

Quantum diffusion of molecular hydrogen in liquid Ne + H₂ mixtures: A quasielastic neutron scattering study

Daniele Colognesi ^{1,*} Ubaldo Bafile ¹ Milva Celli ¹ Leonardo del Rosso ¹

Franz Demmel ² and Martin Neumann ³

¹*Consiglio Nazionale delle Ricerche, Istituto di Fisica Applicata “N. Carrara,” via Madonna del Piano 10, I-50019 Sesto Fiorentino (FI), Italy*

²*ISIS Neutron and Muon Facility, Rutherford Appleton Laboratory, Didcot OX11 0QX, United Kingdom*

³*Fakultät für Physik der Universität Wien, Kolingasse 14-16, A-1090 Wien, Austria*



(Received 13 February 2026; accepted 1 July 2026; published 16 July 2026)

This study presents an analysis of the diffusional dynamics of H₂ impurities in liquid Ne using quasielastic neutron scattering (QENS) and quantum dynamical simulations. By applying a Lorentzian fitting procedure, we identify two key spectral features: peak width (Γ) and intensity (A), both of which are highly dependent on the momentum transfer Q . At low Q values, the experimental results for Γ align well with simulated self-diffusion coefficients. However, at higher Q , QENS data reveals a sublinear variation with respect to Q^2 that characterizes a jump diffusion process. Using the Hall and Ross model, we determine the mean residence time (τ_{CM}) and the standard deviation of jump lengths (l_{CM}). These values provide concrete evidence for the existence of Ne “pseudocages,” i.e., short-lived structures formed by neon atoms that trap H₂ molecules, confirming a hypothesis suggested in a previous research. The study highlights a strong coupling between the H₂ diffusion and its vibration within these pseudocages, driven by the high molecular density of the system. This finding underscores the necessity of moving beyond the well-known Gaussian approximation to accurately describe the microscopic dynamics of semiquantum fluids. In conclusion, this work improves the quality of available neutron spectra for H₂ in liquid Ne, correcting previous misinterpretations that were actually due to instrumental limitations rather than physical anomalies.

DOI: [10.1103/hkg3-y5t8](https://doi.org/10.1103/hkg3-y5t8)

I. INTRODUCTION

Understanding the microscopic dynamics of semiquantum liquids [1] (i.e., liquid systems exhibiting moderate quantum effects such as H₂, D₂, Ne, and their mixtures) is an interesting and partially unsolved problem in physics. Among the various open issues, four are surely worth mentioning:

(i) The violation of the Gaussian approximation (GA) [2]. Many physical models assume that the *self* (i.e., single-particle) scattering law [3] of a liquid system exhibits a Gaussian functional form. However, in semiquantum liquids, experimental data (e.g., on liquid parahydrogen [4]) show significant discrepancies that current approaches cannot fully explain.

(ii) The microscopic origin of non-Markovianity. It is difficult to characterize how memory effects (i.e., non-Markovianity) emerge from the microscopic interactions between the liquid system and its surrounding environment in semiquantum regimes [5]. A complete understanding of

the information flow and system-environment correlations is still lacking. (iii) The handling of the “quantum potential.” In semiclassical hydrodynamic models (such as the Madelung’s [6]), the so-called quantum potential introduces higher-order gradients. These make the equations computationally difficult to handle [7] and lead to numerical instabilities, especially in the presence of quantum vortices.

(iv) Glass transition and dynamical arrest. There is still no first-principles microscopic theory that quantitatively describes the dynamic slowing down toward a glassy state in dense liquids when quantum and statistical fluctuations overlap [8].

In addition, the topic of the self dynamics in binary liquid mixtures (not necessarily exhibiting quantum effects) is of great interest in itself, given the need to understand how the single-particle properties of one component change drastically due to the presence of the other component. For example, in some systems, a “decoupling” phenomenon is observed: one species can diffuse much faster than the other [9], challenging the predictions of the classical hydrodynamic theory (i.e., the Stokes-Einstein law). Local confinement effects are also attracting a certain degree of attention: in a mixture, each particle is trapped in a short-lived pseudocage formed by both identical and different particles. The interest lies in understanding how the mixture microstructure (for example, whether particles tend to aggregate or repel each other) modifies the lifetime of this pseudocage, thereby slowing down or

*Contact author: d.colognesi@ifac.cnr.it

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article’s title, journal citation, and DOI.

accelerating self-diffusion [10]. Finally, the species-specific glass transition is also currently under investigation: In glass-forming binary mixtures, it is possible for one species to “freeze” into a solid state (i.e., the mentioned “dynamic arrest” [10]), while the other continues to move relatively freely through the framework created by the frozen component [11]. Among the various open problems just mentioned regarding semiquantum fluids and the self dynamics of binary mixtures, this article will address both the issue of non-Gaussianity and that of short-lived pseudocages.

Given this situation, any precise experimental determination of dynamic quantities (i.e., transport coefficients and frequency spectra of time-correlation functions) related to semiquantum systems that can be compared with corresponding theoretical and computational predictions becomes very valuable, like, for instance, the recent neutron scattering measurements on pure H_2 [4,12], D_2 [13], and Ne [14], on isotopic $D_2 + H_2$ mixtures [15], as well as on the pseudoisotopic Ne + H_2 [16] and Ne + D_2 [17] systems. In particular, in the cited studies involving hydrogen, the authors have obtained estimates of the self scattering law of the H_2 centers of mass (CMs), $S_{s,CM}(Q, \omega)$, in the pure liquid and in its mixtures with either D_2 or Ne. The mentioned physical quantity $\hbar Q$ and $\hbar\omega$ represent the momentum and the energy transferred from the scattered neutron to the hit nucleus, respectively. These results have been achieved because the coherent cross sections of H_2 , D_2 , and Ne are substantially smaller than the incoherent one pertaining to H_2 , so the contributions to the inelastic signal from collective motions were practically negligible. In addition, the rotational excitations of H_2 can be accurately described and removed (when necessary) from the recorded spectra making use of the generalized Young and Koppel model (GYK) [18]. In Refs. [4,15,16], $S_{s,CM}(Q, \omega)$ was connected to the power spectrum of the simulated *velocity autocorrelation function* (VACF) by means of the GA, providing experimental evidences that, in liquid H_2 , $D_2 + H_2$, and Ne + H_2 , the GA violations are small but still sizable. Another important physical information tentatively extracted from the Ne + H_2 spectra of Ref. [16] (namely, in the $2.25 \text{ \AA}^{-1} \leq Q \leq 3.75 \text{ \AA}^{-1}$ range) was the diffusional behavior of the H_2 molecules in this system. However, we must stress that the employed instrument (i.e., a direct-geometry time-of-flight spectrometer) was a typical *inelastic neutron scattering* (INS) beam line. This means that it was not designed to perform accurate *quasielastic neutron scattering* (QENS) measurements, since neither its Q and ω range, nor the corresponding instrumental resolution $\Delta\omega$, are optimized to accomplish such experiments. In addition, a complete and detailed theory for space-dependent self diffusion in quantum and semiquantum fluids has not been established yet, so it was necessary to simply focus on the *full width at half maximum* (FWHM) of the QENS peak (represented by the symbol Γ). A comparison between experimental and GA-based FWHM results was particularly important since the long-time hydrodynamic limit of the GA implies the so-called continuous diffusion mechanism, while there are some clues that the H_2 self dynamics inside heavier liquids exhibits jump diffusion features due to short-lived pseudocages, which are incompatible with the GA [19]. Experimental and GA-simulated FWHM results for two different mixture samples (i.e., those with hydrogen

concentration, $x[H_2]$, equal to 10% and 3.5%) were plotted in Fig. 10 of Ref. [16] as ratios $\Gamma/(2Q^2)$ versus Q^2 , together with their hydrodynamic limit values (i.e., the self diffusion coefficients, $D_{s,CM}$, obtained from quantum centroid molecular dynamics simulations, namely, $3.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $2.70 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for $x[H_2] = 10\%$ and 3.5%, respectively). A physical interpretation of the GA behavior was apparently straightforward: simulated data show the correct hydrodynamic limit at low- Q values, while, for larger momentum transfers, they exhibit a broadening which grows faster than Q^2 for both H_2 concentrations. This was a known property of the overall GA spectra and had already been described in the scientific literature [20]. As for the experimental data, results were slightly more difficult to be interpreted, even though their general trend looked understandable: the FWHM versus Q^2 grew in an under-quadratic way [i.e., $\Gamma/(2Q^2)$ decreased] for $2.25 \text{ \AA}^{-1} \leq Q \leq 3.3 \text{ \AA}^{-1}$ and then, for higher- Q values, this trend seemed reversed, with the experimental peak width proceeding almost parallel to the GA-simulated one. However, some features were quite puzzling: data for the two mixture samples showed a strikingly similar behavior, but their separation was lower than expected (i.e., about one third) if one considered the respective hydrodynamic limits. In other words, the widths at the lowest Q value (i.e., $2.25 \text{ \AA}^{-1}$) did not seem to exactly approach the quantum-simulated $D_{s,CM}$. In addition, and probably more important, the minimum value of $\Gamma/(2Q^2)$ was located for both samples at $Q = 3.25 \text{ \AA}^{-1}$, which was much larger than the position of the first maximum (i.e., $Q \approx 2.3 \text{ \AA}^{-1}$) of the total static structure factor $S(Q)$. This shift in Q is completely unexpected since the correspondence between the minimum of $\Gamma/(2Q^2)$ versus Q^2 and the first maximum of $S(Q)$ is well established in various simple liquids (Ar, Ne, etc.), both experimentally and through simulation and theoretical work [20–22]. For all the reasons reported, and also because the only other QENS data [23] available in the literature are not usable for our purpose, we have performed a new detailed QENS study on the H_2 single-particle microscopic motion in the Ne + H_2 mixture at two concentration levels and two density values, to clarify the nature of the quantum diffusional mechanism, mainly focusing on its differences from the GA and the Fickian hydrodynamic regime. Subsequently, updated quantum molecular dynamics simulations have also been carried out and their outputs compared with the new experimental results.

The rest of the paper will be organized as follows: Sec. II will deal with the QENS experimental procedure and the subsequent data analysis, while Sec. III will be fully devoted to quantum simulations, concerning both equilibrium and dynamical properties of the mixtures, with a particular reference to their diffusional behavior. In Sec. IV experimental and simulation results will be discussed and used to address the main scientific problems underlined in this introduction. Finally, Sec. V will conclude the present study.

II. QENS EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

QENS measurements were performed on OSIRIS [24], a so-called inverse-geometry near-backscattering spectrometer based on the time-of-flight technique and installed at the

TABLE I. Experimental conditions of the measured samples, including: number “No.,” description, temperature T , hydrogen molar concentration $x[\text{H}_2]$, pressure p , total molecular density n , and integrated proton current “IPC.” Estimated statistical uncertainties are reported in parentheses.

No.	Description	T (K)	$x[\text{H}_2]$ (%)	p (bar)	n (nm ⁻³)	IPC (μA h)
1	Vanadium	295(3)				348.7
2	Empty Al container	30.00(1)				425.7
3	Liquid Ne	30.01(1)	0.00	2.242(6)	34.383(6)	1911.2
4	Liquid Ne	26.95(6)	0.00	0.97(2)	36.07(3)	2372.3
5	Liquid Ne + H ₂ mix.	26.96(5)	3.010(2)	3.52(1)	34.99(3)	2650.7
6	Liquid Ne + H ₂ mix.	30.01(2)	3.010(2)	5.237(3)	33.27(1)	1897.7
7	Liquid Ne + H ₂ mix.	30.00(3)	6.99(7)	6.46(3)	31.93(7)	2077.7

ISIS Neutron and Muon Source (Rutherford Appleton Laboratory, United Kingdom). The final neutron energy is selected by means of Bragg scattering from a large-area pyrolytic graphite (PG) crystal-analyzer array, while scattered neutrons are detected by 42 ³He gas detectors covering a wide angular range: $11^\circ \leq 2\theta \leq 148^\circ$. Our requirements in terms of Q were met by selecting a PG004 analyzer ($\lambda = 3.33 \text{ \AA}$) which gave rise to an accessible energy transfer range $-3.0 \text{ meV} \leq \hbar\omega \leq 5.0 \text{ meV}$ and a momentum transfer range $0.4 \text{ \AA}^{-1} \leq Q \leq 3.5 \text{ \AA}^{-1}$. The available energy resolution amounted to $\Delta\hbar\omega = 99.0 \text{ } \mu\text{eV}$, which is a value sufficient for our purposes.

