperature variation of $\tilde{R}$ for the C-D system. No corrections are visible (from Ref. 41).

$q=2.04\times10^5$ cm^{-1} exhibit no corrections as it can be seen in Fig. 5. The value of the amplitude ratio R has been found to be

$$R=1.055\pm0.05\ ,$$

where all the experimental uncertainties have been accounted for.

TABLE IV. Shear viscosity of the I-W system. $T_c=26.6030\,^\circ$C. Shear rate is about 60 sec^{-1}. Typical relative uncertainty is 0.6%.

$L_N\left[\dfrac{T-T_c}{T_c}\right]$	$\bar{\eta}$ ($10^{-2}P_0$)
−3.084 98	1.601
−3.221 56	1.655
−3.341 35	1.718
−3.507 07	1.797
−3.695 01	1.833
−3.921 59	1.906
−4.216 59	2.018
−4.575 44	2.126
−5.259 56	2.274
−5.821 74	2.368
−6.062 49	2.403
−6.343 51	2.445
−6.744 25	2.502
−7.258 86	2.609
−7.258 86	2.578
−7.240 08	2.568
−7.627 11	2.608
−8.144 81	2.675
−8.015 59	2.677
−7.627 11	2.621
−7.690 73	2.597
−7.151 13	2.581
−7.004 91	2.541
−6.724 61	2.487
−6.510 40	2.465
−6.388 14	2.454
−6.118 47	2.413
−5.884 48	2.379
−5.597 70	2.334
−5.388 15	2.301
−5.222 39	2.279
−5.116 84	2.242
−5.002 98	2.216

E. Nitroethane-3-methylpentane

In Ref. 42 can be found a value for ξ_0, the theoretical exponents being fixed: $\xi_0=(2.13\pm0.05)$ Å. For the *viscosity*, we have taken the data from Ref. 43, multiplied by 1.031 according to Ref. 11. The useful range was 3 mK—7 K. As reported in Table II, it is of no use to look for corrections to scaling, since the effective exponent $Y_{\bar{\eta}}$ is found very close to the theoretical value. Concerning the *linewidth*, three laboratories have already studied this system, and we will successively analyze their data obtained at various q values and $T-T_c$ ranges.

(i) Data from Ref. 11. We have not retained the largest wave vector because of multiple scattering corrections. The data at $q_1=1.92\times10^5$ cm^{-1} have been obtained in the range 0.3 mK—12 K, or $q\xi=25$—0.1. The analysis is made in Table III. Although some of the data have been obtained in a range $q\xi>1$, it is not useful, as stressed in Ref. 3, to consider the q dependence of the corrections $R_{f,w}(X)$ [from formula (44)]. Indeed, the coefficients $R_{f,w}(X)$ are different from unity precisely in a region where the corrections become negligible. Anyway, as is also shown in Fig. 6(a), corrections far from T_c are visible. A value

$$R=1.00\pm0.06$$

can be inferred, which is in agreement with the Ref. 11 analysis which nevertheless applied a MC approach. All uncertainties have been taken into account.

The data obtained in the range 0.4 mK—0.4 K at $q_2=7.04\times10^4$ cm^{-1} are less accurate [Fig. 6(a)]. Therefore, it is of no use making a special analysis of these q_2 data.

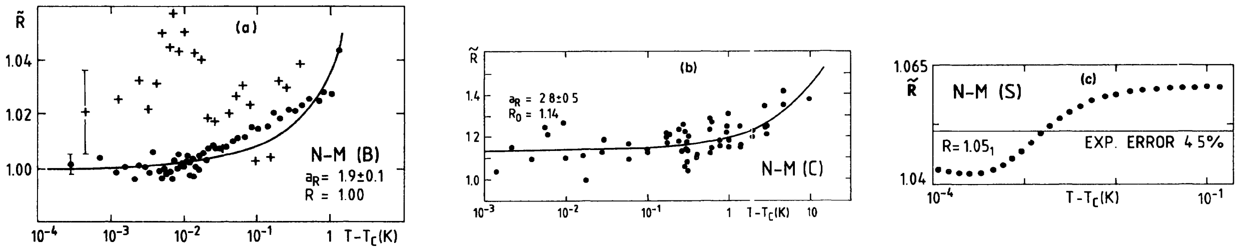

FIG. 6. Temperature variation of $\tilde{R}$ in the N-M system, showing the presence of corrections to scaling. Full line is the best fit with $\bar{\Delta}=0.7$ imposed. All amplitudes (a_R,R) are given with $\bar{\Delta}$ fixed to 0.7. B in (a), C in (b), and S in (c) correspond, respectively, to the data of Refs. 11, 44, and 45. In (a) points represent data obtained at $q_1=1.92\times10^5$ cm^{-1}, and crosses are data at $q_2=7.04\times10^4$ cm^{-1}. Uncertainties on the q_2 data are much larger than the q_1 uncertainties, so the best fit is mainly due to the q_1 data. The systematic distortion which appears in (c) is only due to the use of an analytical function instead of the rough experimental data which were not available. Here corrections to scaling cannot be visible since data have been obtained only close to T_c.

