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INVESTIGATION OF THE DYNAMICAL PROPERTIES OF LIQUID-GAS SYSTEMS BY COHERENT COLD NEUTRON SCATTERING NEAR THE CRITICAL POINT

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BUDAPEST

INVESTIGATION OF THE DYNAMICAL PROPERTIES OF LIQUID-GAS SYSTEMS BY COHERENT COLD NEUTRON SCATTERING NEAR THE CRITICAL POINT

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1. Introduction

In recent years considerable attention has been paid to critical phenomena. Inelastic neutron scattering has become a successful tool in these studies. In fact, our knowledge of the critical fluctuations in magnetic systems is based mainly on neutron scattering results [1] . Is seems therefore reasonable to extend neutron scattering investigations to critical phenomena in liquid-gas systems. The critical region can be characterized by $Q\xi \gg 1$. Here Q stands for the momentum transfer and ξ for the characteristic correlation length of the critical fluctuations [2] .

For the time being no model is available which could be used for describing the neutron scattering in the critical region. However, in the case of $Q\xi \ll 1$, it is expected that the scattering function of the isobaric and adiabatic density fluctuations can be expressed in terms of the hydrodynamical model, as

$$S^{coh}(Q,\omega)=\frac{1}{R^2(\varkappa^2+Q^2)}\left\{\frac{C_p-C_V}{\pi C_p}\;\frac{D_T Q^2}{\omega^2+(D_T Q^2)^2}+\right.$$

$$\left.+\frac{C_V}{\pi C_p}\left[\frac{\Gamma Q^2}{(\Gamma Q^2)^2+(\omega+cQ)^2}+\frac{\Gamma Q^2}{(\Gamma Q^2)^2+(\omega-cQ)^2}\right]\right\} \qquad /1/$$

where R is a length slowly varying with temperature and density [3], $\varkappa^{-1}$ is the two-body correlation length, C_p and C_V are the values of the specific heat at constant pressure and volume, respectively. D_T is the heat diffusion coefficient, c is the velocity of sound, Γ is a coefficient inversely proportional to the lifetime of the sound modes, depending on the shear and bulk viscosities of the system [4].

Even if this model does not hold near the critical temperature T_c and for large values of Q, i.e. if $Q\xi \gg 1$, it may serve as a qualitative guide for the following reasons. Sound modes are expected to exist in the critical region, the dispersion relation $\omega_Q = cQ$ is thought to be still valid, the lifetime Γ^{-1} of the sound modes must be finite and there should exist also isobaric density fluctuations. Moreover, the temperature dependence of the total scattered intensity could be also described by /1/ on introducing at large values of Q, instead of the term $\{R^2/(\varkappa^2+Q^2)\}$ some function $s(Q,T)$ representing the dependence of the total scattered intensity on scattering angle and temperature.

2. Experimental

The experiments were performed on critically loaded CO_2 and CS_2 samples. The transmission for CO_2 was 94 %, that for CS_2 85 %. CO_2 was chosen because its thermodynamic constants near the critical point have been already determined /5/ and CS_2 because it is liquid at room temperature and can be thus conveniently investigated in a wide range of temperatures. Each sample is pure coherent neutron scatterer.

The critical points were determined in CO_2 from small angle /1,5°, 2°, 2,5°/ scattering experiments using Be - filtered cold neutrons and a small angle scattering spectrometer. For CS_2 neutrons of λ = 1,15 Å wavelength and a neutron diffractometer were used.

The inelastic scattering data observed at different temperatures and angles were measured with the time-of-flight spectrometer described in [6] .

For the interpretation of data $\varepsilon = T-T_C/T_C$ was considered, instead of the absolute temperature near the critical point. The critical behaviour of the system was observed in the $10^{-2} \leqq \varepsilon \leqq 10^{-1}$ region.

3. Results and discussion

Fig. 1a shows the critical behaviour exhibited by the cold neutron scattering in CO_2 at small angles with Q = = 0,034 Å, 0,046 Å and 0,058 $Å^{-1}$. A similar type of temperature dependence was observed in CS_2, /Fig. 1b/ for Q_o = = 0,28 $Å^{-1}$. The same effect appears in a wide range of momentum transfer for the values of Q smaller than that corresponding to the first diffraction peak. This region in the case of CS_2 is shown in Fig.2. The inelastic neutron spectra were studied in the momentum transfer region marked by arrow. The changes in intensity are thought to be due to density fluctuation's.