A complete description of the measured samples (including temperature T , hydrogen molar concentration $x[\text{H}_2]$, pressure p , total molecular density n , and integrated proton current IPC) is reported in Table I, where the ancillary measurements on the vanadium calibration standard (i.e., sample No. 1 at room temperature) and the empty container (i.e., sample No. 2 at $T = 30 \text{ K}$) are also listed. Temperature and pressure were directly monitored during the experiment, while the total molecular density was calculated using T , $x[\text{H}_2]$, and p in conjunction with thermodynamic data available in the literature: Ref. [25] for pure neon, and Refs. [26–28] for neon-hydrogen mixtures. Another important issue was the rotational population of the H₂ molecules contained in the experimental samples from No. 5 to No. 7, where the so-called *normal hydrogen* (n-H₂) assumption was employed. This means that the concentration of orthohydrogen (o-H₂) was not in thermodynamic equilibrium at the actual temperatures of the samples ($T \approx 27\text{--}30 \text{ K}$), but it was that of the room temperature mixture: $x[\text{o-H}_2]/x[\text{H}_2] = 0.75$. This was possible since the spontaneous low-temperature orthopara conversion proceeds very slowly, with a typical time of the order of days [29], in the liquid phase with no appropriate paramagnetic catalysts present. However, we experimentally checked the stability of this ratio during the experiment by comparing the overall spectral intensities of a series of partial subruns (see later for details). The scattering container was a can made of an aluminum alloy with a circular-slab geometry (annulus) and consisted in two concentric vertical cylinders giving rise to a 2.0-mm void (to be filled with the liquid sample) exhibiting an average diameter of 20.0 mm. The external diameter of the container (25.2 mm) was quite close to the horizontal beam size (about 22 mm), while the active part of the container (i.e., the portion filled with the liquid samples and amounting to 51.0 mm) was rather bigger than the vertical beam size

(about 44 mm). The can was masked with boron nitride ceramics to exclude its bulky ends which contained only thick metal and no liquid sample. In this way, the portion of can irradiated by neutrons was reduced to approximately 45 mm in length.

As for the pure Ne samples, the preparation of sample No. 4 was quite simple: the temperature of the can was set to $T = 32.5 \text{ K}$ and some neon gas (CK Special Gases Ltd., 99.995% assay, N 4.5 grade) was allowed to condense in it at a pressure of $p \approx 8.5\text{--}9.0 \text{ bar}$, somewhat larger than the corresponding saturated vapor pressure. Then, the container temperature was slowly decreased to $T = 10.0 \text{ K}$ where the pressure reached the final value of $p = 20.5 \text{ mbar}$ with Ne totally frozen in the sample can. At this stage, in view of the value of the initial volume of the neon gas (i.e., 500.0 cm^3) stored in the handling system, we were confident that the scattering container was completely filled with the Ne sample. Later the temperature was raised to 27.0 K , the pressure was adjusted to $p = 0.97 \text{ bar}$, and a neutron measurement of sample No. 4 was started (see Table I). Sample No. 3 was prepared and measured at $T = 30.0 \text{ K}$ following a similar procedure. Moving to the mixture samples we have to note that the preparation of No. 6 was slightly more complex: an appropriate amount of n-H₂ gas (CK Special Gases Ltd., 99.99% assay, N 4.0 grade) was mixed with some neon gas in a buffer volume (500.0 cm^3) at room temperature under a pressure of $p = 18.86 \text{ bar}$. The exact amount of gaseous mixture needed to fill up the sample can with liquid was condensed at $T = 28.0 \text{ K}$. Then, the can was slowly cooled down to $T = 10.0 \text{ K}$, to decrease the vapor pressure of the gas handling line to $p = 20.4 \text{ mbar}$ only. This step, together with the following one, was considered as quite important to prevent a possible sample demixing. Subsequently, the sample container was isolated from the gas handling line and warmed up to the requested experimental temperature (i.e., 30.0 K). An internal pressure, first oscillating in the range $5.2\text{--}5.3 \text{ bar}$, spontaneously built up and stabilized to the values of Table I after a long equilibration time of the order of $1\text{--}1.5 \text{ h}$. Finally, the actual neutron measurement of sample No. 6 started, lasting for about 12 h , evenly divided in six subruns. Samples No. 5 and No. 7 (see Table I) were mixed, condensed, and measured following a procedure analogous to that outlined above, always paying attention to the sample stability by comparing corresponding subruns. An example, related to sample No. 5, of the so-called “raw spectra” $I_{s+c}(Q, \omega)$ (i.e., those including

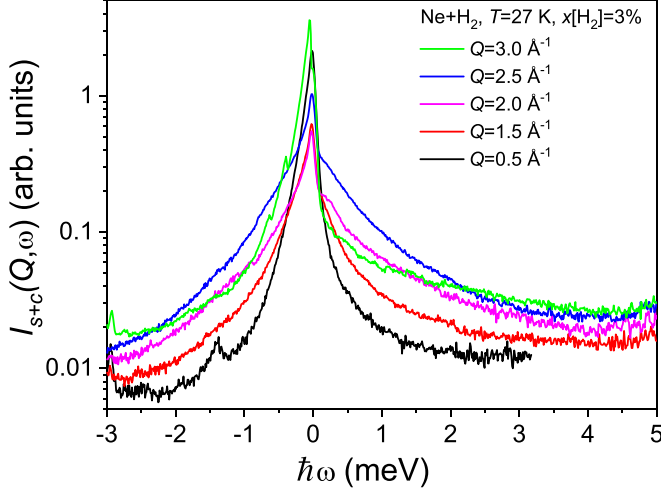


FIG. 1. Examples, related to sample No. 5, of the raw spectra $I_{s+c}(Q, \omega)$, including both mixture and can signal, for some selected Q values ranging from $0.5 \text{ \AA}^{-1}$ (bottom) to $3.0 \text{ \AA}^{-1}$ (top). See Table I and the main text for details.

both can and mixture signal) is reported in Fig. 1 for some selected Q values ranging from 0.5 to $3.0 \text{ \AA}^{-1}$.

A standard neutron scattering data reduction was applied to the $I_{s+c}(Q, \omega)$ spectra from samples No. 3 to No. 7. This procedure was composed of three main steps:

- Empty container scattering removal (carefully taking into account the attenuation due to the sample transmission).
- Sample self-shielding correction.
- Multiple scattering evaluation (found negligible for all the five samples).

In this way the fully processed spectra, $I(Q, \omega)$, were obtained, being directly related to the double differential neutron scattering cross section of the liquids under investigation. In the case of the pure neon samples the analysis ended here: since the Ne incoherent cross section is totally negligible with respect to the coherent one ($\sigma_{\text{inc}}[\text{Ne}] = 0.008 \text{ barn} \ll \sigma_{\text{coh}}[\text{Ne}] = 2.620 \text{ barn}$ [30]), it was possible to associate the $I(Q, \omega)$ for samples No. 3 and No. 4 to the purely coherent scattering law of the respective systems: $I(Q, \omega) = I_{\text{coh}}(Q, \omega)$. In what follows we will call them $I_p(Q, \omega)$ (with “p” standing for “pure Ne”) to prevent possible confusion. On the contrary, as far as the Ne + H₂ mixtures are concerned, the situation looked indeed quite different, since in this case $I(Q, \omega)$ contained both a coherent and an incoherent part: $I(Q, \omega) = I_{\text{coh}}(Q, \omega) + I_{\text{inc}}(Q, \omega)$. So, an additional step beyond the standard neutron scattering data reduction was taken.

(d) We pursued an approximate removal of the coherent spectrum $I_{\text{coh}}(Q, \omega)$ (mainly due to the collective dynamics involving Ne–Ne pairs) from the $I(Q, \omega)$ data to obtain $I_{\text{inc}}(Q, \omega)$, which is given by H₂ only. To this aim, the pure Ne spectra and the partial static structure factors (derived from quantum simulations as shown in Sec. III) were exploited through the following correction scheme:

$$I_{\text{inc}}(Q, \omega) = I(Q, \omega) - I_{\text{coh}}(Q, \omega) \approx I(Q, \omega) - I_p(Q, \omega) \frac{n}{n_p} \frac{S_{\text{Ne-Ne}}(Q)}{S_p(Q)}, \quad (1)$$

where n/n_p is the ratio between the total molecular density of the mixture and that of the corresponding pure Ne sample at the same temperature (see Table I), while $S_{\text{Ne-Ne}}(Q)/S_p(Q)$ is the ratio between the partial Ne–Ne static structure factor of the mixture and the corresponding total static structure factor of the pure Ne sample at the same temperature. This formula takes into account two important effects: the former effect is due to the fact that in the definition of $I(Q, \omega)$ and $I_p(Q, \omega)$ we are not dealing with fully normalized double differential cross sections and so the molecular densities n and n_p have to be still included as scaling factors. This is accounted for by the n/n_p correction factor, which is always slightly lower than unity. The latter effect is the more subtle one and is related to the ω -integral of the Ne–Ne partial scattering law of the mixture, $S_{\text{Ne-Ne}}(Q, \omega)$, which is not identical to that of pure Ne, $S_p(Q, \omega)$. In other words, we have reconstructed the unknown partial scattering law $S_{\text{Ne-Ne}}(Q, \omega)$ using $S_p(Q, \omega)$ in conjunction with $S_{\text{Ne-Ne}}(Q)$, following an approach which closely resembles the well-known Vineyard approximation. However, the above equation is approximate for two reasons: first, the Ne–Ne component of the mixture coherent dynamics is not exactly proportional to $I_p(Q, \omega)$. Second, the small Ne–CM component of the coherent dynamics is not removed from $I(Q, \omega)$ as we will see later in this section.

The new $I_{\text{inc}}(Q, \omega)$ data sets were suitable for a standard QENS data analysis, which was implemented as a constant- Q fitting procedure in the $-3.0 \text{ meV} \leq \hbar\omega \leq 5.0 \text{ meV}$ range through the following formula:

$$I_{\text{inc}}(Q, \omega) = A(Q)[L(Q, \omega) \otimes R(Q, \omega)] + B(Q, \omega), \quad (2)$$

where the symbol $\otimes$ stands for a convolution, $A(Q)$ represents the QENS spectral intensity, and $R(Q, \omega)$ is the energy resolution obtained via a Chesler-Cram fit [31] to the vanadium data transformed to constant- Q spectra. As for the other physical quantities in Eq. (2), $B(Q, \omega)$ is a linear background which accounts for the inelastic (i.e., nonquasielastic) component present in the fitted part of the spectrum, as shown below in Sec. IV, while $L(Q, \omega)$ stands for a detailed-balance corrected Lorentzian curve:

$$L(Q, \omega) = \frac{1}{\pi} \frac{\Gamma(Q)/2}{\hbar^2 \omega^2 + [\Gamma(Q)/2]^2} \frac{2}{\exp(-\frac{\hbar\omega}{k_B T}) + 1}, \quad (3)$$

with $\Gamma(Q)$ being the Q -dependent FWHM and k_B the Boltzmann constant. The advantage of this model over other possible detailed-balance corrections of the Lorentzian peak is the fact that in our case $\int_{-\infty}^{\infty} L(Q, \omega) d\omega = 1$. The fit quality in the whole $0.4 \text{ \AA}^{-1} \leq Q \leq 3.4 \text{ \AA}^{-1}$ range was excellent as shown by the examples in Fig. 2 (related to sample No. 5 for $Q = 1.4 \text{ \AA}^{-1}$ and $2.4 \text{ \AA}^{-1}$). Before concluding this section, it is worth discussing the physical meaning of the fitting parameter $A(Q)$ (see Fig. 3), which, in the framework of our scheme, has been taken to be the product of three factors: an unknown sample-dependent scaling factor C , the molecular form factor $f(Q)$ which is due to the H₂ rotational dynamics, and the Debye-Waller factor $\exp[-2W(Q)]$ which is related to the CM dynamics (see also Sec. IV for details). One can note that the GYK model in itself implies in the present context only the presence of $f(Q)$ and the CM self dynamic structure factor. However, since we focus on the quasielastic

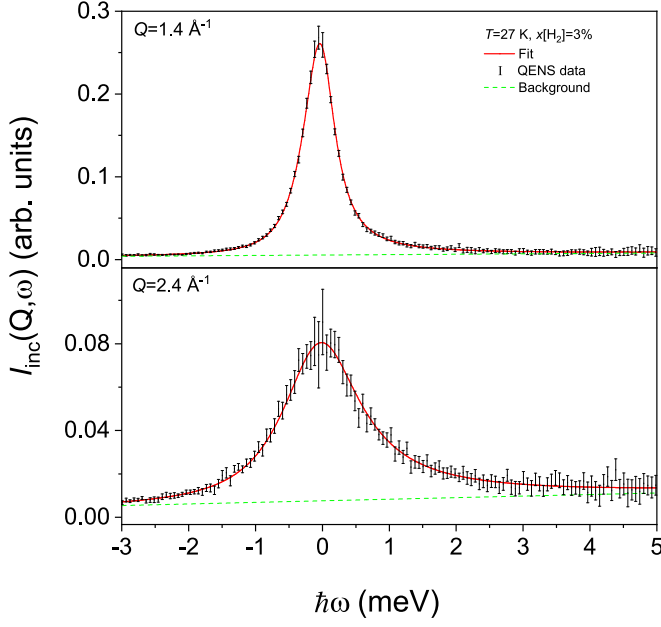


FIG. 2. Examples, related to the spectra at $Q = 1.4 \text{ \AA}^{-1}$ and $Q = 2.4 \text{ \AA}^{-1}$ for sample No. 5, of the QENS fits operated according to Eqs. (2) and (3). Red full line represents the fitting function, black error bars stand for the QENS experimental data, while the linear background is plotted as a green dashed line.

