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Dynamic corrections to transport coefficients of critical binary fluids

D. Beysens

SPSRM, CEN-Saclay, 91191 Gif sur Yvette, France

G. Paladin

Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex, France

and A. Bourgou

Ecole Normale Supérieure, 43 rue de la Liberté, Le Bardo, Tunisia

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Résumé. — Des corrections positives et négatives aux lois d'échelle asymptotiques ont été détectées dans la viscosité et la largeur de raie Rayleigh de plusieurs fluides binaires critiques. L'analyse a été faite dans une approche du groupe de renormalisation, et un exposant effectif de correction $\bar{\Delta} \simeq 0,7$ a été obtenu.

Abstract. — Positive and negative corrections-to-scaling have been detected in the viscosity and the Rayleigh linewidth of several binary fluids. The analysis has been made in the framework of a renormalization group approach, and an effective correction exponent $\bar{\Delta} \simeq 0.7$ has been obtained.

1. Introduction.

It is now well known that the Renormalization Group approach (R-G) leads to an excellent description of systems undergoing a 2nd order phase transition [1]. The agreement with experiments is particularly good for the static properties of binary mixtures, considering either the critical asymptotic behaviour [1] or the corrections-to-scaling [2]. The dynamics of such fluids, described by the model H of reference 3, have been also investigated, confirming the R-G predictions in the region close to the critical point [4]; but non-analytical corrections were not accounted for. On the other hand, the Mode-Coupling (M-C) theory has for a long time been very successful in analysing critical dynamics of pure fluids and binary mixtures [5]. Correction terms, considered as additive background contributions, are included, which in principle allow one to account for the whole critical behaviour. However, even if corrections are overwhelming in pure fluids, this is not the case in binary mixtures. In these mixtures, only 2 transport coefficients are experimentally determined : the shear viscosity $\bar{\eta}$ and the characteristic frequency of the fluctuations of the order parameter (the concentration), i.e. the linewidth Γ of the Rayleigh spectrum. The correction to Γ has to be assumed from the background in $\bar{\eta}$, using basically the Oxtoby-Gelbart method [6]. As noted in references 7, 8, up to now no mixtures have been found which

exhibit corrections large enough to be directly detected, except possibly the Nitroethane-3 Methylpentane (N-M) system. This absence of dynamic corrections also applies to the Triethylamine-Water (T-W) system. However, large negative corrections-to-scaling have been recently found in the specific heat, the order parameter and the susceptibility of this system. The sign, as well as the amplitude of these corrections, is well supported by recent R-G estimations [2, 9]. This will automatically imply negative dynamic corrections, as we will see below, whose sign cannot be explained by the present state of the M-C theory. We have therefore developed a dynamic R-G method including corrections-to-scaling. We have also considered the N-M mixture and we have looked for corrections to the viscosity of the N-M, T-W and the Isobutyric acid-Water (I-W) mixtures. Experimental data were obtained for the T-W and I-W systems.

2. Theoretical

The shear viscosity $\bar{\eta}$, as well as the order parameter transport coefficient, the mass conductivity Λ , is expected to show the behaviour [10]

$$\bar{\eta}(t) = \eta_0(t) t^{-Y_\eta} [1 + a_{\bar{\eta},f} t^{\omega_f \nu} + a_{\bar{\eta},w} t^{\omega_w \nu} + \dots] \quad (1)$$

The amplitude $\eta_0(t)$ exhibits a regular temperature variation. $t = |(T - T_c)/T_c|$ is the reduced temperature and T_c the critical temperature. The exponent $\nu = 0.63$ is that of the correlation length $\xi = \xi_0 t^{-\nu} [1 + a_\xi t^{\omega_\nu} + \dots]$, where $\omega_\nu = 0.50$ is the static Wegner transient exponent.