At room temperature, for scattering angles $\vartheta < 40°$, the width of the quasi-elastic spectra increases with increasing angles, while for angles $\vartheta > 40°$, the width of the quasi elastic spectra decreases owing to the de Gennes [7] narrowing effect. The measured width of the spectra is much smaller than the value predicted from the hydrodynamical approximation taking into account only the heat diffusion process and the classical value [9] of the heat diffusion coefficient, i.e. $D_T = 1{,}26.10^{-3}$ cm^2/sec. The fit of the model yields $D_T = /1,4 \pm 0,3/.10^{-4}$ cm^2/sec.

The scattering spectra exhibit, in addition to the quasi-elastic, an adjacent, apparently inelastic contribution which can be explained by the presence of sound modes with dispersion relation $\omega_Q = CQ$, called Brillouin-Mandelstamm modes in the hydrodynamical model. The velocity of ultrasound measured in CS_2 at room temperature, as $1,5.10^{-5}$ cm/sec. [9] , is in good agreement with the inelastic maxima in the spectra observed at different angles.

At higher temperatures, near the critical point the velocity of sound decreases to the order of $c \approx 1.10^4$ cm/sec and the Brillouin peak appears very close to the central /quasi-elastic/line even at great angles, as seen in Fig. 3 in the spectrum taken at $\vartheta = 50^{\circ}$. At $\varepsilon = 0,04$ the width of the spectra increases rapidly /as Q^2/ with increasing angle up to $\vartheta = 26^{\circ}$, for $\vartheta > 26^{\circ}$ the width continues to change more slowly /Fig. 4./. The values of the half height are marked on the curves by arrows. The solid lines show simple Lorentzians /1/ folded with the ingoing spectrum using the largest reasonable values of D_T . This curve gives for the heat diffusion coefficient at $\vartheta = 20^{\circ}$, $D_T/ \varepsilon = 0,04/ = 3.10^{-4}$ cm^4/sec. It is clearly apparent from the figures that a Lorentzian scattering function cannot describe the measured spectra because it cannot account for the inelastic contributions appearing in the spectra at positions varying with the scattering angle. This inelastic contribution can be interpreted from both scattering on sound modes described by the hydrodynamical model and the relation $\omega_Q = CQ$.

If the classical Van der Waals equation were valid near the critical point, the heat diffusion constant would have the form

$$D_T = \frac{\lambda_0}{\rho_C T R}\left\{|T-T_C| + \frac{3}{4} T_C \left(\frac{V-V_C}{V_C}\right)^2\right\} \qquad /2/$$

where λ_o is the coefficient of heat conduction, ρ_c is the critical density, R is the universal gas constant and V is the specific volume. Using the value of $D_T = 10^{-5}$ cm^2/sec at $\varepsilon = 0{,}004$, calculated from /2/, the heat diffusion contribution to /1/ is shown along with the measured spectrum in Fig. 5. The clearly apparent great discrepancy in the region of large Q , can be explained, at least partially, by the scattering sound modes. Unfortunately the values of c, C_v, C_p and Γ near T_c are not known and the contribution from the sound modes in equation /1/ cannot be evaluated.

The value of c around T_c in CO_2 is known [10] . As an example of the CO_2 runs, the measurements at 60^o are to be seen in Fig. 6. Qualitatively the same effects were observed as in the case of CS_2. The positions of the sound peaks shift towards smaller energies if $\varepsilon \rightarrow 0$, in agreement with the reported data [10] . The horizontal bars in the figure indicate the full width at half height for infinite lifetime of sound modes. The measured distribution is seen to be definitely broader. The narrowing of the central line near T_c should be also observed. This indicates a decrease in D_T near the critical temperature.

Conclusions

It is seen that the scattering spectra measured at different angles cannot be described by a simple Lorentzian function. The large inelastic contributions observed near the quasi-elastic spectra can be explained by the presence of sound modes considered in terms of the proposed hydrodynamical approximation as Brillouin modes. The inelastic contribution varies with the scattering angle as defined by the relation $\omega_Q = cQ$ and exhibits the same temperature dependence as that of the sound velocity, c.

The comparison of the observed inelastic contribution with the adiabatic term in /1/ could not be performed since the separation of the isobaric and adiabatic spectra seems to be extremely difficult without any satisfactory theory and sufficiently reliable thermodynamic data /specific heat, viscosity, thermal conductivity, velocity of sound etc./.