spectral range only, we can reduce such a self scattering law to $\exp[-2W(Q)]L(Q, \omega)$. As far as the form factor $f(Q)$ is concerned, in the case of purely incoherent scattering from liquid or gaseous hydrogen, it is well-known [12] that the following GYK relationship holds for the incoherent elastic rotational transitions of an orthohydrogen molecule at low temperature (i.e., from its initial rotational state $J = 1$ to its final rotational state $J' = 1$):

$$f_{1 \rightarrow 1}(Q) = x[\text{o-H}_2] \frac{4\sigma_c[\text{H}] + 8\sigma_i[\text{H}]/3}{4\pi} \times \left[j_0^2\left(\frac{Qr_0}{2}\right) + 2j_2^2\left(\frac{Qr_0}{2}\right) \right], \quad (4)$$

where $\sigma_c[\text{H}]$ and $\sigma_i[\text{H}]$ are the coherent and incoherent neutron cross section for the proton, respectively [30], while $j_n(\dots)$ represents a spherical Bessel function of n th order, and r_0 stands for the H_2 interatomic distance. One can also include the tiny contribution due to the incoherent elastic rotational transition of a para-hydrogen molecule at low temperature (i.e., from its initial rotational state $J = 0$ to its final rotational state $J' = 0$), $f_{0 \rightarrow 0}(Q)$, which according to the GYK model reads

$$f_{0 \rightarrow 0}(Q) = x[\text{p-H}_2] \frac{4\sigma_c[\text{H}]}{4\pi} j_0^2\left(\frac{Qr_0}{2}\right). \quad (5)$$

In addition, as we have mentioned above, our fitted $I_{\text{inc}}(Q, \omega)$ still contained some small “distinct” components not completely subtracted in Eq. (1), namely, those originated from the correlated dynamics of $\text{H}_2\text{--H}_2$ and $\text{H}_2\text{--Ne}$ molecular pairs. Such components give rise to a slight distortion of the form factor ($f_{1 \rightarrow 1}(Q) + f_{0 \rightarrow 0}(Q)$) which we have approximately included in the final formula for the overall molecular form

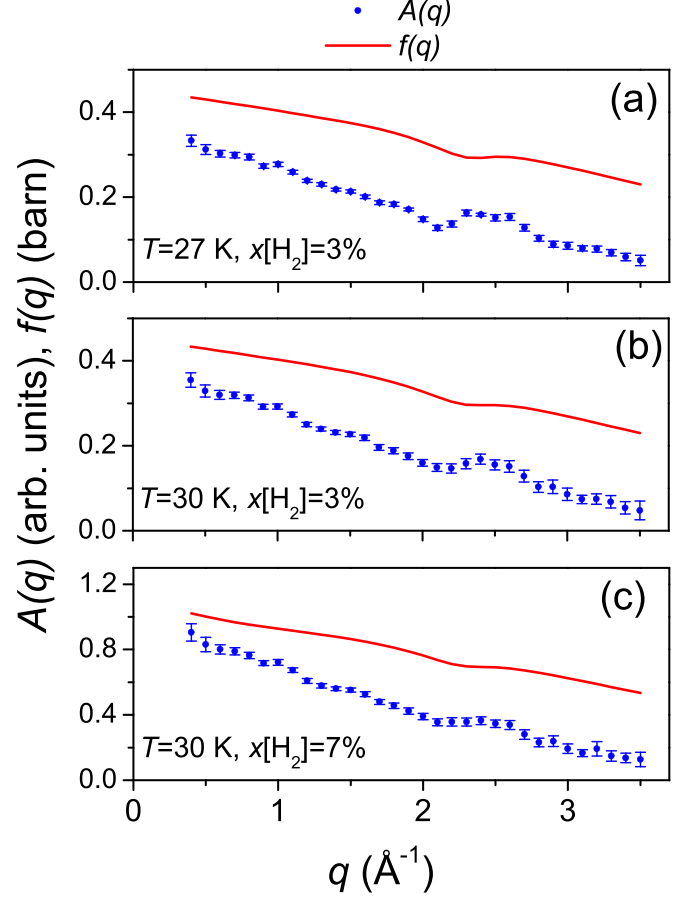


FIG. 3. Experimental QENS spectral intensities $A(Q)$ (blue circles with error bars) and molecular form factor $f(Q)$ for the H_2 rotational dynamics calculated according to the GYK model [18] (red full line) for the three mixture samples: panel (a) represents sample No. 5, panel (b) sample No. 6, and panel (c) sample No. 7 (see Table I for details).

factor $f(Q)$ as

$$f(Q) \approx f_{1 \rightarrow 1}(Q) + f_{0 \rightarrow 0}(Q) + \{x[\text{H}_2]u^2(Q)(S_{\text{CM--CM}}(Q) - 1) + 2b_c[\text{Ne}]u(Q)S_{\text{Ne--CM}}(Q)\}, \quad (6)$$

where $b_c[\text{Ne}]$ represents the Ne coherent scattering length (equal to 4.566 fm [30]), $S_{\text{CM--CM}}(Q)$ and $S_{\text{Ne--CM}}(Q)$ are the (simulated) partial static structure factors for the CM--CM and CM--Ne pairs, respectively, to be defined in Sec. III, while $u(Q)$ is given by [18]

$$u(Q) = 2b_c[\text{H}]j_0\left(\frac{Qr_0}{2}\right), \quad (7)$$

with $b_c[\text{H}] = -3.7390 \text{ fm}$ [30]. Our best estimates of $f(Q)$ for the three mixture samples are reported in Fig. 3.

III. QUANTUM DYNAMICAL SIMULATIONS

To generate the simulated data required for the study of the fully processed QENS experimental spectra, $I_{\text{inc}}(Q)$, from samples Nos. 5–7, we carried out two different types of

TABLE II. Thermodynamic conditions of the simulated samples and other details, including: simulation number, total number of particles N , number of H_2 centers of mass $N[\text{CM}]$, hydrogen molar concentration $x[\text{H}_2]$, temperature T , total molecular density n , type of technique used, type of Ne–Ne pair potential used (either Lennard-Jones [39] or HFD-B [40]), direct self diffusion coefficient $D_{s,\text{CM}}^{(d)}$ for H_2 centers of mass, extrapolated self diffusion coefficient $D_{s,\text{CM}}^{(e)}$ for H_2 centers of mass, mean kinetic energy for H_2 centers of mass $\langle E_k \rangle_{\text{CM}}$, and for Ne atoms $\langle E_k \rangle_{\text{Ne}}$. Estimated statistical uncertainties are reported in parentheses when available.

No.	N	$N[\text{CM}]$	$x[\text{H}_2]$ (%)	T (K)	n (nm^{-3})	Techn.	Ne–Ne pot.	$D_{s,\text{CM}}^{(d)}$ ($10^{-5} \text{ cm}^2/\text{s}$)	$D_{s,\text{CM}}^{(e)}$ ($10^{-5} \text{ cm}^2/\text{s}$)	$\langle E_k \rangle_{\text{CM}}$ (K)	$\langle E_k \rangle_{\text{Ne}}$ (K)
i	500	50	10.00	30.0	31.02	RPMD	LJ	3.420(2)	3.81(1)	93.9(1)	53.03(1)
ii	500	35	7.00	30.0	31.94	RPMD	LJ	3.025(1)	3.35(1)	96.0(1)	53.42(1)
iii	500	15	3.00	30.0	33.22	RPMD	LJ	2.500(3)	2.78(3)	100.5(1)	53.93(1)
iv	500	15	3.00	27.0	34.97	RPMD	LJ	1.758(1)	2.00(3)	103.5(1)	51.00(1)
v	500	0	0.00	27.0	36.07	RPMD	LJ				51.30(1)
vi	256	26	10.16	30.0	30.94	CMD	HFD-B	3.73(1)		87.6(2)	53.09(6)
vii	500	50	10.00	30.0	31.02	CMD	LJ	3.421(2)		91.3(1)	52.92(1)
viii	256	22	8.59	30.0	31.42	CMD	HFD-B	3.49(2)		88.6(2)	53.24(6)
ix	256	20	7.81	30.0	31.66	CMD	HFD-B	3.39(2)		89.0(2)	53.30(6)
x	256	10	3.91	30.0	32.94	CMD	HFD-B	2.70(2)		92.6(2)	53.72(6)
xi	256	9	3.52	30.0	33.07	CMD	HFD-B	2.66(3)		92.8(2)	53.76(6)
xii	256	6	2.34	30.0	33.48	CMD	HFD-B	2.53(3)		94.2(2)	53.89(6)
xiii	256	0	0.00	30.0	34.44	CMD	HFD-B				54.24(6)

quantum dynamical simulations based on the ring polymer representation of quantum mechanical particles, namely:

(a) Centroid molecular dynamics (CMD) [32] is based on an (ideally) quantum mechanical exact evaluation of the instantaneous forces on the polymer centers, which are then propagated according to classical mechanics. Practically, CMD is a simulation tool able to provide excellent approximations of canonical (also known as “Kubo-transformed” [33]) correlation functions in systems exhibiting moderate quantum effects (at $T > 0$), but limited to functions linear in either the particle position or momentum operators. This is surely the case as far as the canonical VACF is concerned. In addition, similarly to standard path integral Monte Carlo [34], which on the contrary is an equilibrium technique, CMD can calculate partial pair correlation functions, $g_{\alpha,\beta}(r)$ (with $\alpha = \{\text{Ne}, \text{CM}\}$ and $\beta = \{\text{Ne}, \text{CM}\}$), as well as the aforementioned partial static structure factors, $S_{\alpha,\beta}(Q)$, and single-particle mean kinetic energies, $\langle E_k \rangle_{\alpha}$ (with $\alpha = \{\text{Ne}, \text{CM}\}$).

(b) Ring polymer molecular dynamics (RPMD) [35] implements an algorithm that is similar to CMD, except it now is the beads on the polymers which are propagated classically. In essence, this means that the forces on the polymer centers are only approximately evaluated at each timestep. Otherwise, RPMD provides the same range of applications, including estimates of the canonical VACF, in addition to $g_{\alpha,\beta}(r)$, $S_{\alpha,\beta}(Q)$, and the mean kinetic energy, $\langle E_k \rangle_{\alpha}$.

The simulations we have carried out, together with their thermodynamic and numerical details, are reported in Table II, where, among the others, the total number of molecules N , the number of H_2 centers-of-mass considered $N[\text{CM}]$, the hydrogen concentration $x[\text{H}_2]$, the temperature T , and the total molecular density n (namely, from Refs. [25–28]) are listed. Our CMD calculations have been performed with a timestep of $\Delta t = 0.005$ ps at a temperature $T = 30$ K, fixed via a Gaussian isokinetic thermostat [36]. The velocity correlation functions were calculated up to a maximum time lag $t_m = 5$ ps and averaged over 10 independent runs of 10^5 timesteps

(i.e., 500 ps) each, for all the thermodynamic states from No. vi to xiii (as reported in Table II). In this way we were able to obtain an estimate of the statistical uncertainty of the results. For the total number of molecules and the Trotter number P [37], we chose $N = 256$ and $P = 64$. A test with $N = 500$ and $P = 64$ was also carried out. As for the RPMD simulations, conditions were similar to the CMD ones, but not identical: molecular dynamics runs have been performed with a timestep $\Delta t = 0.001$ ps up to a maximum time lag $t_m = 2.5$ ps at two temperatures: either $T = 27$ K or 30 K (see Table II for details), fixed by a Langevin thermostat [38]. Our final results represent averages over 20 independent batches made of 1000 individual trajectories each, for all the thermodynamic states from No. i to v (as reported in Table II). For the total number of molecules and the Trotter number, we chose this time $N = 500$ and $P = 64$. Tests with different values of P (namely, $P = 128$ or $P = 32$) have been carried out for both CMD and RPMD simulations, showing insignificant differences with respect to the mentioned calculations with $P = 64$, while the issue of the number of molecules, N , will be dealt with in detail later.

Starting with the equilibrium properties, it is worth specifying how the calculations of the $S_{\alpha,\beta}(Q)$ functions, as well as those for the total static structure factor $S(Q)$, have been implemented in the RPMD and CMD codes:

$$\begin{aligned}
 S_{\text{Ne,Ne}}(Q) &= \frac{1}{N[\text{Ne}]} \sum_{j=1}^{N[\text{Ne}]} \sum_{l=1}^{N[\text{Ne}]} \langle \exp(-i\mathbf{Q} \cdot \mathbf{r}_j) \exp(i\mathbf{Q} \cdot \mathbf{r}_l) \rangle, \\
 S_{\text{Ne,CM}}(Q) &= \frac{1}{N} \sum_{j=1}^{N[\text{Ne}]} \sum_{l=N[\text{Ne}]+1}^N \langle \exp(-i\mathbf{Q} \cdot \mathbf{r}_j) \exp(i\mathbf{Q} \cdot \mathbf{r}_l) \rangle, \\
 S_{\text{CM,CM}}(Q) &= \frac{1}{N[\text{CM}]} \sum_{j=N[\text{Ne}]+1}^N \sum_{l=N[\text{Ne}]+1}^N \langle \exp(-i\mathbf{Q} \cdot \mathbf{r}_j) \exp(i\mathbf{Q} \cdot \mathbf{r}_l) \rangle,
 \end{aligned}$$

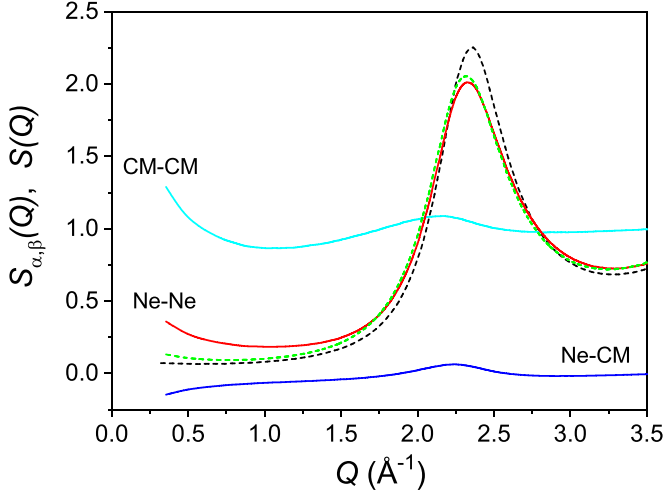


FIG. 4. Partial $S_{\alpha,\beta}(Q)$ and total $S(Q)$ static structure factors for simulation No. ii (i.e., $x[\text{H}_2] = 7\%$ and $T = 30$ K, as in Table II) calculated via RPMD. Red, blue, and cyan full lines represent the Ne–Ne, the Ne–CM, and the CM–CM partial static structure factor, respectively, while green dashed line stands for the total static structure factor. In addition, $S(Q)$ for simulation No. xiii (i.e., pure Ne at $T = 30$ K via CMD) has been included as a black dashed line to highlight the effects of the H_2 presence on the mixture.

$$\begin{aligned}
 S(Q) &= \frac{1}{N} \sum_{j=1}^N \sum_{l=1}^N \langle \exp(-i\mathbf{Q} \cdot \mathbf{r}_j) \exp(i\mathbf{Q} \cdot \mathbf{r}_l) \rangle \\
 &= (1 - x[\text{H}_2])S_{\text{Ne,Ne}}(Q) + 2S_{\text{Ne,CM}}(Q) \\
 &\quad + x[\text{H}_2]S_{\text{CM,CM}}(Q),
 \end{aligned} \tag{8}$$

where $N[\text{Ne}]$ and $N[\text{CM}]$ represent the number of Ne atoms and CMs, respectively. It is important to note that in the definitions above the Ne–CM static structure factor exhibits a normalization different from those pertaining to the Ne–Ne and CM–CM static structure factors. Some selected examples of $S_{\text{Ne,Ne}}(Q)$, $S_{\text{Ne,CM}}(Q)$, and $S_{\text{CM,CM}}(Q)$ are reported in Fig. 4.