TABLE V. Linewidth data for the N-M system by Calmettes (Ref. 44). $q=3.065\ \text{cm}^{-1}$ and $T_c=26.4\,^{\circ}\text{C}$. Numbers in parentheses denote powers of 10, e.g., $1.734\,86(+2)=1.734\,86\times 10^2$.

$L_N(T-T_c)$	Γ (rad sec^{-1})	$\Delta\Gamma$ (rad sec^{-1})	$L_N(T-T_c)$	Γ (rad sec^{-1})	$\Delta\Gamma$ (rad sec^{-1})
1.734 86(−2)	7.366	2.8(−1)	−2.292 63	1.480	3.08(−2)
1.882 18(−2)	7.159	4.6(−1)	−1.751 58	2.288	4.76(−2)
3.478 36(−1)	9.768	5.7(−1)	−1.745 83	2.256	6.72(−2)
3.485 42(−1)	9.028	5.7(−1)	−1.725 97	2.312	8.96(−2)
3.488 95(−1)	8.991	8.0(−1)	−1.725 41	2.246	5.88(−2)
6.928 97(−1)	1.214(+1)	8.9(−1)	−1.410 59	2.910	1.23(−1)
6.933 97(−1)	1.182(+1)	1.0	−1.410 59	2.804	6.44(−2)
1.069 36	1.600(+1)	1.2	−1.309 33	2.865	1.65(−1)
1.069 53	1.731(+1)	1.4	−1.305 27	2.869	1.20(−1)
1.096 94	1.638(+1)	2.5	−1.272 97	3.262	2.18(−1)
1.097 11	1.584(+1)	1.3	−1.212 34	2.882	1.73(−1)
1.595 54	2.529(+1)	1.5	−1.202 31	3.108	2.38(−1)
1.596 15	2.625(+1)	1.2	−1.200 65	3.349	2.32(−1)
2.318 51	4.431(+1)	5.0	−1.172 80	3.000	2.10(−1)
2.318 51	4.436(+1)	1.3(+1)	−1.169 57	3.286	2.54(−1)
−6.571 28	7.853(−2)	1.4(−2)	−1.119 33	3.272	1.00(−1)
−6.096 83	1.187(−1)	5.6(−3)	−1.114 74	3.008	9.80(−2)
−5.546 78	1.627(−1)	1.1(−2)	−1.110 18	3.474	2.21(−1)
−5.167 29	2.387(−1)	1.9(−2)	−8.686 92(−1)	3.784	2.40(−1)
−5.116 00	2.400(−1)	1.4(−2)	−8.675 01(−1)	3.803	2.63(−1)
−5.035 95	2.808(−1)	5.3(−2)	−5.050 09(−1)	4.911	2.54(−1)
−4.656 46	3.399(−1)	2.2(−2)	−4.853 20(−1)	5.683	3.89(−1)
−4.595 22	3.091(−1)	1.6(−2)	−4.853 20(−1)	5.466	3.80(−1)
−4.086 38	4.373(−1)	1.9(−2)	−4.612 42(−1)	5.139	3.92(−1)
−4.039 86	4.406(−1)	3.3(−2)	−4.596 57(−1)	5.715	3.61(−1)
−3.540 46	6.402(−1)	2.5(−2)	−2.275 28(−1)	6.082	4.98(−1)
−3.503 23	6.898(−1)	7.8(−2)	−2.275 28(−1)	6.215	4.56(−1)
−2.813 41	1.009	7.8(−2)	−2.398 54(−2)	7.546	4.62(−1)
−2.806 77	1.083	8.4(−2)	−2.378 05(−2)	7.383	4.28(−1)
−2.302 59	1.486	5.6(−2)	5.484 93(−3)	8.110	4.50(−1)

When both the q_1 and q_2 data are analyzed together (Table III), we nearly recover the q_1 analysis results, as expected following the remarks of the preceding paragraph. A value $\Delta=0.35\pm0.11$ is found, which is low compared to the expected value 0.7. However, the $T-T_c$ range is small, and in order to obtain more information on the corrections it is necessary to consider data obtained in a wider $T-T_c$ range.

