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Universal relations between critical amplitudes : the experimental determination of R_ξ^+

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Résumé. — Nous avons déterminé expérimentalement la constante universelle R_ξ^+ (pour la classe des fluides $n = 1$, $d = 3$) concernant l'amplitude de la partie divergente de la chaleur spécifique. Pour la première fois une bonne précision est atteinte, permettant aux valeurs dans 3 fluides binaires ($R_\xi^+ = 0,29 \pm 0,04$; $0,280 \pm 0,011$; $0,255 \pm 0,013$) d'être comparées à celles du groupe de renormalisation ($0,2696 \pm 0,0008$) et des séries haute température ($0,253 \pm 0,001$), la première valeur étant en meilleur accord avec les résultats expérimentaux.

Abstract. — We have experimentally determined the universal constant R_ξ^+ (for the class of fluids $n = 1$, $d = 3$) concerning the amplitude of the diverging part of the specific heat. For the first time a good accuracy is obtained, which allows the experimental values in 3 binary fluids ($R_\xi^+ = 0.29 \pm 0.04$; 0.280 ± 0.011 ; 0.255 ± 0.013) to be favourably compared to the renormalization group result (0.2696 ± 0.0008) and the high temperature series expansion value (0.253 ± 0.001), the renormalization group result giving a better agreement with the experimental results.

A great deal of theoretical and experimental work has already been done concerning the different critical exponents and the relations between them (*scaling laws*) [1]. In the field of critical phenomena, the knowledge of critical amplitudes is of the same universal interest, but only a few papers deal with the subject (theory : Refs. [2-6]). Ten universal relations can be evidenced [4] through the renormalization group (R-G) approach. This paper is concerned with the specific heat in binary fluids (dimensionality $d = 3$, scalar order parameter $n = 1$), which diverges with the exponent α , and whose universal amplitude ratio in the homogeneous phase is R_ξ^+ . Some attempts have already been made to experimentally determine R_ξ^+ [7-8], but the methods used ; specific heat, density and thermal diffusivity, did not provide even a significant determination of the α exponent [9]. The refractive index measurements [9] that we carried out increased the accuracy by at least one order of magnitude, while being insensitive to perturbations, especially gravity effects. In this paper we report accurate measurements of the correlation length in the same sample used in Ref. [9], which allows an accurate

determination of the universal ratio R_ξ^+ to be made in 3 binary fluids.

The relationship concerning the diverging part of the specific heat at constant pressure p and critical concentration x_c : C_{p,x_c}^0 , in the homogeneous phase (+), can be written :

$$R_\xi^+ = \left[\frac{\alpha \rho_c C_{p,x_c}^0}{k_B} \right]^{1/3} \xi_0^+.$$

Here $\alpha = 0.110$ [1, 9] is the critical exponent, k_B the Boltzmann constant, and ρ_c the critical density. ξ_0^+ is the amplitude of the correlation length $\xi^+ = \xi_0^+ t^{-\nu}$, with ν the universal exponent, and $t = (T - T_c)/T_c$ the reduced temperature. T_c is the absolute critical temperature. Taking into account possible non analytical corrections, with exponent ω_ν , the total specific heat varies as :

$$C_{p,x_c} = C_{p,x_c}^{\text{reg}} + C_{p,x_c}^0 t^{-\alpha} \left[1 + \sum_j b_j t^{j\omega_\nu} \right]$$

where C_{p,x_c}^{reg} is the regular part of the specific heat. Thus R_ξ^+ is expected to be an universal constant for a given class of systems. For fluids,

$$R_\xi^+ = 0.2696 \pm 0.0008$$

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from a R-G calculation [4-5], whereas a high temperature series expansion (H.T.S.) gives 0.253 ± 0.001 [2].

