Experimental Report

08/10/2013

Proposal:	**6-02-499**	**Council:**	4/2012
Title:	Violation of the Gaussian approximation in the incoherent inelastic spectrum of parahydrogen-deuteriumquantum mixtures		

This proposal is a new proposal

Researh Area: Physics

Main proposer: **COLOGNESI Daniele**

Experimental Team: COLOGNESI Daniele
BAFILE Ubaldo
CELLI Milva

Local Contact: ORECCHINI Andrea

Samples: deuterium plus para-hydrogen / D_2 + H_2

Instrument	**Req. Days**	**All. Days**	**From**	**To**
IN4	6	5	14/11/2012	19/11/2012

Abstract:

In the proposed experiment two parahydrogen plus deuterium liquid mixtures (namely: c[p-H2]=30%, n=40.724 mol/l and c[p-H2]=50%, n=39.357 mol/l) will be investigated at T=20 K through incoherent inelastic neutron scattering on the chopper spectrometer IN4C using an incident wavelength of 1 Å, obtained employing the Cu (220) Bragg reflection. In addition, a pure normal deuterium sample (n=42.508 mol/l) will be also measured and used as a reference. The authors have a documented experience in the study of semi-quantum liquids and have recently proved the breakdown of the Gaussian approximation (i.e. the direct connection between the velocity auto-correlation function and self-dynamic structure factor) in pure liquid hydrogen. Now this study could represent a significant step forward in the knowledge of the applicability range and the limits of the Gaussian approximation, since the amount of D_2 modifies the self dynamics of H_2 in a highly non-trivial way, acting both on its pseudo-phononic and its diffusive parts in a tuneable way.

Violation of the Gaussian approximation in the incoherent inelastic spectrum of parahydrogen-deuterium quantum mixtures

D. Colognesi, U. Bafile, M. Celli, and F. Formisano

Abstract

A well-known approach to the self-dynamics of liquids is based on the so-called Gaussian approximation, where it is assumed that the motion of a molecule is fully determined by a unique function of time directly related to the velocity autocorrelation function. Experimental inquiries into the presence of non-Gaussian dynamics are scarce, particularly concerning low-temperature liquids exhibiting moderate quantum effects (*i.e.* H_2, D_2, and Ne). Though experimental evidence of the breakdown of the Gaussian approximation in liquid H_2 has been obtained by the present authors few years ago, the density behavior of this phenomenon and its link with the self-diffusion coefficient are still unknown. These two issues have been tackled by a new neutron investigation on three liquid H_2-D_2 isotopic mixtures with different H_2 concentrations.

Introduction

Understanding the microscopic dynamics of liquid systems exhibiting moderate quantum effects, such as H_2, D_2 and Ne, is still one of the open problems in condensed matter physics [1]. Given this situation, any precise experimental determination of their dynamic quantities (i.e. time-correlation functions or their frequency spectra) that can be compared to corresponding theoretical predictions becomes highly valuable, like, for instance, a recent experiment on liquid H_2 performed by the present authors [2]. In this study we have obtained experimental spectra on the microscopic single-particle dynamics of *parahydrogen* (p-H_2) in its liquid mixtures with *normal deuterium* (n-D_2). This hydrogen-based liquid system has been selected because of the peculiar molecular hydrogen properties when H_2 is interacting with thermal neutrons: as explained in detail in the literature [3], it is possible to single out the self-dynamics of the p-H_2 molecular *centres-of-mass* (CoM) (*i.e.* $S_{s,cm}(Q,E)$ with Q and E being the wave-vector and energy transfers, respectively) in a condensed system by means of inelastic neutron scattering. Then it is a common practice to try to connect $S_{s,cm}(Q,E)$ to the power spectrum of the *velocity auto-correlation function* (VACF). This connection is generally attempted by means of the well-known *Gaussian approximation* (GA) [4]. In this respect, the mentioned work on pure liquid p-H_2 [2], making use of IN4C, was able to detect clear experimental evidences of a GA breakdown four times larger than in liquid Ar, possibly due to the more quantum nature of the former system. Thus the purpose of the present experiment has been to investigate the GA when applied to p-H_2 mixtures with n-D_2: here the quantum character of H_2 is stronger than in the pure liquid, as shown by comparing the respective zero-point CoM mean kinetic energy values [5]. In addition, one can observe a lower value of the H_2 self-diffusion coefficient, D_s, since the diffusive motion of H_2 is hindered by an increased density and, possibly, by the formation of short-lived D_2 cages around the molecule. Advanced quantum Monte Carlo calculations of the mixture dynamics have been already performed by

Prof. M. Neumann (Univ. of Vienna) in order to yield simulated VACF spectra to be used as inputs for testing the GA via a comparison with the experimental data (see Fig. 1).