(ii) Data from Ref. 44 and Table V. With an investigated temperature range of 1 mK–10 K at a wave vector of $q=3.065\ \text{cm}^{-1}$, all data, even close to T_c, lie in the hydrodynamic region ($q\xi<0.18$). We have made the t variation of $\tilde{R}$ visible by applying (46).

Corrections, up to 20%, are visible in Fig. 6(b), whose estimation is in agreement with that performed above in (i) for the same system, i.e., $\bar{\Delta}=0.7\pm0.1$ and when $\bar{\Delta}=0.7$ is imposed, $a=2.8\pm0.5$. However, R is somewhat different since here

$$R=1.14\pm0.07$$

(all uncertainties are accounted for).

(iii) Data from Ref. 45. We considered the best fit $\Gamma(t)$ describing the data. They cover the range 0.1 mK–0.2 K, which prevents corrections to scaling from being important [see Fig. 6(c)]. We have estimated

$$R=1.05\pm0.09\ .$$

The uncertainty is higher, because we could not analyze the rough experimental data.

As a conclusion on this particular system, corrections to scaling seem to be evidenced, with data from two different origins, and the correction amplitudes agree with each other. However, the values of R, which include a third independent determination, lie in the range 1–1.14; the mean value

$$R=1.06$$

is in satisfactory agreement with all determinations, considering the experimental uncertainties. The disagreement in these experimental values can be attributed to differences in calibrations of Γ and q, and to small differences in the mixture composition. This should affect only R, and not its temperature variations.

F. Triethylamine-water

This system was seen to show important corrections-to-scaling[2] terms in the specific heat, order parameter,

TABLE VI. Shear viscosity of the T-W system. $T_c = 18.1700\,^\circ\mathrm{C}$. Shear rate is about 30 sec^{-1}. For absolute values, multiply $\bar{\eta}$ by 0.93. Typical relative uncertainty is 0.9%.

$L_N(T_c-T)$	$\bar{\eta}$ $(10^{-2}P_0)$	$L_N(T_c-T)$	$\bar{\eta}$ $(10^{-2}P_0)$
2.353 28	6.652	−1.078 80	4.184
2.423 03	6.937	−1.139 42	4.184
2.306 58	6.463	−1.203 96	4.174
2.238 58	6.241	−1.203 96	4.283
2.488 23	7.235	−1.283 72	4.228
2.373 04	6.727	−1.335 59	4.244
2.474 01	7.195	−1.443 91	4.321
2.124 65	5.943	−1.562 54	4.345
2.064 33	5.766	−1.553 04	4.197
2.001 48	5.620	−1.541 76	4.211
1.932 97	5.473	−1.609 42	4.306
1.879 47	5.375	−1.968 95	4.269
1.827 77	5.373	−1.873 38	4.232
1.771 56	5.213	−1.754 44	4.306
1.702 93	5.210	−2.282 75	4.320
1.639 00	5.044	−1.123 92	4.207
1.581 04	4.975	−7.687 25(−1)	4.196
1.516 23	4.895	−8.989 33(−1)	4.172
1.439 84	4.802	−1.690 09	4.184
1.353 26	4.721	4.173 96(−1)	4.350
1.266 95	4.652	1.371 53(−1)	4.264
1.175 57	4.584	1.052 64(−1)	4.208
9.555 13(−1)	4.480	−6.831 90(−1)	4.147
8.329 11(−1)	4.394	−3.649 52	4.474
6.931 45(−1)	4.344	−3.649 52	4.557
6.931 49(−1)	4.359	−3.882 29	4.576
5.394 15(−1)	4.439	−2.975 86	4.441
5.827 24(−2)	4.316	−3.688 73	4.592
−3.562 34(−2)	4.310	−3.688 73	4.539
−1.415 59(−1)	4.249	−3.218 78	4.460
−2.984 01(−1)	4.216	−2.882 34	4.372
−8.209 72(−1)	4.244	−2.748 81	4.349
−4.683 99(−1)	4.199	−2.673 60	4.376
−7.100 82(−1)	4.310	−2.525 68	4.399
−9.597 11(−1)	4.196	−2.375 12	4.304
−1.053 82	4.221	−4.604 80	4.685
−8.989 33(−1)	4.217	−4.342 52	4.662
−8.915 89(−1)	4.159		
−9.545 02(−1)	4.212		
−1.018 87	4.196		