The three interparticle interactions, i.e., Ne–Ne, Ne– H_2 , and H_2 – H_2 , have been assumed to be pairwise additive following this simple scheme:

(a) The Ne–Ne interaction was represented by two different isotropic pair potentials: either a Lennard-Jones potential using the parametrization by Morales and Nuevo [39] (which has already proved to effectively simulate the Ne– H_2 mixtures [34]) employed for the RPMD calculations (plus the CMD simulation, No. vii), or the HFD-B potential of Aziz and Slaman [40], utilized for the rest of the CMD calculations. A detailed comparative discussion on these two potentials can be found in Appendix B of Ref. [16], where we explained why, in agreement with Ref. [34], we found some clues that the Lennard-Jones Ne–Ne potential (within the mentioned parametrization) is slightly superior to the HFD-B one in reproducing the microscopic dynamic features probed by our neutron scattering experiments.

(b) The Ne– H_2 interaction, i.e., that between a CM and a Ne atom, was modeled taking the spherical average of the orientation-dependent potential developed by Faubel

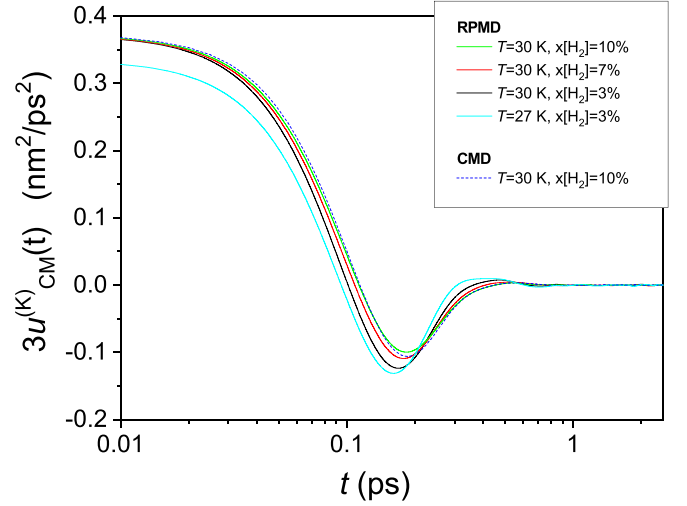


FIG. 5. Canonical VACFs for the H_2 CM from simulations No. i (green full line), No. ii (red full line), No. iii (black full line), and No. iv (cyan full line), all calculated via RPMD (see Table II for details). In addition, $u_{\text{CM}}^{(K)}(t)$ from simulation No. vii obtained via CMD has been included as a blue dashed line.

et al. [41], following the approach suggested by Challa and Johnson [34].

(c) The H_2 – H_2 interaction, i.e., that between two CMs, was described using the isotropic Silvera and Goldman potential [42].

As mentioned above, in our case the CMD and RPMD techniques produced two primary physical output quantities, i.e., $u_{\alpha}^{(K)}(t)$ with $\alpha = \{\text{Ne}, \text{CM}\}$, which approximate the two respective Kubo-transformed VACFs. Some selected examples of $u_{\text{CM}}^{(K)}(t)$ are plotted in Fig. 5, while the preliminary estimates (dubbed “direct”) of the self diffusion coefficients $D_{s,\text{CM}}^{(d)}$, obtained from the time integration $D_{s,\text{CM}}^{(d)} = \int_0^{t_m} u_{\text{CM}}^{(K)}(t) dt$, are reported in Table II and Fig. 6. Direct CM self diffusion coefficients for simulations No. i and No. vii, calculated with the same values of T , $x[\text{H}_2]$, N , and employing the same Ne–Ne Lennard-Jones potential, turned out to be identical within the errors, showing that the two simulation techniques, i.e., CMD and RPMD, are fully compatible for this class of semiquantum systems. This was also confirmed by the satisfactory comparison between the two $u_{\text{CM}}^{(K)}(t)$ functions related to the mentioned samples, which are plotted in Fig. 5. However, regarding the $D_{s,\text{CM}}^{(d)}$ estimates at identical (or similar) T and $x[\text{H}_2]$ values, but obtained using different values of N (i.e., either 500 or 256) and Ne–Ne pair potentials (i.e., either Lennard-Jones or HFD-B), the situation looks rather unsatisfactory as shown in Table II, where data from simulations No. vi and Nos. viii–xii are clearly larger than the corresponding figures for simulations Nos. i–v. This disagreement was not completely unexpected, at least as far as N is concerned, since it is well known that finite-size effects play a big role in the evaluation of D_s . Unfortunately, the standard way to correct for such effects making use of the viscosity [43] was not applicable in our case due to two main problems (namely, the classicality of the correction formulas and the lack of reliable shear viscosity data for our Ne + H_2 mixtures). So, we had to resort to a linear extrapolation of

TABLE III. Experimental estimates of the self diffusion coefficient $D_{s,\text{CM}}$ and the exponent of the Debye-Waller factor α_{CM}^2 for the three measured mixture samples described in Table I, together with the residence time τ_{CM} , the jump length parameter l_{CM} , and self diffusion coefficient $D_{s,\text{CM}}^{(\text{hr})}$ derived from fits using the Hall and Ross model. Corresponding values of the residence time λ_{CM}^{-1} and the self diffusion coefficient $D_{s,\text{CM}}^{(\text{ss})}$ fitted according to the Singwi and Sjölander model are also included. Estimated statistical uncertainties are reported in parentheses when relevant.

No.	T (K)	$x[\text{H}_2]$ (%)	n (nm^{-3})	$D_{s,\text{CM}}$ ($10^{-5} \text{ cm}^2/\text{s}$)	α_{CM}^2 ($\text{\AA}^2$)	τ_{CM} (ps)	l_{CM} ($\text{\AA}$)	$D_{s,\text{CM}}^{(\text{hr})}$ ($10^{-5} \text{ cm}^2/\text{s}$)	λ_{CM}^{-1} (ps)	$D_{s,\text{CM}}^{(\text{ss})}$ ($10^{-5} \text{ cm}^2/\text{s}$)
5	26.96	3.01	34.99	1.90(6)	0.128(6)	0.33(5)	0.36(2)	1.96(3)	0.18(3)	1.97(3)
6	30.01	3.01	33.27	2.74(5)	0.128(6)	0.37(3)	0.46(2)	2.85(3)	0.21(2)	2.86(3)
7	30.00	6.99	31.93	3.26(7)	0.139(6)	0.42(2)	0.53(1)	3.34(3)	0.25(1)	3.39(4)

$D_{s,\text{CM}}^{(d)}$ as a function of $N^{-1/3}$, making use of RPMD data (always evaluated using $P = 64$ and the Ne-Ne Lennard-Jones pair potential) at different values of N : 108, 256, and 500, augmented by additional short runs with $N = 4000$. Also, since concentrations of 7 and 3% could not be represented by integer numbers of H_2 molecules for these systems, the $x[\text{H}_2] = 0.07$ result for the $N = 256$ sample was obtained from a linear interpolation of separate runs with 17 and 18 H_2 particles, and analogously for $x[\text{H}_2] = 0.03$ and the $N = 108$ system. It is worth noting that in the case of $N = 256$ and 108, to increase the statistical accuracy of the result, the number of averaged trajectories was taken five and ten times longer than with $N = 500$. The y-intercept of such linear fits, corresponding to $N = \infty$, was assumed to be the extrapolated self diffusion coefficient, $D_{s,\text{CM}}^{(e)}$, for the H_2 CM (see Table II and Fig. 6).

As for the single-particle mean kinetic energy, the results reported in Table II show that quantum effects are sizable in both species, but while for Ne they represent only a modest correction to the classical equipartition value ($\frac{3}{2}k_B T$) of the order of 17–18%, for H_2 CM this percentage grows to the large value of 52–55%, which means that more than a half

of $\langle E_k \rangle_{\text{CM}}$ exhibits a purely quantum origin. This difference is also visible in the mean kinetic energy variation as a function of T and n : $\langle E_k \rangle_{\text{Ne}}$ is mildly sensitive to both physical quantities, while $\langle E_k \rangle_{\text{CM}}$ seems almost independent of T , but extremely sensitive to the changes of n , which determine the degree of local confinement felt by an H_2 molecule in the liquid mixture. In addition, as mentioned earlier and explained in detail in the Appendix B of Ref. [16], $\langle E_k \rangle_{\text{CM}}$ seems influenced by the choice of the Ne-Ne pair potential, with LJ providing larger values than HFD-B. From a quantitative point of view, the $\langle E_k \rangle_{\text{Ne}}$ value for pure Ne at $T = 27$ K in Table II favorably compares with the experimental measurement reported by Peek *et al.* [44], i.e., (52.8 ± 3.7) K as well as with that reported by Azuah *et al.* [45], namely, (52.9 ± 2.5) K, both obtained via deep inelastic neutron scattering at $T = 25.8$ K (and saturated vapor pressure). In addition, the agreement with the neutron measurement by Fradkin *et al.* [46] operated on isotopic ^{20}Ne at $T = 27$ K (and saturated vapor pressure), is virtually identical to our RPMD simulation result at the same temperature: $\langle E_k \rangle_{\text{Ne}} = (51.3 \pm 0.4)$ K. Moving to H_2 , molecular density values similar to those pertaining to our simulated mixtures can be found in the solid phase of pure hydrogen, e.g., at $T = 19 - 20$ K and $p > 500$ bar [47] but inelastic neutron scattering on these samples reveals center-of-mass mean kinetic energy values which are substantially higher than those in Table II. For example, at $T = 19.4$ K and $n = 31.29 \text{ nm}^{-3}$, $\langle E_k \rangle_{\text{CM}} = (102 \pm 5)$ K [48], while from our RPMD calculations at $T = 30$ K one can easily interpolate a figure of about (94.4 ± 0.1) K. The origin of this discrepancy is probably related to the lightweight mass of H_2 : despite the fact that Ne- H_2 and Ne-Ne pair potentials are similar, the H_2 molecules forming a cage of neighbors are considerably more delocalized (i.e., larger) than Ne, so a particle in the center of the cage in pure H_2 is more confined than in a Ne-rich mixture.

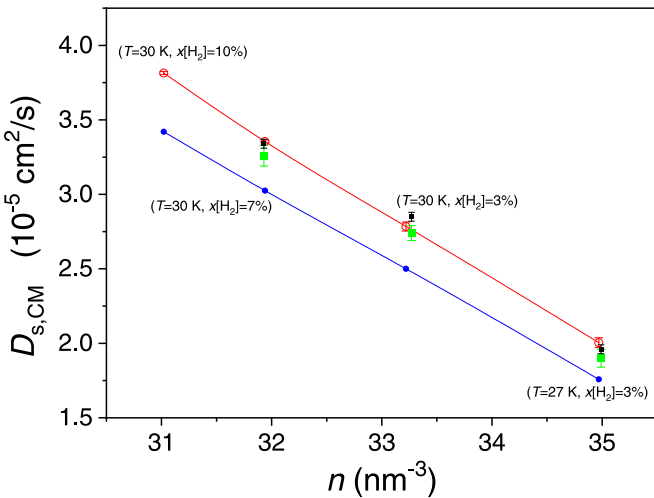


FIG. 6. Comparative plot of the self diffusion coefficients for the H_2 CM vs n taken from Tables II (circles, RPMD simulations) and III (squares, QENS data): blue full circles are $D_{s,\text{CM}}^{(d)}$, red empty circles are $D_{s,\text{CM}}^{(e)}$, green full squares are $D_{s,\text{CM}}$, and, finally, black full squares are $D_{s,\text{CM}}^{(\text{hr})}$. Lines are just guides for the eye.