The transient exponents are $\omega_f \simeq 1.1$, $\omega_w \simeq 1.2$ [11]. They are related to the derivatives of the Wilson functions for the parameters f and w [4, 11] of the perturbative expansion. From a 2nd order ε -expansion computation [4], the universal exponent Y_η assumes the value 0.041. From M-C, the value is 0.042 [12]. The analysis of experimental data at various concentrations [10] implies the value 0.04, which seems therefore to be the most probable value. The line-width $\Gamma(q, t)$ of the Rayleigh spectrum satisfies the Kawasaki-Stokes relation [13]; in the critical limit (wavevector $q \rightarrow 0$, $\xi \rightarrow \infty$ $q\xi \equiv X$ arbitrary),

$$\Gamma(q, t) = R(q, t) \cdot [k_B T / 6 \pi \bar{\eta} \xi] q^2 \Omega(x) \quad (2)$$

k_B is the Boltzmann constant. Ω is a universal scaling function which has to satisfy the requirements

$$\Omega(x) |_{x \rightarrow \infty} \propto X^{(Y_\eta + \nu)/\nu}, \quad \Omega(0) = 1. \quad (3)$$

For this reason we used the approximant of reference 14 instead of the Kawasaki function $\Omega_K = 3/4 \cdot X^{-2} \cdot \{1 + X^2 + (X^3 - X^{-1}) \cdot \tan^{-1}(X)\}$, but with the universal values of the Fisher exponent $\eta = 0.0315$ [1] and with $Y_\eta = 0.04$:

$$\Omega_P = [\Omega_K]^{1 - (Y_\eta/\nu) - \eta} \cdot [x^2 + 1]^{(Y_\eta/\nu) + (\eta/2)}. \quad (4)$$

The amplitude ratio R is also universal and with suitable normalization conditions [4, 11, 14], $R = 6 \pi f^{*-1} = 1.075$ according to a one loop fixed dimensional computation [14]. f^* is the fixed point value of the renormalized parameter f . Therefore it is possible to define a $R(t, q)$ which should exhibit the same corrections-to-scaling as the parameter f [4, 11] and reaches the asymptotic value $R_0 = 6 \pi f^{*-1}$ in the limit $q \rightarrow 0$, $t \rightarrow 0$:

$$R(q, t) = R_0 \{1 + a_{R,f} t^{\omega_f \nu} R_f(X) + a_{R,w} t^{\omega_w \nu} R_w(X) + \dots\}. \quad (5)$$

Up to now the scaling functions $R_{f,w}(X)$ have not been computed but they must satisfy the conditions [3, 11] $R_{f,w}(X) |_{X \rightarrow \infty} \propto X^{\omega_{f,w}}$, $R_{f,w}(0) = 1$ which correspond to (3). The experiments analysed below were mostly carried out in a temperature range where the $R_{f,w}(X)$ are not far from unity (see below).

It seems nearly impossible to distinguish between the values of the exponents ω_f and ω_w , so we had to introduce an effective exponent $\bar{\Delta} \equiv \omega_{\text{eff}} \cdot \nu$ and effective amplitudes $a_{\bar{\eta}}$ and a_R . Then (1) and (2) become

$$\bar{\eta}(t) = \eta_0(t) t^{-Y_n} \{ 1 + a_{\bar{\eta}} t^{\bar{\Delta}} \} \quad (6)$$

and

$$\Gamma(q, t) = R_0 \frac{k_B T}{6 \pi \bar{\eta} \xi} q^2 \Omega(X) [1 + a_R t^{\bar{\Delta}} R_{\text{eff}}(X)] . \quad (7)$$

It is worth noting that the M-C analysis leads to a rather similar relation for the linewidth [6],

$$\Gamma(q, t) = R_0 \frac{k_B T}{6 \pi \bar{\eta} \xi} q^2 \Omega_K(X) \left\{ 1 + b \frac{X^2 + 1}{\Omega_K(X)} t^\nu \right\}, \quad (8)$$

where $R_0 = 1.027$ [15]. The background amplitude is related to the critical part of the viscosity [6]. Although (7) and (8) are similar in their formulation since $\bar{\Delta} \sim \nu$, their meaning is quite different. In particular a_R can be either positive or negative, whereas b is essentially positive.

In the following, $R_{\text{eff}}(X)$ will be set to unity. We have checked that this simplification does not affect the linewidth data interpretation by re-analysing these data using an approximant which satisfies the correct limit conditions : in analogy with the M-C background, $R_{\text{eff}}(X) = [\Omega_K/(X^2 + 1)]^{-\bar{\Delta}/\nu}$.