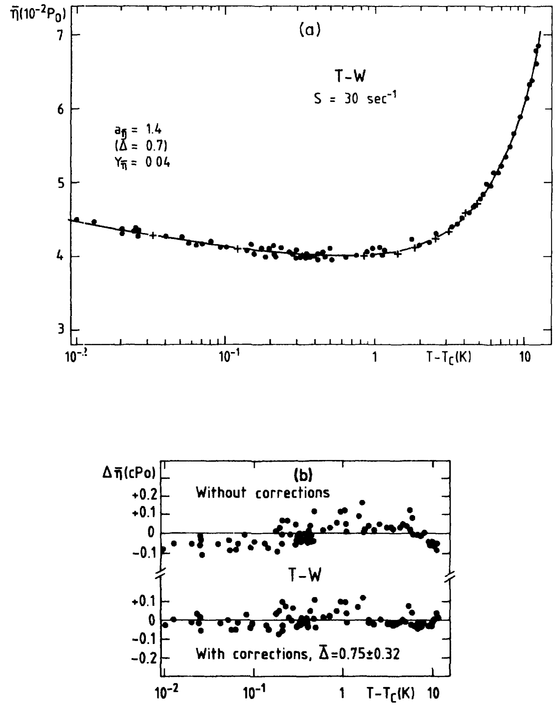

FIG. 7. (a) Shear viscosity $\bar{\eta}$ of the T-W system vs temperature. Shear rate is about $S=30\ \mathrm{sec}^{-1}$. Data affected by shear ($T-T_c<0.01$ K) have been discarded. ●, our data; +, Ref. 46 data. Full line is the best fit with $\bar{\Delta}=0.7$ and $Y_{\bar{\eta}}=0.04$ imposed. (b) Deviation $\Delta\bar{\eta}$ between the shear viscosity data and formula (42), imposing $Y_{\bar{\eta}}=0.04$. When corrections are not allowed, distortions appear.

and susceptibility. Direct measurements of the correlation length in a wide range of temperature do not exist at the present time, one of the reasons being the lack of knowledge of a correlation function which includes corrections to scaling. However, turbidity measurements close to T_c are available,[29] and with a few approximations it is possible to infer values for ξ. The correlation length correction a_ξ can be inferred from the other corrections, for instance, from the susceptibility correction $a_\chi=-5.1\pm0.6$ and the universal ratio[46] $a_\xi/a_\chi=0.68\pm0.03$. Then the value $a_\xi=-3.5\pm0.6$ can be deduced, which leads, when imposed in the analysis of the data of Ref. 29, to the value $\xi_0=(1.28\pm0.05)$ Å.

Our *viscosity data* (Table VI and Fig. 7) cover the range 0.01—12 K and agree with the Ref. 47 data, checking both the viscosimeter calibration and the density behavior. The analysis, performed in Table II, shows that the exponent $Y_{\bar{\eta}}$ can reach the value 0.04 only if corrections to scaling are considered.

Linewidth measurements have been obtained in the range 10 mK—10 K (Table VII and Fig. 8), at $q=(2.04\pm0.01)\times10^5$ and $(1.91\pm0.01)\times10^5\ \mathrm{cm}^{-1}$. The $q\xi$ range is 1.5—0.02, therefore the data lie mainly in the hydrodynamic region. In Table III is reported the

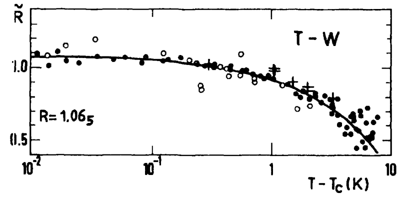

FIG. 8. Temperature variation of $\tilde{R}$ in the T-W system. Amplitudes (a_R, R) are given with $\bar{\Delta}=0.7$ imposed. Full line is the best fit with $\bar{\Delta}=0.7$ imposed. ●, set 1; ○, set 2. The accuracy of set 2 is lower. For sake of comparison, data from Ref. 39 (+) have been reported.

TABLE VII. Linewidth data for the T-W system. $q_1=2.04\times10^5$ cm^{-1} and $q_2=1.91\times10^5$ cm^{-1}. Thermal variation of q comes from $n-n_c$ as given in the text or in Ref. 36.