IV. DISCUSSION OF THE SCIENTIFIC RESULTS

The fitted values of $\Gamma(Q)$, plotted in Fig. 7, can be directly used to provide experimental estimates of $\hbar D_{s,\text{CM}}$ through the extrapolation at $Q = 0$ of the values of $\Gamma(Q)/(2Q^2)$. Results, reported in Table III as well as in Fig. 6, exhibit good agreement with the extrapolated self diffusion coefficients, $D_{s,\text{CM}}^{(e)}$, derived from simulations No. ii to No. iv, although in the case of $x[\text{H}_2] = 7.00\%$ the RPMD value appears slightly overestimated. The general Q -trend of $\Gamma(Q)$ for all the three mixture samples is clearly characterized by a strong deviation from the Fickian behavior (which is linear in Q^2) prompting us to

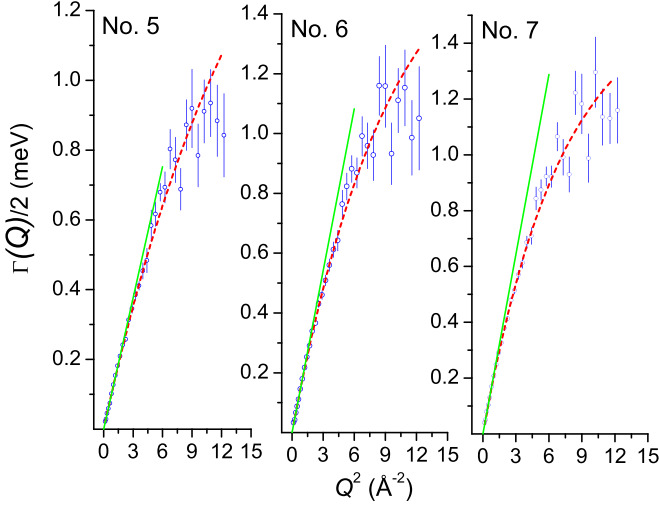


FIG. 7. Variation with Q^2 of the HWHMs of the QENS peaks for samples from No. 5 to No. 7 as in Table I. Blue empty circles represent experimental data, red dashed lines are fits using the Hall and Ross model [49], while green full lines stand for the low- Q Fickian behavior. See main text and Table III for details.

apply a more realistic diffusional model like, for example, that proposed by Hall and Ross [49] and suitable for disordered systems:

$$\Gamma(Q) = \frac{2\hbar}{\tau_{\text{CM}}} \left[1 - \exp\left(-\frac{Q^2 l_{\text{CM}}^2}{2}\right) \right], \quad (9)$$

where τ_{CM} is the mean residence time between two subsequent H_2 jumps and l_{CM} is related to the jump length in the way that $3l_{\text{CM}}^2$ is the value of the three-dimensional mean square jump length. By imposing that the Hall and Ross (HR) model has the correct low- Q limit, one immediately finds that $D_{s,\text{CM}} = l_{\text{CM}}^2/(2\tau_{\text{CM}})$, giving rise to a two-parameter fitting model, e.g., based on l_{CM} and τ_{CM} . Results for the two-parameter HR fits are reported in Table III and Fig. 7. In the former, one can easily appreciate the good agreement between low- Q and HR estimates of the self diffusion coefficient. In the latter it is possible to evaluate the fit quality which, although not excellent, can be considered as satisfactory, since the following reduced χ^2 values were obtained: 1.39, 1.19, and 1.37 for samples No. 5, No. 6, and No. 7, respectively.

The next step was the study of the Debye-Waller factor, $\exp[-2W(Q)]$, which accounts for the nondiffusional (and nonrotational) part of the CM dynamics, i.e., that related to the vibrations of an H_2 CM about its instantaneous equilibrium position inside the short-lived Ne pseudocages. In the case of a harmonic solid, it is well-known [3] that $W(Q) \propto Q^2$, so it was convenient to plot $-\ln(A(Q)/f(Q)) = 2W(Q) - \ln(C)$ versus Q^2 , with C being the aforementioned sample-dependent scaling factor, as shown in Fig. 8. The behavior of $2W(Q)$ as a function of Q^2 is essentially monotonically increasing, although a trough is clearly visible in all three panels of the figure in the $4.5 \text{ \AA}^{-2} \leq Q^2 \leq 8.0 \text{ \AA}^{-2}$ range, which, as shown in Fig. 4, exactly corresponds to the first sharp diffraction peak of $S_{\text{Ne,Ne}}(Q)$. However, the low- Q part of $2W(Q)$ (say, up to $Q^2 = 4.41 \text{ \AA}^{-2}$) grows quite linearly and can be fitted according to the simple model $-\ln$

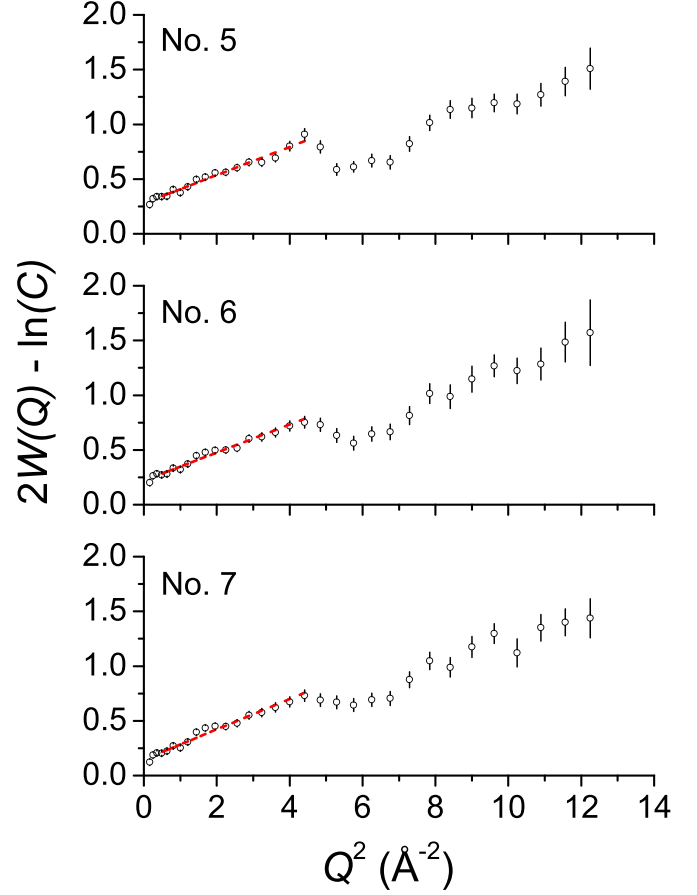


FIG. 8. Variation with Q^2 of the exponent of the Debye-Waller factor, $2W(Q)$, for the QENS peaks of samples from No. 5 to No. 7 as in Table I. Black empty circles represent experimental data, while red dashed lines are linear fits in the $0.16 \text{ \AA}^{-2} \leq Q^2 \leq 4.41 \text{ \AA}^{-2}$ interval. The quantity $\ln(C)$ represents an unknown sample-dependent intercept. See main text and Table III for details.

$(A(Q)/f(Q)) = \alpha_{\text{CM}}^2 Q^2 - \ln(C)$, where α_{CM}^2 and $\ln(C)$ represent the two fitting parameters. The rationale behind this linear functional form will be provided below. Results can be considered as satisfactory, since the following reduced χ^2 values were obtained: 1.00, 1.07, and 1.16 for samples No. 5, No. 6, and No. 7, respectively, while the corresponding estimates of α_{CM}^2 are reported in Table III.

Another diffusional model, due to Singwi and Sjölander (SS) [50], has also been tested. It is based on the concept of random jump diffusion and assumes an alternation between oscillatory motion and directed motion expressed by the formula:

$$\Gamma(Q) = 2\hbar \frac{\lambda_{\text{CM}}[1 - e^{-2W(Q)}] + D_{s,\text{CM}}Q^2}{1 + \lambda_{\text{CM}}^{-1}D_{s,\text{CM}}Q^2}, \quad (10)$$

where λ_{CM}^{-1} represents the typical timescale in which the CM motion is very similar to what would occur in a solid. However, such an equation is not suitable for our data set. In fact, the SS model was originally built starting from the hypothesis that a particle vibrates about its mean position for a period λ_{CM}^{-1} as in a solid, and then diffuses for a period μ_{CM}^{-1} . This two-time approach gives rise to quite a long and complicated

TABLE IV. Comparison between spatial and temporal quantities related to either the vibrational (Ω_E^2 , $2\pi/\Omega_E$ from RPMD, $3\alpha_{\text{CM}}^2$ from QENS, and $3\alpha_{\text{CM},s}^2$ from RPMD) or the diffusional (τ_{CM} and $3l_{\text{CM}}^2$ from QENS) dynamics of the H_2 centers of mass in the investigated mixture samples described in Tables I (neutron experiment, Arabic numbers) and II (quantum simulations, Roman numbers). For the meaning of the various symbols see the main text and Table III.

No.	T (K)	$x[\text{H}_2]$ (%)	Ω_E^2 (ps $^{-2}$)	$2\pi/\Omega_E$ (ps)	$3\alpha_{\text{CM}}^2$ (Å ^{2})	$3\alpha_{\text{CM},s}^2$ (Å ^{2})	τ_{CM} (ps)	$3l_{\text{CM}}^2$ (Å ^{2})
5-iv	26.96–27.00	3.01–3.00	395(5)	0.316(2)	0.39(2)	0.346(1)	0.33(5)	0.39(5)
6-iii	30.01–30.00	3.01–3.00	352(2)	0.335(1)	0.38(2)	0.352(1)	0.37(3)	0.64(5)
7-ii	30.00–30.00	6.99–7.00	307(2)	0.359(1)	0.42(2)	0.354(1)	0.42(2)	0.84(5)

formula where the peak shape is no longer a Lorentzian function. Subsequently, it is assumed by the authors [50,51] that $\lambda_{\text{CM}}^{-1} \gg \mu_{\text{CM}}^{-1}$, so that the diffusion process is taken as instantaneous and one may consider the model as describing a fast jump diffusion. In this way, the μ_{CM} dependence disappears and the Lorentzian peak shape is recovered, with Eq. (10) describing its width Γ as a function of Q . Unfortunately, as we will see below, the two timescales, i.e., λ_{CM}^{-1} and μ_{CM}^{-1} in the SS formalism, are actually very close to each other, and so the SS approach cannot be applied in the reduced form of Eq. (10). Nevertheless, a simpler formula for the SS model does exist and is obtained by fixing $W(Q) = 0$ in Eq. (10):

$$\Gamma(Q) = 2\hbar \frac{D_{s,\text{CM}}Q^2}{1 + \lambda_{\text{CM}}^{-1}D_{s,\text{CM}}Q^2}. \quad (11)$$

It is still supposed to describe periodic jumps occurring between potential energy minima where the scattering particle performs an oscillatory motion. However, in spite of its popularity in the QENS data analysis (see, e.g., Ref. [52]), in our context it is to be considered as essentially heuristic. We have exploited it in the same way as we made use of the HR model for fitting the QENS results. The fit quality turned out as slightly worse than that pertaining to HR, since in the present case the following reduced χ^2 values were obtained: 1.46, 1.34, and 1.56 for samples No. 5, No. 6, and No. 7, respectively. Results for this type of fit are reported in Table III, where one can easily appreciate the good agreement between SS and HR estimates of the self diffusion coefficient, while, as for the mean residence time, τ_{CM} appears substantially larger than λ_{CM}^{-1} , with the latter not being considered in the rest of the present work.

At this stage it is possible to compare the two diffusional quantities τ_{CM} and $3l_{\text{CM}}^2$ (which are temporal and spatial, respectively) with the corresponding VACF-related quantities ($2\pi/\Omega_E$) and the three-dimensional $3\alpha_{\text{CM}}^2$, where Ω_E is the Einstein frequency, directly connected to the short-time second derivative of $u_{\text{CM}}^{(K)}(t)$ [33]:

$$\Omega_E^2 = -\frac{\ddot{u}_{\text{CM}}^{(K)}(0)}{u_{\text{CM}}^{(K)}(0)}. \quad (12)$$