Acknowledgments

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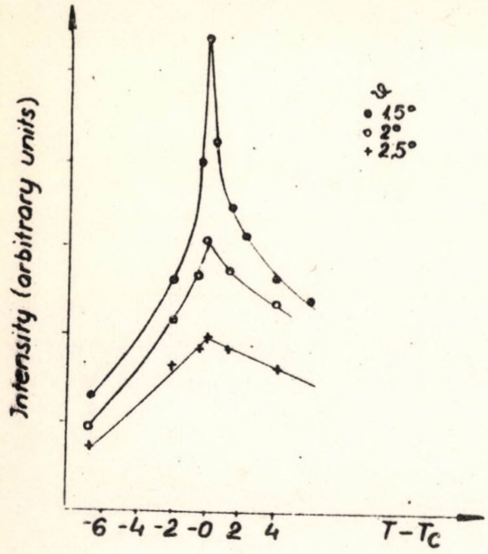

Fig. 1.a

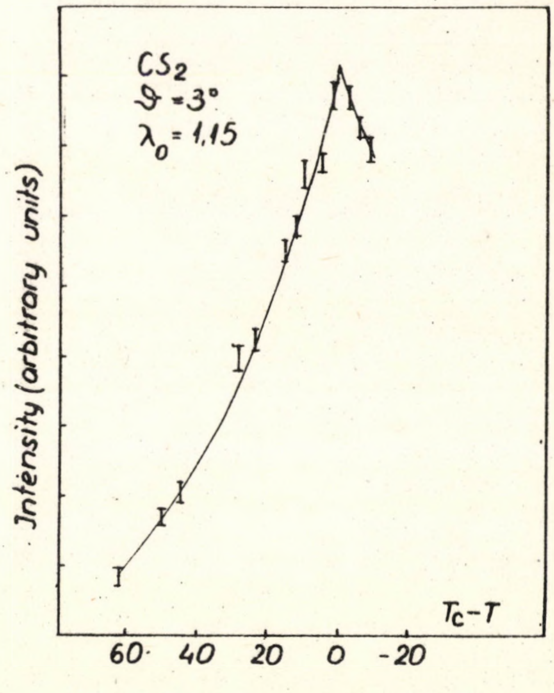

Fig. 1.b

Fig. 1.a. Critical Scattering of Be Filtered Cold Neutrons by CO_2. Temperature dependence of intensity at different scattering angles.

Fig. 1.b. Temperature dependence of scattered neutrons with $\lambda_0 = 1,15$ Å by CS_2 at $\vartheta = 3^{\circ}$ scattering angles.

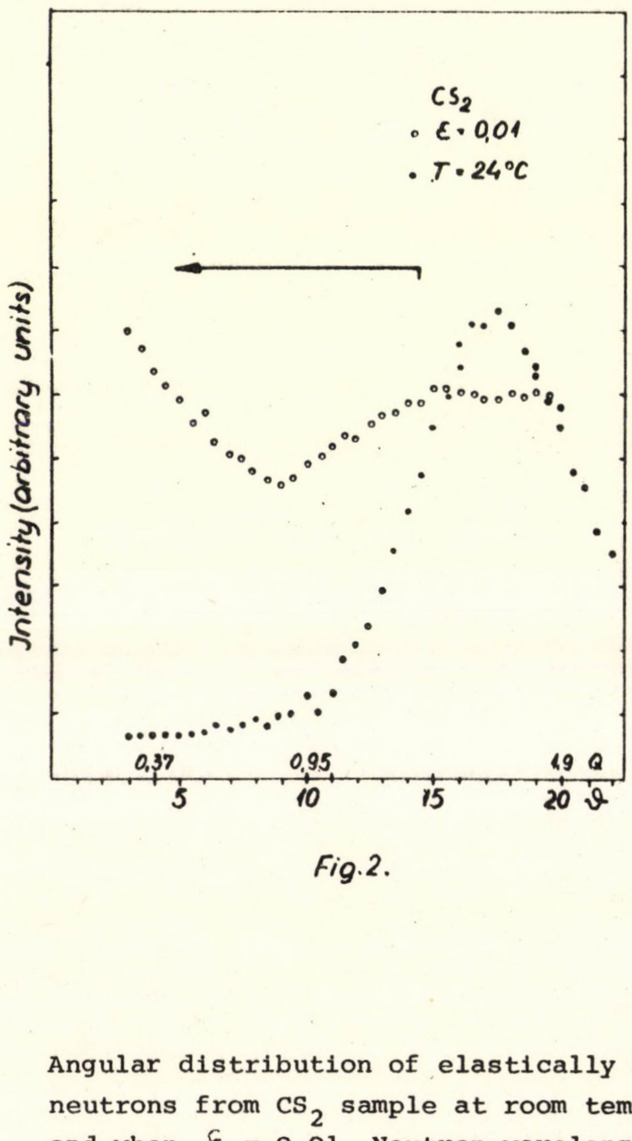

Fig.2.