$L_N(T_c-T)$	Γ (10^6 rad sec^{-1}) set 1 (q_1)	$\Delta\Gamma$ (10^6 rad sec^{-1})
1.757 57	1.535(−2)	2.6(−3)
1.852 12	1.533(−2)	5.6(−3)
1.835 98	1.250(−2)	3.7(−3)
1.812 76	1.075(−2)	2.2(−3)
1.771 27	1.128(−2)	3.0(−3)
1.715 65	1.562(−2)	3.1(−3)
1.976 90	1.524(−2)	4.8(−3)
2.040 87	1.937(−2)	7.8(−3)
1.976 90	1.731(−2)	6.2(−3)
1.943 67	1.393(−2)	4.0(−3)
1.926 77	1.388(−2)	4.6(−3)
1.890 14	1.307(−2)	3.2(−3)
1.873 23	1.843(−2)	5.4(−3)
1.684 05	1.219(−2)	1.9(−3)
1.655 81	9.433(−3)	2.5(−3)
1.637 11	1.190(−2)	2.2(−3)
1.607 00	1.282(−2)	2.1(−3)
1.606 90	1.388(−2)	2.4(−3)
1.587 87	1.329(−2)	1.6(−3)
1.536 07	1.282(−2)	1.8(−3)
1.535 21	1.041(−2)	2.0(−3)
1.481 67	1.086(−2)	1.5(−3)
1.427 51	9.615(−3)	2.0(−3)
1.330 60	1.000(−2)	1.2(−3)
1.305 71	1.086(−2)	2.2(−3)
1.287 66	1.250(−2)	1.2(−3)
1.190 07	1.006(−2)	9.1(−4)
1.190 07	1.095(−2)	9.6(−4)
1.168 23	1.000(−2)	1.7(−3)
1.141 45	1.111(−2)	5.9(−4)
1.059 28	1.079(−2)	9.3(−4)
9.686 20(−1)	9.523(−3)	5.8(−4)
8.705 84(−1)	9.259(−3)	6.8(−4)
8.697 46(−1)	9.615(−3)	1.7(−3)
7.609 49(−1)	8.333(−3)	5.5(−4)
6.399 07(−1)	8.163(−3)	3.1(−4)
5.840 61(−1)	7.440(−3)	1.0(−3)
5.009 60(−1)	7.246(−3)	5.0(−4)
3.374 04(−1)	6.885(−3)	1.5(−4)
1.800 74(−1)	6.097(−3)	3.5(−4)
6.607 37(−2)	5.882(−3)	2.7(−4)
−2.705 74(−2)	5.636(−3)	3.0(−4)
−1.061 33(−1)	5.229(−3)	2.1(−4)
−1.739 90(−1)	5.050(−3)	2.4(−4)
−3.350 46(−1)	4.545(−3)	1.3(−4)
−3.350 46(−1)	4.545(−3)	1.3(−4)
−4.568 02(−1)	4.299(−3)	8.8(−5)
−5.311 89(−1)	4.079(−3)	1.3(−4)
−7.590 62(−1)	3.571(−3)	3.2(−4)
−7.592 75(−1)	3.472(−3)	5.7(−5)
−1.066 23	2.849(−3)	5.1(−5)
−1.072 93	2.849(−3)	6.4(−5)
−1.241 31	2.564(−3)	6.3(−5)
−1.385 07	2.347(−3)	5.2(−5)
−1.512 74	2.212(−3)	4.2(−5)
−1.730 45	1.953(−3)	2.4(−5)
−1.965 36	1.644(−3)	2.1(−5)
−2.061 17	1.533(−3)	3.7(−5)
−2.395 74	1.293(−3)	1.3(−5)
−2.777 31	1.038(−3)	1.3(−5)
−3.011 75	9.090(−4)	1.3(−5)
−3.011 75	9.090(−4)	1.3(−5)
−3.338 07	8.064(−4)	1.0(−5)
−3.684 67	6.802(−4)	1.1(−5)
−3.931 95	6.410(−4)	1.5(−5)
−4.104 07	6.476(−4)	1.0(−5)
−4.247 12	5.773(−4)	9.6(−6)
−4.482 47	5.952(−4)	8.5(−6)
−4.709 93	5.494(−4)	8.6(−6)
	set 2 (q_2)	
−1.298 28	1.811(−3)	1.9(−4)
−1.316 77	1.845(−3)	2.0(−4)
2.159 18(−1)	5.494(−3)	1.8(−3)
7.843 58(−1)	7.042(−3)	2.9(−3)
5.312 16(−1)	5.694(−3)	1.9(−3)
−2.850 19(−1)	4.032(−3)	9.7(−4)
−2.863 50(−1)	3.906(−3)	9.1(−4)
−5.568 70(−1)	3.906(−3)	9.1(−4)
−5.568 70(−1)	3.401(−3)	6.9(−4)
−7.721 90(−1)	2.890(−3)	5.0(−4)
−7.940 73(−1)	2.994(−3)	5.3(−4)
−9.467 50(−1)	2.717(−3)	4.4(−4)
−1.398 37	2.040(−3)	2.4(−4)
−1.551 17	1.853(−3)	2.1(−4)
−2.040 22	1.420(−3)	1.2(−4)
−3.352 41	7.530(−4)	3.4(−5)
−4.268 70	5.096(−4)	1.5(−5)
−3.912 02	5.903(−4)	2.0(−5)
−4.828 31	4.504(−4)	1.2(−5)

analysis of such data. We used the viscosity fit with corrections to scaling ($Q=0.730$ in Table II), and dynamic corrections appeared with an amplitude nearly four times that found in the N-M systems. We also tried a fit with $a_\xi=0$, which lead to a lower fit quality. The conclusion is that dynamic corrections appear clearly in the linewidth only because the static corrections have been imposed.