Experimental Neutron Scattering Procedures

We have measured the inelastic neutron scattering spectra of liquid mixtures of p-H_2 and n-D_2 at $T\approx$20.2-20.4 K in the region of the first H_2 rotational line (*i.e.* J=0$\rightarrow$$J$=1) in an extended range of Q. Due to the possible dependence of the GA validity on the n-D_2 concentration via the density change, we have performed the measurements at three different mixture compositions, namely: c[p-H_2]=24% (n=24.40 nm^{-3}), c[p-H_2]=32% (n=24.01 nm^{-3}), and c[p-H_2]=50% (n=23.24 nm^{-3}). In addition, a pure n-D_2 sample (n=25.52 nm^{-3}) has been measured and used as a reference. Short runs on the corresponding frozen samples ($T\approx$13.7-14.7 K) have been also recorded for calibration purposes. The experiment has been carried out using a HOPG(004) monochromator at λ=1.153 Å (E_i=61.53 meV), covering an E spectral region between -40 and 56 meV, which allows to measure a wide spectral interval around the first rotational transition of molecular p-H_2 (we remind that, due to the recoil effects, the first rotational transition is shifted to a considerable higher energy with respect to 14.7 meV). The interesting Q-interval ranges between 1.5 Å^{-1} and 6.0 Å^{-1}. The available energy resolution, of the order of 3.2-3.8 meV, is largely sufficient for our purposes, due to the broadening and shifting of the rotational line caused by recoil effects. Data analysis is at the moment still in progress.

TAB. I: Experimental conditions of the neutron measurements performed on IN4C, including: temperature T, counting time τ, *molecular density n,* p-H_2 *concentration (molar)* c[H_2], *and pressure p.*

SAMPLE	T (K)	τ (s)	n (nm^{-3})	c[H_2] (%)	p (mbar)
empty cell	20.70	43090	-	-	-
n-D_2, liquid	20.26	58008	25.52	0	358
25% p-H_2, liquid	20.22	50400	24.40	24	600
33% p-H_2, liquid	20.39	39600	24.01	32	640
50% p-H_2, liquid	20.26	46180	23.24	50	759

Bibliography

[1] P. A. Egelstaff, *An introduction to the Liquid state* (Clarendon Press, Oxford, 1994).
[2] M. Celli *et al.*, Phys. Rev. B **84**, 140510R (2011).
[3] J. A. Young and J. U. Koppel, Phys. Rev. **A33**, 603 (1964).
[4] A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 986 (1962).
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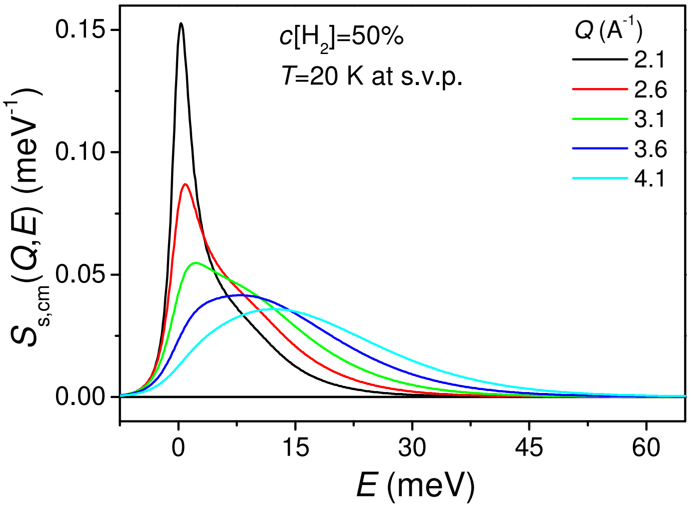

FIG.1. Simulated self H_2*-CoM spectra for an* H_2-D_2 *mixture (namely c*$[H_2]$*=50%) at T=20 K (and saturated vapor pressure), obtained applying the GA to the output of the Ring-Polymer Molecular Dynamics calculation of the* H_2 *VACF. These types of spectrum will be crucial for the detection of the non-Gaussian behavior of the measured* H_2-D_2 *mixture samples.*