Fig. 2. Angular distribution of elastically scattered neutrons from CS_2 sample at room temperature and when $\mathcal{E}$ = 0,01. Neutron wavelength λ_0 = 1,15 Å.

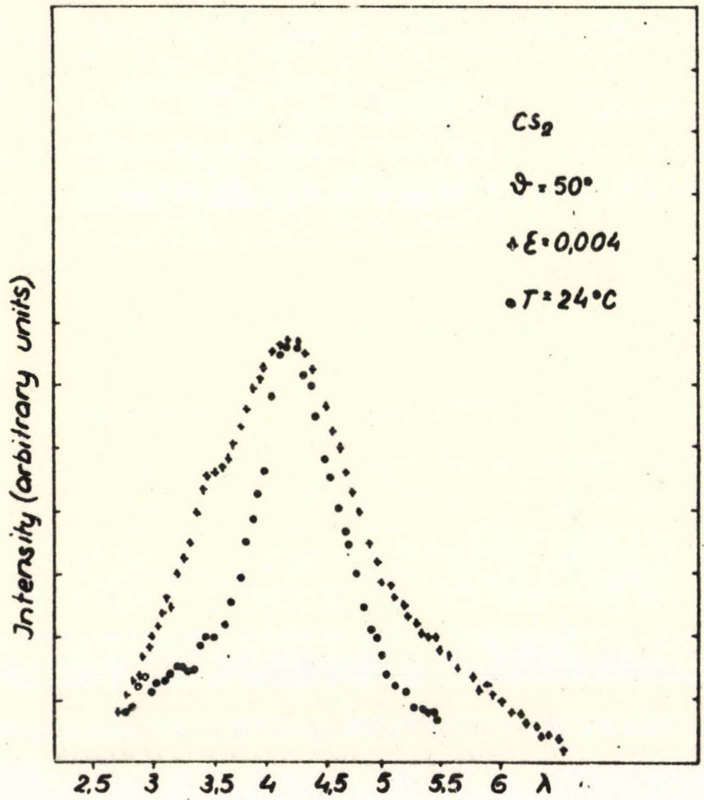

Fig. 3.

Fig. 3. The scattered neutron spectra on CS_2 at room temperature and near to critical point.

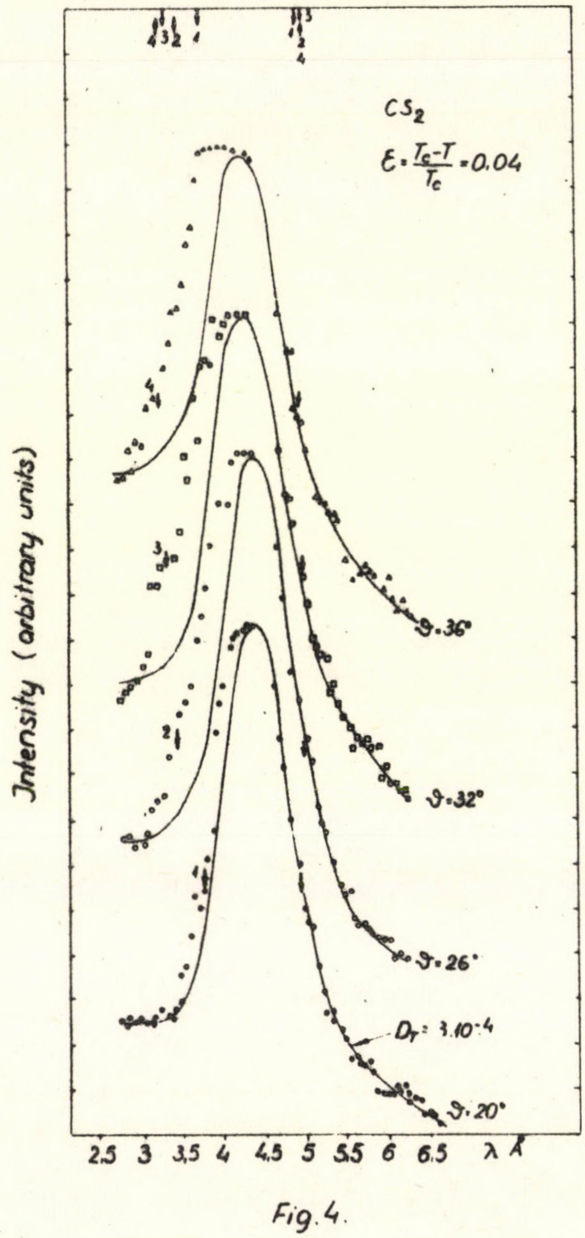

Fig. 4.