Finally, it is interesting to note that the sign of the corrections in this T-W system always shows an opposite sign when compared to that in other systems, in both statics (corrections <0) and dynamics ($a_{\bar\eta}>0$, $a_\Gamma<0$). This may be connected to the nature of the critical point, a lower one, which changes the sign of t.[48] It is known that such systems have the particularity of revealing strong deviations from ideality.

The value of$R$ can be estimated from Table III, with $\bar{\Delta}=0.7$, and is

$$R=1.06\pm0.06$$

(all experimental uncertainties included). This value is more reliable than the former value $R=1.21$ which was given in Ref. 7; the disagreement is chiefly due to new viscosity data and to the use of a different fitting procedure which now includes corrections to scaling in both ξ and R.

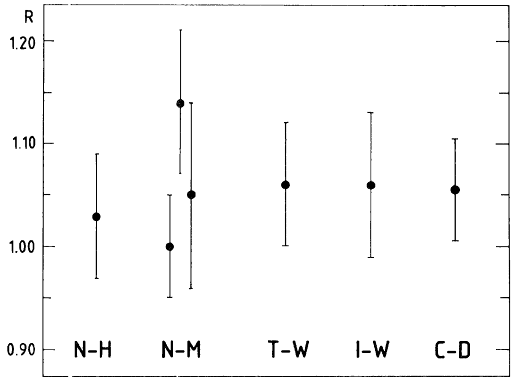

FIG. 9. Dynamic amplitude ratio R when corrections to scaling are taken into account and using the function Ω_P.

V. GENERAL CONCLUSION

The values of the universal ratio R in binary fluids that we have found here lie in the range 1—1.14 (Table VIII and Fig. 9). These values are lower than those published in Ref. 7 where the mean value was 1.16, and agree well with others in pure fluids[49,50] or polymers.[51] This change is due, first, to the elimination in the analysis of systems where we could not check both the viscosity and the linewidth calibrations; second, to the use of new information (correlation length for N-H, viscosity calibrations for I-W and T-W), and finally to the use of an analysis which includes static and dynamic corrections to scaling (T-W). We would like to emphasize that a great number of parameters enter in the determination of R; some of them, such as the correlation length, are measured indirectly, and thus the experimental uncertainty is probably higher than 6% in the best case. For this reason, a comparison with the theoretical predictions $R=1.027$ (MC) and $R=1.038$ (RG) has little significance.

Another result of this work is the apparent relevance of corrections to scaling in both the viscosity and the linewidth. Both MC and RG theories predict corrections, with exponent $\nu=0.63$ for MC and $\bar{\Delta}\simeq0.7$ for RG. Although we have shown that the formulations were similar, their meaning is quite different since MC corrections are essentially positive.

Moreover, we have shown that according to MC the ratio of corrections $a_{\bar{\eta}}/a_{\Gamma}$ should be universal and equal to $2x_{\bar{\eta}}$. Let us compare in greater detail these predictions with experiments.

(i) Exponent of the corrections. The exponent $\bar{\Delta}$ has been found to be in the range 0.35—0.75 (Table VIII), with most of the values closer to 0.7. However, the experimental accuracy is not sufficient to distinguish between MC ($\bar{\Delta}\equiv\nu=0.63$) or RG ($\bar{\Delta}\simeq0.7$).

(ii) Sign of corrections. Concerning the linewidth, the correction in the N-M system is positive ($a_R\sim2$), but for T-W it is negative ($a_R\sim-8$).

The analysis of the viscosity results is more complicated. Indeed the divergence with exponent $Y_{\bar{\eta}}\simeq0.04$ is very weak and its precise theoretical value is not definitely admitted. The existence of corrections will induce an "effective" exponent $Y_{\bar{\eta}}^{\text{eff}}$, larger than the theoretical one if $a_{\bar{\eta}}<0$, and smaller if $a_{\bar{\eta}}>0$. According to MC, one expects $a_{\bar{\eta}}>0$, and therefore all the effective exponents should be lower than the theoretical value. It follows that the corrections should be weaker for the larger experimental values. This will lead in the present study to a theoretical value $Y_{\bar{\eta}}\gtrsim0.045$ (I-W mixture, Table VIII). This value seems large compared to that we considered as the most probable: $Y_{\bar{\eta}}\simeq0.04$. Now, if one imposes $Y_{\bar{\eta}}$ to be 0.04, positive corrections (T-W system) or negative corrections (I-W) are detected.