Estimates of all these four quantities are reported in Table IV. In the following, for the sake of brevity, we will use the term “vibrational” for quantities related to the VACF. The comparison between the two temporal ones, namely, $(2\pi/\Omega_E)$ and τ_{CM} , is straightforward since the average vibrational period turns out to be just slightly smaller than the mean residence time between two subsequent jump. Physically, this situation

can be easily described as an H_2 molecule oscillating only once in its short-lived Ne pseudocage before jumping into a different one. This means that due to the high system density, diffusion and vibrations are very strongly coupled for the H_2 CMs. Such a coupling also explains a rather counterintuitive fact visible in Tables III and IV: as T grows, the residence time τ_{CM} becomes larger. However, if $(2\pi/\Omega_E)$ and τ_{CM} are linked together, they are both driven by the system molecular density n , since Ω_E is strongly density-dependent. Unfortunately, this captivating picture must remain at a qualitative and heuristic level. In fact, if quantitatively translated into a rigorous mathematical model like that including the so-called “itinerant oscillators,” this idea gives rise to highly implausible results as it has been recently proved in the case of the Ne + D_2 mixtures [53]. However, the comparison between the two spatial quantities, namely, $3\alpha_{\text{CM}}^2$ and $3l_{\text{CM}}^2$, confirms our previous interpretation, since they turned out to be rather similar (even identical in the case of sample No. 5). However, the former quantity appears to be scarcely sensitive to the density and temperature changes of the mixtures, while the latter, which is given by $6D_{s,\text{CM}}\tau_{\text{CM}}$, is clearly dominated by the changes of $D_{s,\text{CM}}$ which surpass those coming from τ_{CM} . Differently from $3l_{\text{CM}}^2$, whose meaning is physically quite straightforward, the concept of $3\alpha_{\text{CM}}^2$ in a liquid is more subtle, since in diffusing systems the exponent of the Debye-Waller factor is not at all proportional to the mean square displacement. However, following the GA approach presented in Ref. [2], it is possible to give a physical interpretation of α_{CM}^2 : the self intermediate scattering function $I_s(Q, t)$ is approximated by the Gaussian term $\exp[-Q^2\gamma_1(t)]$, where $\gamma_1(t)$ represents the time-dependent mean square displacement given by the double time integral of the single-particle VACF. The asymptotic behavior of $\gamma_1(t)$ for very large values of t reads $D_s|t| - C_1$, so it means that GA simply states that in a liquid system $\exp[-2W(Q)] \approx \exp\{Q^2\text{Re}[C_1]\}$, where $\text{Re}[C_1] = -\alpha_{\text{CM}}^2$. Following the procedure sketched in the Appendix, one can explicitly write for our H_2 -CM a relationship between α_{CM}^2 and the spectrum $\tilde{u}_{\text{CM}}^{(K)}(\omega)$:

$$\alpha_{\text{CM}}^2 = \frac{\hbar}{k_B T} \int_0^\infty \frac{d}{d\omega} \left[\omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) \tilde{u}_{\text{CM}}^{(K)}(\omega) \right] \frac{d\omega}{\omega}, \quad (13)$$

In addition, one can also establish a connection between the Debye-Waller factor in a liquid and the more common one used for the solid state, $\exp[-2W_{\text{sol}}(Q)]$:

$$2W_{\text{sol}}(Q) = \frac{\hbar Q^2}{2M} \int_0^\infty Z(\omega) \coth\left(\frac{\hbar\omega}{2k_B T}\right) \frac{d\omega}{\omega}, \quad (14)$$

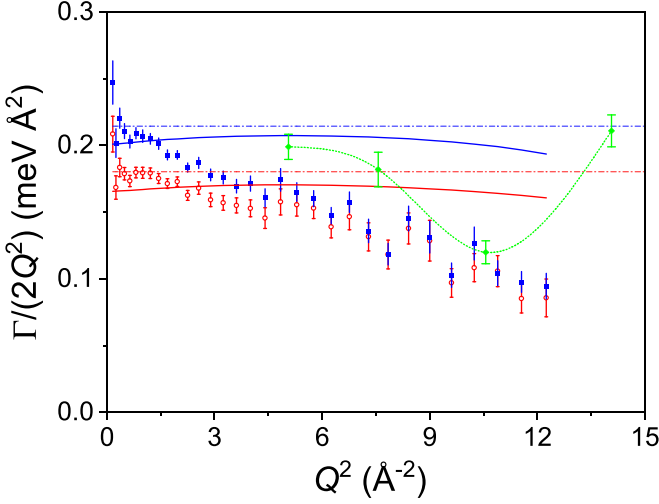


FIG. 9. Ratios between the spectral full width at half maximum, Γ , and $2Q^2$ as a function of Q^2 for $T = 30$ K and $x[\text{H}_2] = 3\%$ (red) or 7% (blue). Full lines represent the GA-simulated results exploiting simulation Nos. iii and ii, respectively (see Table II). Experimental data are plotted as empty circles and full squares for samples No. 6 and No. 7, respectively (see Table I). Thin dash-dotted lines indicate the experimental hydrodynamic limit values, $\hbar D_{s,\text{CM}}$, obtained from Table III. Experimental data from Ref. [16] ($T = 30.1$ K and $x[\text{H}_2] = 3.4\%$) are also reported as green circles (joint by a dotted green line which is just a guide for the eye).

where M is the particle mass and $Z(\omega)$ is the well-known density of phonon states, which is proportional to $\tilde{u}_{\text{CM}}^{(K)}(\omega)$. It turns out that Eq. (14) can be recovered from Eq. (13) through integration by parts if the diffusion is totally negligible and thus $\tilde{u}_{\text{CM}}^{(K)}(0) = 0$. This fact can be easily appreciated by writing: $\lim_{\omega \rightarrow 0} \tilde{u}_{\text{CM}}^{(K)}(\omega) = \pi^{-1} D_{s,\text{CM}}$. Other details about the implementation of Eq. (13) are given in the Appendix, especially those concerning the long-time behavior of the VACF and its possible effects on $\tilde{u}_{\text{CM}}^{(K)}(\omega)$. For all the reasons stated in the Appendix, one can conclude that the RPMD simulation values of $3\alpha_{\text{CM}}^2$, calculated on the basis of Eq. (13), dubbed $3\alpha_{\text{CM},s}^2$ and reported in Table IV, have to be considered as more than just qualitative, although they turn out to be 9–16% underestimated with respect to the corresponding QENS quantities.

We are now in a position to try solving the problem, presented in the introduction, concerning the FWHMs of QENS and GA spectra, both evaluated at $T = 30$ K in the $2.25 \text{ \AA}^{-1} \leq Q \leq 3.75 \text{ \AA}^{-1}$ range (namely, $5.06 \text{ \AA}^{-2} \leq Q^2 \leq 14.06 \text{ \AA}^{-2}$). A new and updated version of Fig. 10 in Ref. [16] is reported here in Fig. 9, where the data from the old INS spectrometer (taken with $\Delta\hbar\omega \approx 2.37$ meV) has been complemented by those obtained from the present QENS instrument (taken with $\Delta\hbar\omega \approx 0.10$ meV). The effect of such a resolution improvement is actually relevant: although we did not have access to QENS data for $Q^2 > 12.25 \text{ \AA}^{-2}$, no sign of the anomalous growth of $\Gamma/(2Q^2)$ is visible for both samples No. 6 and No. 7. In the case of the GA, this discrepancy between INS- and QENS-simulated data is even more striking: the FWHMs of the latter spectra plotted versus Q^2 are roughly flat with a tiny initial positive slope followed

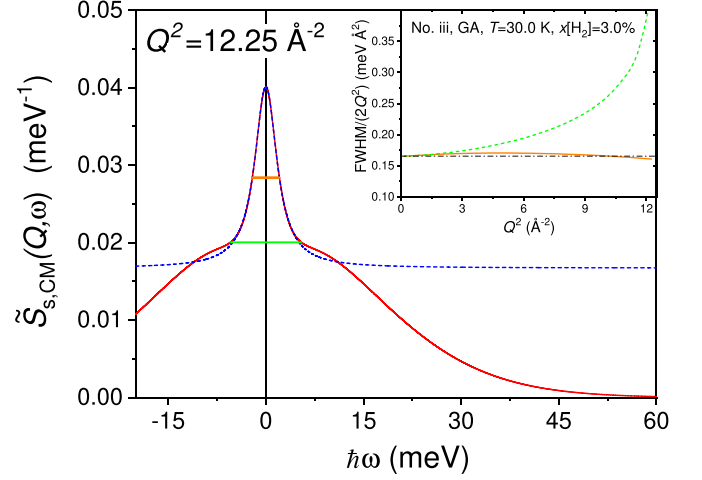


FIG. 10. Symmetric part of the GA-simulated self scattering law of the H_2 CM at $Q^2 = 12.25 \text{ \AA}^{-2}$ for simulation No. iii in Table II (red full line), together with its diffusional component (blue dashed line). The green horizontal line marks the FWHM of the whole peak, while the orange one is related to the FWHM of the diffusional component only. In the inset, the values of $\text{FWHM}/(2Q^2)$ for the whole peak (green dashed line) and those of $\text{FWHM}/(2Q^2)$ for the diffusional component only (orange full line) are reported as a function of Q^2 for the same simulation as above. The value of $\hbar D_{s,\text{CM}}^{(d)}$ is also plotted as a black dot-dashed line.

by an equally small decrease, while, by contrast, Fig. 10 in Ref. [16] showed an intense monotonic growth for both H_2 concentrations (namely, 3.4% and 10%). The reason for the large differences observed by comparing the two scenarios, i.e., INS in Ref. [16] and QENS in Fig. 9, can be related to the merging of the diffusional and the inelastic part of the spectra operated by the INS spectrometer due to its large energy resolution. Since the same effect takes place once the GA-simulated spectra are folded with an appropriate resolution function which mimics that of the corresponding spectrometer, it is interesting to show an example of these two spectral parts without any resolution broadening and calculated in an ω range substantially larger than the interval available on OSIRIS. In Fig. 10 we have plotted the symmetric part of the GA-simulated self scattering law of the H_2 center of mass, $\tilde{S}_{s,\text{CM}}(Q, \omega)$, for simulation No. iii, defined, following Eq. (3), as

$$\tilde{S}_{s,\text{CM}}(Q, \omega) = \frac{1}{2} S_{s,\text{CM}}(Q, \omega) \left[\exp\left(-\frac{\hbar\omega}{k_B T}\right) + 1 \right]. \quad (15)$$

The wavevector transfer value corresponding to $Q^2 = 12.25 \text{ \AA}^{-2}$ has been selected since in Fig. 10 of Ref. [16] this corresponds to a situation where the GA estimates of $\Gamma/(2Q^2)$ already exhibit large extra-intensities if compared to the $\hbar D_{s,\text{CM}}$ of the simulated mixture. Since here the plotted scattering law does not include any additional broadening, it is possible to separate the purely diffusional component from the inelastic one via a simple two-Lorentzian fit. In this way two distinct FWHMs can be evaluated: one for the whole peak, and one (i.e., Γ) related to the diffusional component only (after treating the inelastic signal as an additional background), with the former substantially larger than the

latter. This achievement fully explains the discrepancy between the curves in Fig. 10 of Ref. [16] and those reported in Fig. 9, since the old INS data, due to the instrumental resolution, contain information on the whole peak, while, on the contrary, the present QENS data, owing to their limited ω range, contain information on the diffusional part only. In the inset of Fig. 9 such an effect is shown for the entire Q^2 range by comparing the values of $\text{FWHM}/(2Q^2)$ for the whole peak with those of $\text{FWHM}/(2Q^2)$ for the diffusional component only. While the latter stay very close to $D_{s,\text{CM}}$ in the whole Q^2 range, the former grow in a highly superlinear way, as reported for the GA in the literature [20,21], and also in agreement with the GA curves in Fig. 10 of Ref. [16]. In addition, it is also possible to study the Q -evolution of the area, $I(Q)$, of the diffusional GA component through the same fitting model used for the corresponding QENS data, namely: $-\ln I(Q) = \alpha_{\text{CM}}^2 Q^2 - \ln(C)$. Results for $3\alpha_{\text{CM}}^2$ are $(0.424 \pm 0.009) \text{ \AA}^2$ and $(0.40 \pm 0.04) \text{ \AA}^2$ for sample No. 6 and No. 7, respectively, showing a reasonably good agreement with corresponding data extracted from the QENS spectra and the VACFs, reported in Table IV.

The only issue related to Fig. 10 in Ref. [16] (Fig. 9 in the present study) which is still unexplained is the position of the minimum of $\Gamma/(2Q^2)$ at $Q_m^2 \approx 10.5 \text{ \AA}^{-2}$. In fact, according to the literature [20–22], it should coincide with the first maximum of $S(Q)$. Now, looking at Fig. 4, one can easily locate the four maxima of $S(Q)$ and $S_{\alpha,\beta}(Q)$ in the range $2.0 \text{ \AA}^{-1} \leq Q \leq 2.5 \text{ \AA}^{-1}$ (i.e., $4.0 \text{ \AA}^{-2} \leq Q^2 \leq 6.3 \text{ \AA}^{-2}$), which does not match the observed Q_m value. Even though Q_m was somehow dubious, being derived from a heuristic spline interpolating four data points only, it would be worthwhile to further investigate this intriguing question by studying the experimental FWHM for the whole peak and its variation along with Q . Rigorously speaking, this cannot be done using the present QENS data since their narrow ω range prevents the possibility to isolate the whole spectral peak, to analyze it via a fitting procedure, and finally to remove the experimental energy resolution in an accurate way. However, an approximated attempt can be carried out using our $I_{\text{inc}}(Q, \omega)$ spectra by means of a fitting procedure, which modifies Eq. (2) by replacing the linear background $B(Q, \omega)$ (2 fitting parameters) with a cubic one, $C(Q, \omega)$, containing four fitting parameters. Subsequently, using these new fit results, the unbroadened spectral function $L(Q, \omega)$ is symmetrized by removing the correction for the detailed balance, while $C(Q, \omega)$ is also symmetrized by keeping only the even powers of ω . This procedure gives rise to a new spectrum, $P(Q, \omega)$:

$$P(Q, \omega) = \frac{1}{2} \left\{ L(Q, \omega) \left[\exp\left(-\frac{\hbar\omega}{k_B T}\right) + 1 \right] + C(Q, \omega) + C(Q, -\omega) \right\}. \quad (16)$$

Finally, the FWHM of the whole $P(Q, \omega)$ peak is evaluated for each Q value. Results for sample No. 6 are reported in Fig. 11 clearly showing that the FWHM of the whole spectral peak becomes progressively larger than the diffusional Γ as Q grows bigger than about $1.5 \text{ \AA}^{-1}$. However, there is no evidence of a minimum of $\text{FWHM}/(2Q^2)$ for Q values close

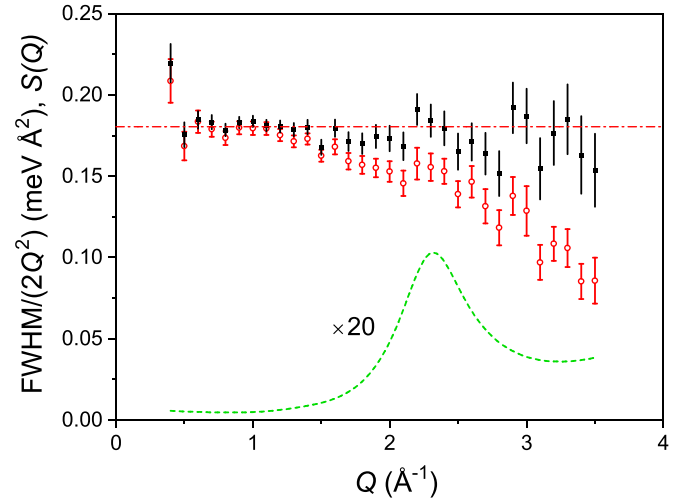


FIG. 11. Ratios between the spectral full width at half maximum and $2Q^2$ as a function of Q for sample No. 6 (see Table I). Experimental data are plotted as red empty circles and black full squares for the diffusional part only (as in Fig. 9) and the whole peak, respectively. The red dash-dotted line exhibits the experimental hydrodynamic limit value, $\hbar D_{s,\text{CM}}$, obtained from Table III. Finally, the green dashed line represents the simulation of the total static structure factor $S(Q)$ for simulation No. iii (see Table II), divided by 20 for graphic reasons.

to the first maximum of $S(Q)$, as reported, for example, by Sköld *et al.* in the case of liquid Ar at 85.2 K [54].