3. Experimental.

The kinetic viscosity $\bar{\eta}/\rho$ (ρ density) was measured with a Cannon-tilting viscosimeter. The calibration was checked by using pure water. The T-W and I-W mixtures were prepared with components from the same origin as in [16]. The critical concentrations are 0.321 mass fraction of triethylamine and 0.389 mass fraction of acid. The critical temperatures are 291.320 K (T-W) and 299.753 K (I-W). Note that the critical point is a lower consolute point for T-W. The viscosimeter was sealed, and placed in a thermally regulated water bath (± 1 mK stability), whose temperature was measured by a calibrated quartz thermometer. The shear rates were about 30 s^{-1} for T-W, and 60 s^{-1} for I-W. The refractive index variation ($n - n_c$) near T_c reflects the ρ -behaviour with a high accuracy [8], so we took the data both from [16] and [17] to infer ρ . For T-W the linewidth measurements were performed with the sample used in reference 2, placed in a copper oven with ± 0.1 mK thermal regulation. We used a homodyne light scattering technique [wavevector $q = (2.04 \pm 0.01) \times 10^5 \text{ cm}^{-1}$]. The signal was analysed by a clipped photon correlator. Care was taken to prevent heating by the laser beam. Typical experimental uncertainties in Γ and $\bar{\eta}$ are 1.5 %. All data will be reported elsewhere.

4. Results.

The data were fitted using Tournarie's statistical refining method [18]. *Viscosity* data for N-M are from reference 19 with the calibration of reference 20. As an ultimate check of our viscosimeter calibration, we verified that our T-W and I-W data agreed with those of references 21, 22.

We fitted the data to formula 6. As $\eta_0(t)$ is a regular function near T_c , we used either a polynomial expansion $\eta_0(t) = \eta_1[1 + X_1 t + X_2 t^2 + X_3 t^3 + \dots]$ with $\eta_1, X_1, X_2, \dots$ as free parameters, or an Arrhenius law, $\eta_0(t) = \eta'_1 \exp E/(1 + t)$, with η'_1 and E as free parameters. We checked that the results for the parameters $Y_n, a_{\bar{\eta}}, \bar{\Delta}$ in (6) did not depend on the exact form assumed for η_0 . The analysis was made in 2 steps :

i) *No corrections* : $a_{\bar{\eta}} = 0$ imposed. *N-M system* : $Y_n = 0.03995 \pm 0.00016$ was obtained, using the Arrhenius form. This value is in good agreement with 0.0398 ± 0.0002 found in

reference 10 where the polynomial function was used. *I-W system* : $Y_{\eta} = 0.0487 \pm 0.0015$. *T-W system* : $Y_{\eta} = 0.032 \pm 0.001$.

Since Y_{η} is universal, corrections-to-scaling should explain the discrepancies. Consequently, the most probable value $Y_{\eta} = 0.04$ was assumed in the subsequent analysis, where corrections were taken into account.

ii) *Corrections*, $Y_{\eta} = 0.04$ imposed, $a_{\bar{\eta}}$ and $\bar{A}$ free. *N-M system* : no corrections, in accordance with the above $Y_{\bar{\eta}}$ result. *I-W system* : $\bar{A} = 0.45 \pm 0.4$, $a_{\bar{\eta}} = -0.40 \pm 5$. *T-W system* : $\bar{A} = 0.75 \pm 0.32$, $a_{\bar{\eta}} = 1.4 \pm 3.0$. The large uncertainty in the amplitudes $a_{\bar{\eta}}$ is due to the fitting procedure of the viscosity data which correlates $a_{\bar{\eta}}$ and E in formula 6. However we found, when imposing the value $\bar{A} = 0.7$, $a_{\bar{\eta}} = -0.80 \pm 0.05$ for I-W, and $a_{\bar{\eta}} = 1.45 \pm 0.2$ for T-W.

Figure 1 shows the distortion which results when $Y_{\eta} = 0.04$ and when corrections-to-scaling are neglected.

Linewidth : the data were analysed according to (7) with R_0 , $\bar{A}$, a_R as adjustable parameters. Among the different possibilities for describing $\bar{\eta}$ and ξ we choose the fits with the best quality which maintained the theoretical exponent values : $\xi = 2.13 t^{-0.63}$ (Å) and $\bar{\eta} = 2.21 \times 10^{-4} t^{-0.03995} \exp[2.76/(1+t)] P_0$ for N-M, and $\bar{\eta} = 5.91 \times 10^{-8} t^{-0.04} [1 + 1.4 t^{0.7}] \times \exp[13.1/(1-t)] P_0$ for T-W. We considered for this system the turbidity data analysis of reference 23 which assumed a correction to ξ which led to $\xi = 1.28 t^{-0.63} [1 + a_{\xi} t^{0.5}]$ Å. The value $a_{\xi} = -3.5$ was deduced from the universal ratios of references 2, 9.