TABLE VIII. Values of the universal amplitude ratio R, of the effective exponents $\bar{\Delta}$ and $Y_{\bar{\eta}}^{\text{eff}}$, and of the correction amplitudes a_R and $a_{\bar{\eta}}$ when the values $\bar{\Delta}\simeq0.7$ and $Y_{\bar{\eta}}=0.4$ have been imposed.

System	R[a]	$\bar{\Delta}_R$[a]	a_R[a]	$Y_{\bar{\eta}}^{\text{eff}}$[b]	$\bar{\Delta}_{\bar{\eta}}$[b]	$a_{\bar{\eta}}$[b]
N-H	1.03 ±0.06			0.0397±0.0004		
I-W	1.06 ±0.07			0.0455±0.002	0.65±0.4	−2.1 ±0.5
C-D	1.055±0.05[c]			0.0415±0.0005[c]		
N-M	1.00 ±0.05	0.35±0.1	1.9±0.1	0.0398±0.0003		
	1.14 ±0.07	0.7 ±0.1	2.9±0.5			
	1.05 ±0.09[d]					
T-W	1.06 ±0.06	0.68±0.05	−7.8±0.3	0.031 ±0.002	0.75±0.3	1.45±0.2

[a] From Table III.

[b] From Table II.

[c] From Ref. 41.

[d] From Fig. 6.

(iii) Amplitude ratio of corrections. In the N-H and C-D systems no corrections are visible. It is possible, using the determination of the linewidth correction, to infer a value for the viscosity correction. In the N-M mixture one obtains $a_{\bar{\eta}} = a_R/8 \simeq 0.3$. This low value is not experimentally detectable. For the T-W mixture the absolute value of the ratio is $|a_{\bar{\eta}}/a_R| \sim \frac{1}{6}$. To conclude about these corrections, the MC predictions seem compatible with the experiment results in N-H, C-D, and N-M, but not in I-W and T-W.

More work with pure fluids, which belong to the same universality class and are currently studied in the framework of a MC analysis assuming backgrounds, should give interesting results. Let us note the viscosity RG analysis of Ref. 21 for ethane, leading to the value $\bar{\Delta} = 0.45 \pm 0.09$, with a positive amplitude.

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APPENDIX A: THE SCALING FUNCTION Ω

It is interesting to discuss in greater details the form of the scaling function Ω. The first approximation (Kawasaki[8]) consisted in considering both a constant viscosity $[x_{\bar{\eta}} = 0,\ E_0(q\xi) = 1]$ and the Ornstein-Zernicke static susceptibility $(\eta = 0,\ X(q\xi) = [1 + (q\xi)^2]^{-1})$. It follows, estimating the MC integral (7a) for the critical part of the conductivity $\Delta\Lambda_c$;

$$x_\Lambda = 1\ ,\quad L_0(x) = \frac{\Omega_K(x)}{(x^2+1)} \tag{A1}$$

with $x \equiv q\xi$.

Then, in terms of the relation (39), i.e., $\Omega = \tilde{R}_0/E_0$, the Kawasaki result corresponds to

$$\Omega(x) = R_0(x) = \Omega_K(x)\ . \tag{A2}$$

A reasonable assumption for the scaling function E_0 is suggested by Ref. 19:

$$E_0(x) = [X(x)]^{x_{\bar{\eta}}/2}\ . \tag{A3}$$

In the Bhattacharjee approximant (10) the Fisher-Burford susceptibility is used,

$$X(x) = \frac{(1+\phi^2 x^2)^{\eta/2}}{1 + (1 + \eta/2\phi^2)^2}\ , \tag{A4}$$

where $\eta = 0.024$, $\phi = 0.014$. In fact, in Ref. 11 an approximation for E_0 was proposed which is very similar to (A3): $E_0(x) = C(x)[(x/2)^2 + 1]^{x_{\bar{\eta}}/2}$. Here C is a numerically computed factor which takes into account the difference between the Fisher-Burford susceptibility (A4) and the Ornstein-Zernicke susceptibility. Let us note that C is always very close to unity: $C(q\xi = 100) = 1.012$, $C(q\xi = 0) = 1.003$. On the other hand, Ref. 11 assumed the *first-order* approximation $\tilde{R}_0 = \Omega_K$ obtained for $x_{\bar{\eta}} = 0$, $\eta = 0$. It is possible to find in this way[11,12]

$$\Omega_B(x) = \frac{\tilde{R}_0(x)}{E_0(x)} = \Omega_K(x) C(x) [(x/2)^2 + 1]^{x_{\bar{\eta}}/2}\ . \tag{A5}$$