In a recent work [9], together with an accurate determination of α and ω_v , we have obtained the quantity $(\alpha \rho_c C_{p,x_c}^0 / k_B)$ in 3 binary fluids, Nitroethane-Isooctane (N-I), Isobutyric Acid-Water (I-W), and Triethylamine-Water (T-W). But it was not possible to obtain meaningful values of R_ξ^+ due to the lack of data concerning ξ_0^+ . So we measured ξ_0 in the *same* samples already used in [9], by light scattering techniques. Two kinds of measurements were carried out :

(i) **Dynamic measurements**, that we performed with a digital correlation technique in the hydrodynamic regime, i.e. in the region where the correlation length $\xi = \xi_0^+ t^{-\nu}$ is lower than q^{-1} (with $\nu = 0.630$ the critical exponent and q the transfer light wavevector), where it is now well assessed [8, 11, 12] that the relaxation time τ of the concentration fluctuations is

$$\tau = 5 \pi \eta \xi_0^+ t^{-\nu} / k_B T q^2 .$$

Fig. 1. — Relaxation time τ over viscosity η versus $T - T_c$ in the hydrodynamic regime, for the mixtures Triethylamine-Water and Isobutyric Acid-Water.

T is the absolute temperature and η the shear viscosity, well known for the systems we considered (I-W [13], T-W [14]). We imposed the R.G. value $\nu = 0.630$ (the discrepancy between R. G. and H.T.S. values is negligible when considering the experimental uncertainties). Figure 1 shows the experimental results at a scattering angle of 90° . Only few points have been recorded for the system I-W, since a previous determination [15] gave about the same ξ_0^+ value (3.60 ± 0.07 Å). Concerning the N-I mixture, we could not use this technique, the nearly perfect matching in refractive index of the components ($\approx 10^{-3}$) preventing good coupling between the concentration fluctuations and the scattered light. So we had to perform other measurements, i.e. :

(ii) **Static measurements**, from the scattered light intensity. We used a Fabry-Perot spectrometer (double-passed) with a 6 GHz free spectral range, in order to separate the central peak due to concentration and entropy fluctuations from the other contributions (Brillouin lines, depolarized lines, ...) which are not negligible in this particular mixture. The corresponding intensity measures the sum of the susceptibility $\chi_q(t)$ plus other contributions due to

Fig. 2. — Intensity of the Rayleigh peak in the Nitroethane-Isooctane system, normalized to the Brillouin lines.

Table I. — Experimental data concerning the determination of R_ξ^+ , for values of the ratio : diverging part of the refractive index/regular part, ranging from 3.8 % to 270 %. The R.G. approach gives 0.2696 ± 0.0008 [5], the H.T.S. value is 0.253 ± 0.001 [2].

System	Non analytical corrections	Divergent Regular	$k_B^{-1} \alpha \rho_c C_{p,x_c}^0 (\times 10^{21} \text{ cm}^3)$	$\xi_0^+ (\text{Å})$	R_ξ^+
N-I	no	0.037 7 (°)	1.8 ± 0.5 (°)	2.4 ± 0.15 (°)	0.29 ± 0.04
I-W	no	— 0.281 (°)	0.46 ± 0.03 (°)	3.62 ± 0.07 (°)	0.280 ± 0.011
T-W	yes	2.70 (°)	8.4 ± 0.3 (°)	1.25 ± 0.05 (°)	0.255 ± 0.013

(°) From static measurements (Fig. 1).

(°) From dynamic measurements (Fig. 2).

(°) From refractive index data of Ref. [9].

entropy fluctuations, dust, etc... which are at most weakly $(1 + t)$ dependent. Figure 2 shows that the corresponding intensity is well described near T_c by $\chi_q(t) \propto t^{-\gamma}/(1 + q^2 \xi^2)^{1-\eta/2}$ where $\eta \simeq 0.035$ [10]. The fit was performed with γ , η , ν fixed to their R. G. values [10], the discrepancies between R. G. and H. T. S. leading to about the same results within the experimental uncertainties.

In table I are summarized the experimental results concerning the determination of R_ζ^+ . It clearly appears that the values found are in significant agreement

with the predicted values. Moreover the R.G. value shows a somewhat better agreement than the H.T.S. value. This result can be compared with the determination of ω_v in Ref. [9], where also better agreement is obtained with the R.G. calculation.

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