V. CONCLUSIONS

In this study we have measured the QENS spectra of hydrogen mixed with liquid neon (namely, at $T = 27 \text{ K}$ and 30 K) for two values of the H_2 molar concentration (namely, 3% and 7%), making use of the OSIRIS neutron spectrometer [24]. These low-energy parts of the double-differential neutron scattering cross section are strictly related to the self dynamic structure factors of the H_2 center of mass, $S_{s,\text{CM}}(Q, \omega)$, for the three mixture samples [3]. To quantitatively extract the $S_{s,\text{CM}}(Q, \omega)$ estimates, QENS data have been corrected for the usual experimental effects (i.e., empty can contributions, self-shielding attenuation etc.) and, after subtracting an adequate (although approximated) contribution due to the Ne–Ne coherent scattering, have been interpreted in the framework of the GYK model [18] for taking into account the effects stemming from the rotational ortho-hydrogen dynamics. In this way, we obtained a complete description of $S_{s,\text{CM}}(Q, \omega)$ in the wavevector transfer range $0.4 \text{ \AA}^{-1} \leq Q \leq 3.5 \text{ \AA}^{-1}$ and in the energy transfer range $-3.0 \text{ meV} \leq \hbar\omega \leq 5.0 \text{ meV}$, with an energy transfer resolution (FWHM) amounting to $\Delta\hbar\omega = 99.0 \text{ \mu eV}$, ready to be studied to extract information of the H_2 diffusional dynamics in the aforementioned liquid systems. In fact, after a straightforward Lorentzian fitting procedure, we managed to determine the two basic spectral features related to the H_2 diffusion, namely, the intrinsic QENS peak width, Γ , and the corresponding peak intensity, A , both strongly dependent on Q . The low- Q Γ estimates turned out to be in a good agreement with the self diffusion coefficients simulated via quantum calculations, especially when the latter

were corrected for finite-size effects through an extrapolation procedure. In addition, at larger Q values, the peak width values exhibited typical sublinear variations as a function of Q^2 , which have been interpreted as a clear mark of a jump diffusion process with the help of the Hall and Ross fitting model [49], providing estimates of the mean residence time, τ_{CM} , and the jump length parameter, l_{CM} . These two quantities represent a sound and objective characterization of the short-lived Ne pseudocages in our system, which have been simply hypothesized in a previous study [16]. In particular, the former physical quantity, τ_{CM} , was found to be almost identical to the average vibrational period of an H_2 trapped in such a Ne pseudocage, and the latter, l_{CM} , turned out rather similar to α_{CM} of H_2 , which in turn controls the intensity of $A(Q)$ via a Debye-Waller factor. These two similitudes were interpreted as the result of a strong coupling between the diffusion and the vibration of the H_2 CM caused by the high molecular density of the system. The cited quantum calculations, obtained through RPMD and CMD, provided, as in the case of other semiquantum mixtures [4,15,16,53], accurate estimates of the partial static structure factors, $S_{\alpha,\beta}(Q)$, as well as of the canonical velocity autocorrelation functions, $u_{\alpha}^{(K)}(t)$ (with $\alpha = \{\text{Ne}, \text{CM}\}$ and $\beta = \{\text{Ne}, \text{CM}\}$). The latter functions, similarly to what was found in Refs. [15,16,53], exhibit the typical behavior of a dense fluid, i.e., a rapid drop to values lower than zero (understood as the backflow caused by bouncing on the pseudocage walls), followed by a slow decrease characterized by a longer tail. These $u_{\text{CM}}^{(K)}(t)$ were employed, in conjunction with the well-known Gaussian approximation [2], to evaluate the $S_{s,\text{CM}}(Q, \omega)$ spectra in the same (Q, ω) range as the experimental one, at identical thermodynamic and ω -resolution conditions, to be analyzed in an analogous way. In particular, the FWHMs obtained from the GA data showed a low- Q behavior quite close to that found in the QENS fit results, while, as Q grew, their respective trends became more and more distinct, with the former $\Gamma/(2Q^2)$ staying always very close to the $\hbar D_{s,\text{CM}}^{(d)}$ value, while the latter decreased in a substantial way following a strongly non-Gaussian trend well described by a jump diffusion model. It was this kind of discrepancies between QENS and GA data sets that, in the conclusions of previous spectroscopic studies [4,15,16,55] on various semiquantum liquids, pointed to the necessity of going beyond the GA for an accurate description of the microscopic self dynamics in these fluids. In this respect, the present QENS experiment has underpinned in a quantitative way the strict connection, already hypothesized in Refs. [16,55], between caging effects due to heavy particles (like Ne atoms) surrounding diluted lightweight particles (like H_2 or D_2 molecules) and the observed breakdown of the GA.

In conclusion, we can point out that the present study substantially improves the quality of the existing neutron spectra of H_2 impurities in liquid Ne [16,23,55], especially in terms of the energy transfer resolution in the quasielastic region of the (Q, ω) kinematic plane. In particular, we have filled the gap present in Ref. [16], allowing to correct the interpretation of the supposedly anomalous Q -dependence of Γ , which actually did not exhibit a deep physical origin but was just an instrumental effect. However, there is still an aspect which has not yet been totally clarified by the present experiment

and might reveal an interesting difference between simple liquids and binary mixtures: in similar systems (e.g., liquid Ar [54]) a dip in $\text{FWHM}/(2Q^2)$ as a function of Q is observed at wave numbers corresponding to the first maximum of the static structure factor $S(Q)$, while in the present mixtures this feature seems completely absent. As we are aware that our QENS data are not ideal for such an analysis, we think that in principle one would need further high-resolution neutron scattering measurements in broader ω and Q ranges, for example $-20 \text{ meV} \leq \hbar\omega \leq 50 \text{ meV}$ and $0.5 \text{ \AA}^{-1} \leq Q \leq 5 \text{ \AA}^{-1}$, for properly addressing this problem. Unfortunately, this type of measurements seems experimentally unfeasible at the moment.

ACKNOWLEDGMENTS

We gratefully acknowledge the important scientific and technical support provided by the ISIS staff. We are also greatly indebted to the late Dr. Eleonora Guarini (Univ. of Florence, Italy) for several fruitful scientific discussions on the subject of the microscopic dynamics of liquids. The cited neutron scattering experiments have been made possible by the CNR-STFC Agreement (Grant No. 2020-2027), concerning collaboration in scientific research between the ISIS Neutron and Muon Source of STFC (UK) and CNR (Italy). This research was also partially funded by the European Union—Next Generation EU from the Italian Ministry of Environment and Energy Security POR H2 AdP MMES/ENEA with involvement of CNR and RSE, PNRR—Mission 2, Component 2, Investment 3.5 “Ricerca e sviluppo sull'idrogeno” (Grant No. PRR.AP015.017 H2-AdC ENEA/CNR POR IDROGENO, CUP: B93C22000630006).

DATA AVAILABILITY

The data that support the findings of this article are openly available at [56], embargo periods may apply.

APPENDIX: DEBYE-WALLER FACTOR AND LONG-TIME TAIL IN DENSE LOW-TEMPERATURE LIQUIDS

In Sec. IV, Eq. (13), derived from Eq. (54) of Ref. [2] via Fourier transform, has been presented. A few details about this derivation are probably worthwhile. The definition of C_1 in the mentioned equation of Ref. [2] (specialized for $n = 1$) is the following:

$$C_1 = \int_0^\infty t u(t) dt, \quad (\text{A1})$$

but it is not immediately applicable since it contains the fully quantum $u(t)$ rather than the Kubo-transformed one, $u^{(K)}(t)$, provided by our RPMD/CMD simulations. However, the real and the imaginary part of $u(t)$ can be expressed (see Eqs. (83), (84), and (85) of Ref. [2]) in terms of $f(\omega)$ which is proportional to the Fourier spectrum of $u^{(K)}(t)$ (although normalized to unity as in Eq. (86) of Ref. [2]). So, inserting the mentioned Eqs. (84) and (85) into Eq. (54) (specialized for $n = 1$) and

using standard algebraic manipulations, one writes

$$-\alpha^2 = \text{Re}[C_1] = \frac{\hbar}{2M} \int_0^\infty t dt \int_0^\infty d\omega \cos(\omega t) \omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) f(\omega) = \frac{\hbar}{2M} \int_0^\infty dt \int_0^\infty \frac{d}{d\omega} [\sin(\omega t)] \omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) f(\omega) d\omega. \quad (\text{A2})$$

Note that, due to two different definitions of the velocity autocorrelation function in Ref. [2], our present formulas and those in such a paper sometimes differ by a factor 3. Then integrating Eq. (A2) by parts, one obtains

$$-\alpha^2 = \text{Re}[C_1] = \frac{\hbar}{2M} \int_0^\infty t dt \left\{ \left[\sin(\omega t) \omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) f(\omega) \right]_0^\infty - \int_0^\infty \sin(\omega t) \frac{d}{d\omega} \left[\omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) f(\omega) \right] d\omega \right\}, \quad (\text{A3})$$

where, assuming quite reasonably that $\lim_{\omega \rightarrow \infty} \omega \coth[\hbar\omega/(2k_B T)] f(\omega) = 0$, one can totally drop the boundary term. Finally, using the well-known distribution theory identity $\int_0^\infty \sin(\omega t) dt = \text{PV}(1/\omega)$ (where symbol PV stands for the Cauchy principal value), one arrives to Eq. (13).

In the derivation above, as explicitly stated by the authors of Ref. [2], it is assumed that $\tilde{u}^{(K)}(\omega)$, being an even function of ω , can be expanded in powers of ω^2 as

$$\lim_{\omega \rightarrow 0} \tilde{u}^{(K)}(\omega) = \pi^{-1} D_s + c_2 \omega^2 + c_4 \omega^4 + \dots, \quad (\text{A4})$$

where c_2 and c_4 are constants related to the moments of $u^{(K)}(t)$. However, eight years later, in 1970, Alder and Wainwright discovered the slow power decay proportional to $t^{-3/2}$ of the VACF in moderately dense hard-sphere fluids using classical molecular dynamics simulations [57]. Subsequently, this effect has been found in a number of liquid systems [20,58], and has been explained by using classical kinetic theory [59]. In the ω domain, this decay corresponds to the following limit:

$$\lim_{\omega \rightarrow 0} \tilde{u}^{(K)}(\omega) = \pi^{-1} D_s - c_{1/2} \omega^{0.5} + \dots, \quad (\text{A5})$$

where $c_{1/2}$ is a positive constant. In the case of a quantum

fluid, however, this aspect seems less clear [60,61], but we do not wish to enter into a theoretical debate since our sole point here is the following: if the long-time tail spectrum were characterized by Eq. (A5), the integral in Eq. (13) would diverge at $\omega = 0$ and, consequently, $3\alpha_{\text{CM}}^2$ would be ill-defined. This possibility led us to further investigate the long-time tail problem in the specific case of our dense, low-temperature, liquid samples. Taking into account the detailed studies of Refs. [62] [63] on the temperature and density dependence of the long-time tail in Lennard-Jones systems, one can approximately estimate the onset of such a tail in the VACF for our three mixture samples using, e.g., standard Lennard-Jones parameters for the H₂-Ne interaction obtained via the Lorentz-Berthelot combining rule [58]: $\epsilon = 36.83$ K and $\sigma = 2.85$ Å. By inspecting the thermodynamic state in Ref. [63] closest to our experimental conditions (i.e., $T = 33.15$ K, $n = 34.49$ nm⁻³ for our combined ϵ and σ), one realizes that no persistent long-time tail behavior proportional to $t^{-3/2}$ is present in the VACF, as shown in the lowest curve of Fig. 4 in the cited paper [63]. For this reason, although the aforementioned calculations were obtained via classical molecular dynamics, we believe that the use of Eq. (13) is fully justified in the present context of our dense Lennard-Jones-like mixtures.