However, the Bhattacharjee function (A5) uses the $\tilde{R}_0$ and E_0 functions which are computed at different perturbative orders. We think that Ω_P, as defined in (33), is more correct than Ω_B, since all the "one-loop" forms of the scaling functions have been left unchanged. In fact, we only inserted in (33) the two-loop exponent values ($\eta = 0.0315$, $x_{\bar{\eta}} \simeq 0.063$) instead of the one-loop values ($\eta = 0$, $x_{\bar{\eta}} = 0.07$). In order to make a comparison between the different approximants Ω_K, Ω_B, and Ω_P of the function Ω, we have plotted $R(t) = \Gamma_{\text{expt}}[k_B T \Omega(q\xi) q^2 / 6\pi\bar{\eta}\xi]^{-1}$ in a range close to the critical point, where either corrections to scaling or background terms are negligible. Figure 10 shows that the Kawasaki function Ω_K gives clear distortions since it does not take into account the viscosity divergence. The Paladin-Peliti [Eq. (32)] and Bhattacharjee-Ferrell [Eq. (A5)] functions provide better agreement.

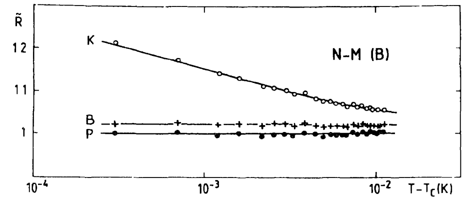

FIG. 10. $\tilde{R} = \Gamma_{\text{exp}}/[k_B T \Omega_{K,B,P} q^2/6\pi\bar{\eta}\xi]$ plotted vs t in the range (0.1—10) mK. Experimental data Γ_{expt} are from Ref. 11 at $q_1 = 1.92 \times 10^5\ \text{cm}^{-1}$. K,B,P represent either the Kawasaki, Bhattacharjee-Ferrell, or Paladin-Peliti function. One expects $\tilde{R}$ to be a constant in this t range, the correction to scaling being negligible.

APPENDIX B: EXPANSION OF THE CROSSOVER VISCOSITY FUNCTION

We follow here the notation of Ref. 14(c), which is slightly different from our notation. The background contribution to the diffusion coefficient is now[14(c)]

$$\bar{D}_B \frac{k_B T}{16\bar{\eta}\xi} \frac{(1+q^2\xi^2)}{q_c^* \xi} = \Delta D_{\text{cr}} \left[\frac{(1+x^2)}{\Omega(x)} \right] \tfrac{3}{8}\pi \frac{1}{q_c^*}\ . \tag{B1}$$

Therefore, we see that

$$\left[\frac{\Lambda_B}{\Lambda_0} \right] \xi_0 = (\tfrac{3}{8}\pi) \frac{1}{q_c^*} = \frac{1}{q_c} \tag{B2}$$

which differs from the wave vector q_c defined in the relations (14) and (15) by a factor $\frac{3}{8}\pi$. The crossover function H of Bhattacharjee *et al.* has the following form:

$$H = \tfrac{1}{12}\sin 3\psi_D - \frac{1}{4q_C\xi}\sin 2\psi_D + \frac{1}{(q_C\xi)^2}[1 - \tfrac{5}{4}(q_C\xi)^2]\sin\psi_D - \frac{1}{(q_C\xi)^3}\{[1 - \tfrac{3}{2}(q_C\xi)^2]\psi_D - |(q_C\xi)^2 - 1|^{3/2} L(w)\}\ , \tag{B3}$$

where

$$\psi_D = \arccos(1+q_D^2\xi^2)^{-1/2} , \tag{B4}$$

$$w = \left| \frac{q_C\xi-1}{q_C\xi+1} \right|^{1/2} \tan\frac{\psi_D}{2} , \tag{B5}$$

$$L(w) = \begin{cases} \ln\dfrac{1+w}{1-w} & \text{if } q_C\xi > 1 \\ 2\arctan|w| & \text{if } q_C\xi \leq 1 . \end{cases} \tag{B6}$$

In the experimental region $q_C\xi$ and $q_D\xi$ are larger than 1 and we can expand H in powers of $1/q_C\xi$ and $1/q_D\xi$. This work has been done using a computer. The first term of the expansion is analytical:

$$e^{-Hx_{\bar\eta}} = 1 + (\tfrac{3}{8}\pi)\frac{1}{q_C^*\xi}2x_{\bar\eta} + \cdots = 1 + 2x_{\bar\eta}\left[\frac{\Lambda_B}{\Lambda_0}\right]\xi^{-1} + \cdots . \tag{B7}$$

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