Fig. 4. Inelasticaly scattered neutron spectra on CS_2 at ε = 0,04 and different angles. The solid lines in the figure indicate the folding of in going spectra with Lorentzian scattering function, when $D_T = 3.10^{-4}$ cm^2/sec at $\vartheta = 20^o$ and D_T = $= 4.10^{-4}$ cm/sec in other cases. The arrows show the positions of the measured half width values at different angles.

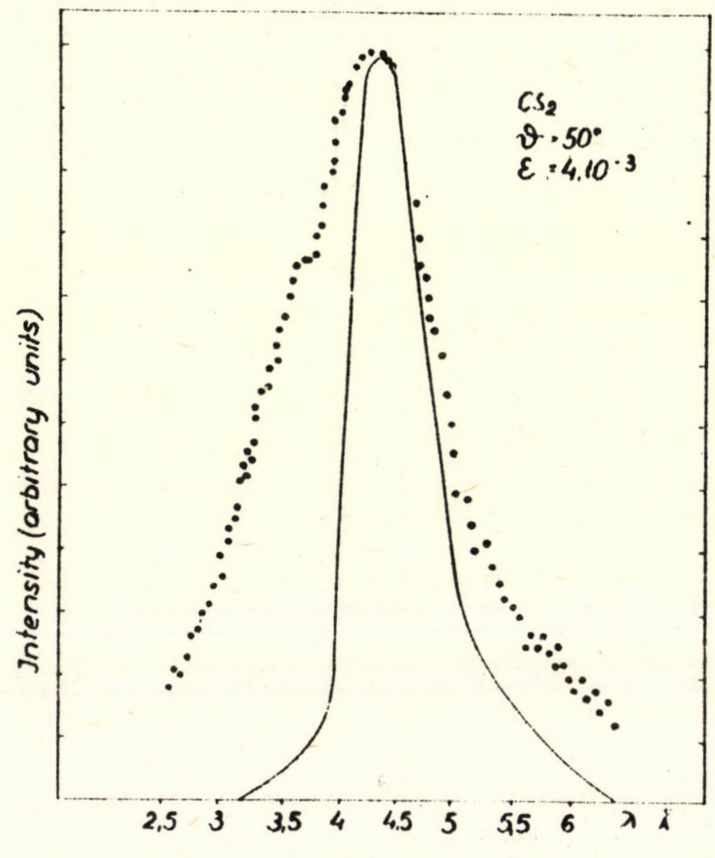

Fig. 5.

Fig. 5 The measured scattered neutron spectra near to critical point with $\varepsilon = 4.10^{-3}$ and the calculated one with $D_T = 10^{-5}$ cm^2/sec.

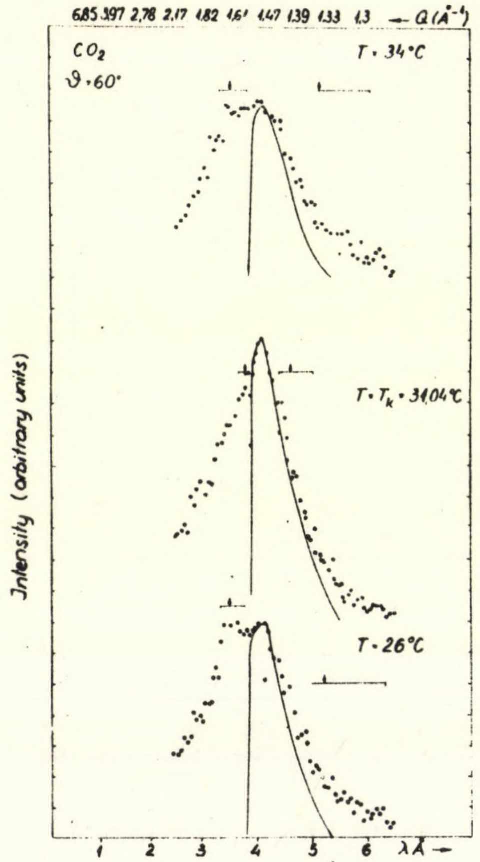

Fig.6.

Fig. 6. The inelastically scattered neutron spectra at $\vartheta = 60^{o}$ at different temperatures $\mathcal{E} = 1.10^{-3}$, $\mathcal{E} = 1,3.10^{-4}$ and $\mathcal{E} = 1,6.10^{3}$. The solid lines in the figure indicate the ingoing spectrum, the arrows the positions of the Brillouin scatterings.

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