-
- [1] A. F. Andreev and Y. A. Kosevich, Kinetic phenomena in semiquantum liquids, *Zh. Eksp. Teor. Fiz.* **77**, 2518 (1979) [*Sov. Phys. JETP* **50**, 1218 (1979)].
 - [2] A. Rahman, K. S. Singwi, and A. Sjölander, Theory of slow neutron scattering by liquids. I, *Phys. Rev.* **126**, 986 (1962).
 - [3] S. W. Lovesey, *Theory of Neutron Scattering from Condensed Matter, Volume 1: Nuclear Scattering* (Clarendon Press, Oxford, UK, 1984).
 - [4] M. Celli, U. Bafle, D. Colognesi, A. De Francesco, F. Formisano, E. Guarini, M. Neumann, and M. Zoppi, Non-Gaussian self-dynamics of liquid hydrogen, *Phys. Rev. B* **84**, 140510(R) (2011).
 - [5] A. Bulgac, M. Kafker, I. Abdurrahman, and G. Wlazłowski, Quantum turbulence, superfluidity, non-Markovian dynamics, and wave function thermalization, *Phys. Rev. Res.* **6**, L042003 (2024).
 - [6] E. Heifetz and E. Cohen, Toward a thermo-hydrodynamic like description of Schrödinger equation via the Madelung formulation and Fisher information, *Found. Phys.* **45**, 1514 (2015).
 - [7] R. E. Wyatt, *Quantum Dynamics with Trajectories: Introduction to Quantum Hydrodynamics* (Springer, New York, NY, 2010).
 - [8] V. N. Novikov and A. P. Sokolov, Role of quantum effects in the glass transition, *Phys. Rev. Lett.* **110**, 065701 (2013).
 - [9] T. Yamaguchi, Decoupling between solvent viscosity and diffusion of a small solute induced by self-motion, *J. Phys. Chem. Lett.* **12**, 7696 (2021).
 - [10] C. P. Royall and S. R. Williams, The role of local structure in dynamical arrest, *Phys. Rep.* **560**, 1 (2015).
 - [11] M. Majka and P. F. Góra, Effective one-component model of binary mixture: Molecular arrest induced by the spatially correlated stochastic dynamics, *Sci. Rep.* **9**, 19661 (2019).
 - [12] T. R. Prisk, S. Hanna, and R. T. Azuah, Self-diffusion of liquid hydrogen: A quasi-elastic neutron scattering study, *J. Low Temp. Phys.* **201**, 451 (2020).
 - [13] F. J. Bermejo, F. J. Mompeán, M. García-Hernández, J. L. Martínez, D. Martín-Marero, A. Chahid, G. Senger, and M. L. Ristig, Collective excitations in liquid deuterium: Neutron-scattering and correlated-density-matrix results, *Phys. Rev. B* **47**, 15097 (1993); E. Guarini, F. Barocchi, A. De Francesco, F. Formisano, A. Laloni, U. Bafle, M. Celli, D. Colognesi, R.

- Magli, A. Cunsolo, and M. Neumann, Collective dynamics of liquid deuterium: Neutron scattering and approximate quantum simulation methods, *ibid.* **104**, 174204 (2021).
- [14] A. A. van Well and L. A. de Graaf, Density fluctuations in liquid neon studied by neutron scattering, *Phys. Rev. A* **32**, 2396 (1985).
- [15] D. Colognesi, U. Bafle, M. Celli, M. Neumann, and A. Orecchini, Hydrogen self-dynamics in liquid H₂-D₂ mixtures studied through inelastic neutron scattering, *Phys. Rev. E* **92**, 012311 (2015).
- [16] D. Colognesi, U. Bafle, M. Celli, M. Neumann, E. Guarini, and M. D. Le, Hydrogen self-dynamics in diluted liquid mixtures with neon: An inelastic neutron scattering study, *Phys. Rev. E* **99**, 012138 (2019).
- [17] D. Colognesi, U. Bafle, E. Guarini, T. Guidi, and M. Neumann, Microscopic collective dynamics in liquid neon-deuterium mixtures: Inelastic neutron scattering and quantum simulations, *Phys. Rev. E* **105**, 054603 (2022).
- [18] J. A. Young and J. U. Koppel, Slow neutron scattering by molecular hydrogen and deuterium, *Phys. Rev.* **135**, A603 (1964); V. F. Sears, Theory of cold neutron scattering by homonuclear diatomic liquids: I. Free Rotation, *Can. J. Phys.* **44**, 1279 (1966); M. Zoppi, Neutron scattering of homonuclear diatomic liquids, *Physica B* **183**, 235 (1993).
- [19] M. Beé, *Quasielastic Neutron Scattering, Principles and Applications in Solid State Chemistry, Biology and Materials Science* (Adam Hilger, Bristol, 1988).
- [20] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon Press, Oxford, UK, 1994).
- [21] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, London, UK, 1980).
- [22] G. Wahnström and L. Sjögren, Incoherent scattering function in simple classical liquids, *J. Phys. C: Solid State Phys.* **15**, 401 (1982).
- [23] O. J. Eder, S. H. Chen, and P. A. Egelstaff, Molecular motion of hydrogen in liquid argon and neon, *Proc. Phys. Soc.* **89**, 833 (1966).
- [24] M. T. F. Telling and K. H. Andersen, Spectroscopic characteristics of the OSIRIS near-backscattering crystal analyser spectrometer on the ISIS pulsed neutron source, *Phys. Chem. Chem. Phys.* **7**, 1255 (2005); M. T. F. Telling, S. I. Campbell, D. Engberg, D. Martín y Marero, and K. H. Andersen, Correction: Spectroscopic characteristics of the OSIRIS near-backscattering crystal analyser spectrometer on the ISIS pulsed neutron source, *ibid.* **18**, 8243 (2016).
- [25] R. Katti, R. T. Jacobsen, R. B. Stewart, and M. Jahangiri, Thermodynamic properties of neon for temperatures from the triple point to 700 K at pressures to 700 MPa, *Adv. Cryog. Eng.* **31**, 1189 (1986).
- [26] C. K. Heck and P. L. Barrick, Liquid-vapor phase equilibria of the neon-normal hydrogen system, in *Advances in Cryogenic Engineering*, edited by K. D. Timmerhaus (Springer, Boston, MA, 1966), Vol. 11, p. 349.
- [27] D. Güsewell, F. Schmeissner, and J. Schmid, Density and sound velocity of saturated liquid neon-hydrogen and neon-deuterium mixtures between 25 and 31 K, *Cryogenics* **10**, 150 (1970); New data on liquid neon-hydrogen mixtures, **11**, 311 (1971).
- [28] W. B. Streett, An experimental study of the equation of state of liquid mixtures of neon + normal hydrogen, *J. Chem. Thermodyn.* **5**, 313 (1973).
- [29] Y. Y. Milenko, R. M. Sibileva, and M. A. Strzhemechny, Natural ortho-para conversion rate in liquid and gaseous hydrogen, *J. Low Temp. Phys.* **107**, 77 (1997).
- [30] V. F. Sears, Neutron scattering lengths and cross sections, *Neutron News* **3**, 26 (1992).
- [31] S. N. Chesler and S. P. Cram, Iterative curve fitting of chromatographic peaks, *Anal. Chem.* **45**, 1354 (1973).
- [32] J. Cao and G. A. Voth, The formulation of quantum statistical mechanics based on the Feynman path centroid density. II. Dynamical properties, *J. Chem. Phys.* **100**, 5106 (1994).
- [33] H. Kim, Relationship between Kubo-transformed and classical correlation functions, *Chem. Phys. Lett.* **436**, 111 (2007).
- [34] S. R. Challa and J. K. Johnson, Molar excess volumes of liquid hydrogen and neon mixtures from path integral simulation, *J. Chem. Phys.* **111**, 724 (1999).
- [35] I. R. Craig and D. E. Manolopoulos, Quantum statistics and classical mechanics: Real time correlation functions from ring polymer molecular dynamics, *J. Chem. Phys.* **121**, 3368 (2004).
- [36] C. P. Dettmann and G. P. Morriss, Hamiltonian formulation of the Gaussian isokinetic thermostat, *Phys. Rev. E* **54**, 2495 (1996).
- [37] H. F. Trotter, On the product of semi-groups of operators, *Proc. Amer. Math. Soc.* **10**, 545 (1959).
- [38] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, 2nd ed. (Oxford University Press, Oxford, UK, 2017).
- [39] J. J. Morales and M. J. Nuevo, Path integral molecular dynamics methods: Application to neon, *J. Comput. Chem.* **16**, 105 (1995).
- [40] R. A. Aziz and M. J. Slaman, The Ne-Ne interatomic potential revisited, *Chem. Phys.* **130**, 187 (1989).
- [41] M. Faubel, F. A. Gianturco, F. Ragnetti, L. Y. Rusin, F. Sondermann, U. Tappe, and J. P. Toennies, The H₂-Ne interaction, *J. Chem. Phys.* **101**, 8800 (1994).
- [42] I. F. Silvera and V. V. Goldman, The isotropic intermolecular potential for H₂ and D₂ in the solid and gas phases, *J. Chem. Phys.* **69**, 4209 (1978).
- [43] I.-C. Yeh and G. Hummer, System-size dependence of diffusion coefficients and viscosities from molecular dynamics simulations with periodic boundary conditions, *J. Phys. Chem. B* **108**, 15873 (2004); S. H. Jamali, L. Wolff, T. M. Becker, A. Bardow, T. J. H. Vlucht, and O. A. Moulton, Finite-size effects of binary mutual diffusion coefficients from molecular dynamics, *J. Chem. Theory Comput.* **14**, 2667 (2018).
- [44] D. A. Peek, M. C. Schmidt, I. Fujita, and R. O. Simmons, Single-particle kinetic energies in liquid neon, *Phys. Rev. B* **45**, 9671 (1992).
- [45] R. T. Azuah, W. G. Stirling, H. R. Glyde, and M. Boninsegni, Momentum distribution and final state effects in liquid neon, *J. Low Temp. Phys.* **109**, 287 (1997).
- [46] M. A. Fradkin, S.-X. Zeng, and R. O. Simmons, Final-state effects in neutron scattering from liquid neon, *Phys. Rev. B* **49**, 15563 (1994).
- [47] R. D. McCarty, J. Hord, and H. M. Roder, Selected properties of hydrogen, NBS Monogr. **168** (1981), and references therein.

- [48] M. Zoppi, D. Colognesi, and M. Celli, Density dependence of mean kinetic energy in liquid and solid hydrogen at 19.3 K, *Eur. Phys. J. B* **23**, 171 (2001).
- [49] P. L. Hall and D. K. Ross, Incoherent neutron scattering functions for random jump diffusion in bounded and infinite media, *Mol. Phys.* **42**, 673 (1981).
- [50] K. S. Singwi and A. Sjölander, Diffusive motions in water and cold neutron scattering, *Phys. Rev.* **119**, 863 (1960).
- [51] S. N. Purohit, Discussion of the quasi elastic scattering of neutrons in incoherent liquids, *Phys. Chem. Liq.* **1**, 13 (1968).
- [52] I. P. Silverwood and V. G. Sakai, Propane diffusion in ZSM-5 pores measured by quasielastic neutron scattering under macroscopic flow, *Chem. Eng. Sci.* **186**, 116 (2018).
- [53] D. Colognesi, U. Bafle, E. Guarini, and M. Neumann, Microscopic self-dynamics in liquid Ne-D₂ mixtures: Quantum features and itinerant oscillators reexamined, *Phys. Rev. E* **109**, 045104 (2024).
- [54] K. Sköld, J. M. Rowe, G. Ostrowski, and P. D. Randolph, Coherent- and incoherent-scattering laws of liquid argon, *Phys. Rev. A* **6**, 1107 (1972).
- [55] M. Celli, D. Colognesi, A. J. Ramirez-Cuesta, and M. Zoppi, Breakdown of the Gaussian approximation in semi-quantum liquids, *Physica B* **350**, E1083 (2004); M. Celli, D. Colognesi, M. Zoppi, and A. J. Ramirez-Cuesta, Microscopic self dynamics in liquid hydrogen and in its mixtures with deuterium and neon: A neutron scattering study, *J. Low Temp. Phys.* **138**, 887 (2005).
- [56] <https://edata.stfc.ac.uk/home>.
- [57] B. J. Alder and T. E. Wainwright, Decay of the velocity autocorrelation function, *Phys. Rev. A* **1**, 18 (1970).
- [58] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Academic Press, Burlington, MA, 2006).
- [59] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, Asymptotic time behavior of correlation functions, *Phys. Rev. Lett.* **25**, 1254 (1970).
- [60] R. Jung, G.-L. Ingold, and H. Grabert, Long-time tails in quantum Brownian motion, *Phys. Rev. A* **32**, 2510 (1985).
- [61] T. R. Kirkpatrick and D. Belitz, Diffusion, long-time tails, and localization in classical and quantum Lorentz models: A unifying hydrodynamic approach, *Phys. Rev. B* **110**, 184203 (2024).
- [62] S. Bellissima, M. Neumann, E. Guarini, U. Bafle, and F. Barocchi, Time dependence of the velocity autocorrelation function of a fluid: An eigenmode analysis of dynamical processes, *Phys. Rev. E* **92**, 042166 (2015).
- [63] S. Bellissima, M. Neumann, E. Guarini, U. Bafle, and F. Barocchi, Density of states and dynamical crossover in a dense fluid revealed by exponential mode analysis of the velocity autocorrelation function, *Phys. Rev. E* **95**, 012108 (2017).