Fig. 1. — Deviations $\Delta\bar{\eta}$ between the experimental viscosity and expression 6, assuming $Y_{\eta} = 0.04$ with and without corrections-to-scaling. 0.1 cPo corresponds for T-W to a relative uncertainty of 2 % and 0.05 cPo corresponds for I-W to 2.5 %.

The analysis was performed in the same t -range for both the linewidth and the viscosity in order to avoid spurious artificial deviations due to extrapolations. The N-M data are from references 20, 24. The data of reference 24, obtained at $q = 3.065 \text{ cm}^{-1}$ are always in the region $q\xi < 0.2$. We have retained the most accurate data of reference 20, obtained at $q = 1.92 \times 10^5 \text{ cm}^{-1}$. We now follow the same scheme as above.

i) *No corrections*, $a_R = 0$ imposed (i.e. $R(t) = R_0$, R_0 is a constant). As shown in figure 2 important systematic distortions appear.

ii) *Corrections*, $\bar{A}$ and a_R free. The distortions now vanish. *N-M system*, reference 20 data : $\bar{A}$ cannot be accurately determined in the small t -range investigated ($\bar{A} \sim 0.5 \pm 0.4$). However figure 2 shows that a correction does exist. When the value $\bar{A} = 0.7$ is imposed, one finds $a_R = 2.0 \pm 0.1$ and $R_0 = 1.00$. The data of reference 24 leads to $\bar{A} = 0.7 \pm 0.1$, $R_0 = 1.14$, $a_R = 2.8 \pm 0.5$ when $\bar{A} = 0.7$ is imposed. The a_R values obtained for $\bar{A} = 0.7$ are then in agreement. *T-W system* : $\bar{A} = 0.56 \pm 0.05$. With $\bar{A} = 0.7$ imposed, $a_R = -8.4 \pm 0.3$ and $R_0 = 1.08$.

Fig. 2. — Variations of $R(t) = \Gamma \exp[k_B T / 6 \pi \bar{\eta} \xi] q^2 \Omega_p$ versus $T - T_c$. (B) and (C) refer to the data of references 20 and 24 respectively. The full line is the best fit to equation 7 with $\bar{A} = 0.7$ imposed. The amplitudes are given with $\bar{A} = 0.7$. For T-W, crosses correspond to the data of reference 29.

For the T-W mixture the correction is negative, and therefore it seems that it cannot be regarded as a background contribution.

The above linewidth analysis concerns the R -variations and does not depend on the precise value of R_0 , considered as a free parameter. For instance, one can see that the amplitudes of the corrections for N-M are comparable for both experimental data (B) and (C) (Fig. 2), although a 14 % discrepancy in R_0 remains. This disagreement is presumably due to small differences in the mixture composition, and in the calibration of Γ and q , which affect only R_0 . On the other hand, the R_0 -value for T-W is somewhat different from that previously published in references 7, 8, although the linewidth data remain in agreement (Fig. 2). This is due to a different method of analysis where corrections to ξ and R were ignored. In the same way, the average value $R_0 = 1.16$ of references 7, 8 must be revised accordingly, and should give a value closer to 1, in better agreement with recent experiments [20, 25-28] analysed by the M-C theory. This revision will be made in a future publication. Finally, owing to the experimental uncertainties in R_0 ($\sim 6\%$), neither the M-C ($R_0 = 1.027$) nor the R-G ($R_0 = 1.075$) values can be rejected.

5. Conclusion.

The R-G analysis of viscosity data in 3 binary fluids shows that corrections-to-scaling are present, in so far as the universality of the exponent Y_η is admitted. The same kind of analysis for the linewidth of 2 mixtures makes visible corrections-to-scaling. They are negative in one system, and consequently it seems that it cannot be regarded as a background. An effective exponent $\bar{\Delta} = 0.45 - 0.75$ has been obtained, which favourably compares with theory. Finally, the values found for the amplitude R_0 range from 1 to 1.14, as expected from the M-C or the R-G theory.

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