

Maxwell's Demon Observing Creation of a Molecular Vibration

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Dedicated to Professor Jörg Fleischhauer on the occasion of his 75th birthday

Quantum correlations and associated quantum information concepts (e. g. quantum discord, entanglement, quantum Maxwell's demon) provide novel insights in various quantum-information processing tasks, quantum-thermodynamics processes, open-system dynamics, quantum molecular dynamics, and general many-body physics. We investigate a new effect of correlations accompanying collision of two quantum systems A and B , the latter being part of a larger (interacting) system $B + \mathcal{D}$. In contrast to the usual case of a classical 'environment' or 'demon' (which can have only classical correlations with $A + B$ during and after the collision), the quantum case exhibits striking new features. Here, in the frame of incoherent inelastic neutron scattering (INS) and vibrational dynamics of molecules, we report experimental evidence of a new phenomenon: quantum deficit of momentum transfer in an elementary neutron–molecule collision, in particular, in INS from single H_2O molecules confined in channels with sub-nanometer diameter. The INS findings are in clear contrast to conventional theoretical expectations, but are naturally (albeit qualitative) interpreted in the frame of modern theory of quantumness of correlations, thus also proposing a new operational meaning of quantum discord and related measures.

Key words: Quantum Maxwell's Demon; Quantumness of Correlations; Quantum Discord; Inelastic Neutron Scattering; Molecular Vibrations.

1. Introduction

Correlations between physical (chemical, biological etc.) systems are created by interactions and thus are ubiquitous in nature. They play a significant role in classical and quantum physics. The emergent behaviour of many complex systems cannot simply be derived from their individual components, since their properties fundamentally depend on the delicate correlations between their subsystems; cf. [1].

To prevent possible confusion, it should be emphasized that the well-known quantum mechanical correlations due to the indistinguishability of identical particles play no role in the following investigations. Namely we will consider only quantum correlations between *distinguishable quantum systems*. For instance, below we will consider specific quantum correlations, created by incoherent inelastic neutron scattering (INS), between a neutron and a proton of molecular H_2O stretching vibrational modes. Additionally, classical correlations (e. g. as appearing in classical statistical mechanics of condensed systems) are also excluded from our considerations.

In certain cases, quantum correlations are in blatant contrast to every expectation based on classical physics. A particular kind of quantum correlations which have been shown to exhibit distinctive non-classical features are known as quantum entanglement [2–7]. Nowadays quantum entanglement (QE) is recognized to be a basic resource for quantum information, computing and communication, and thus plays a central role in the field of quantum information processing (QIP); see e. g. [8].

The correlations between two quantum systems A and B are associated with information, as for instance in the case of DNA, where (classical) correlations between base pairs encode genetic information. In classical statistical physics and thermodynamics, the crucial role of correlations became obvious when Maxwell [9], in an attempt to clarify the limitations of thermodynamics, introduced his famous demon, who plays an important role in present-day information theory, cf. [10]. Generally, thermodynamics and information theory possess several links, as e. g. indicated by the formal similarity of the formulas of the Shannon and the von Neumann entropies, cf. [6, 8, 10]. Finally

Landauer [11] and Bennett [12, 13] succeeded to 'exorcize' Maxwell's demon through the so-called Landauer erasure principle. There is no doubt that the intricate relation between information theory and thermodynamics also implies a thermodynamic cost for information acquisition. Likewise, any information acquisition process is expected to be ultimately limited by the Second Law of thermodynamics. In short, as Landauer puts it: 'information is physical'; cf. [10, 11, 14].

In 2001, the thus far latest chapter in the story of the relation between 'correlations' and 'information' began with the pioneering works by Ollivier and Zurek [15] and Henderson and Vedral [16] showing that, beyond QE, there exists another, more general kind of quantum correlations. Nowadays these correlations are popularly known as 'quantum discord' (QD) [17], or more generally referred to as 'quantumness of correlations'. Discord and related concepts (like e. g. quantum (work) deficit, measurement-induced disturbance etc.) have recently entered the field of QIP and are subject to considerable investigations regarding their operational meaning; see e. g. [18]. As they concern the physics of Maxwell's demon, they also have entered the foundations of quantum thermodynamics (cf. [10, 18–20]).

In the present paper, we consider the possible connection of these quantum phenomena (i. e. entanglement, discord, decoherence, dynamics of correlations, etc.) within a concrete experimental context, namely elementary scattering processes. We will particularly point out the 'energetic costs' of quantumness of correlations and their experimental measurability, which then establishes additional physical insight into the phenomenon. We employ the developed concepts to interpret experimental results obtained from neutron scattering – qualitatively, for the time being – which contradict predictions of conventional theory. It appears that these results illustrate a new operational meaning (or interpretation) of quantumness of correlations in the context of a real scattering experiment, like INS.

2. Quantumness of Correlations and Decoherence – Thermodynamic and Energetic Consequences

Decoherence is the ubiquitous phenomenon that destroys quantum correlations (state superpositions, quantum interference, quantum phases) thus leading to the 'appearance of a classical world in quantum the-

ory'; cf. [21]. Representing an irreversible process, decoherence is time-oriented, i. e. it breaks the time-inversion invariance of the Schrödinger equation. In macroscopic systems, it is known to be much faster than energy dissipation (e. g. due to friction). Numerous decoherence models, based on a broad variety of physical motivations, have been proposed and investigated in the scientific literature; see [21, and references therein].

Quantum correlations, their decoherence, and the associated 'quantum Maxwell's demon' observing the dynamics of correlations, are intrinsically related to the concept of 'quantum heat engine'; see e. g. [19, 22]. The latter has attracted considerable interest since it provides novel insights into the fundamental physics of heat–information–energy conversion. Some selective examples from the literature (which are in conceptual context with the experimental INS topic considered below) are mentioned in the following.

2.1. Lloyd Model

Lloyd [22] analyzed the effects of the quantum Maxwell's demon. He found that a quantum device acquiring information in a measurement process and the associated decoherence disturb the system and act as a source of thermodynamic inefficiency. The latter is shown to be intrinsically related to the destruction of non-diagonal matrix elements of the system's density matrix ρ . In special processes with ρ remaining always diagonal, the quantum demon reaches the well-known Carnot efficiency. In other words, the extra gained information by quantum measurement and decoherence has been identified as the cause of *decrease* of the efficiency of the Carnot engine [22].

2.2. Scully et al. Model

The above interesting result pointing out the role of decoherence and/or loss of quantum correlations should be contrasted with the following result of Scully et al. [19]. These authors proposed and analyzed a new kind of quantum Carnot engine powered by a special quantum heat bath, in which quantum correlations (or coherences) constitute the crucial ingredient. Surprisingly, in this quantum model it is possible to extract work even from a single thermal bath. In this heat engine the piston is driven by radiation pressure. The working fluid (say, analogous to steam of a conventional machine) finds its counterpart in the radiation,

which is generated by a beam of hot atoms (constituting the thermal reservoir). In the 'regular' case of two-level thermal atoms, the engine's efficiency cannot exceed the well-known Carnot limit. In the case of hot specific three-level atoms constituting a heat bath things look quite different, i. e. when the nearly degenerate lower levels feature a small amount of quantum coherence. The corresponding quantum phase ϕ can be varied as a control parameter to effectively increase the temperature of the radiation field. In this scenario work is obtained even when only one single heat bath is present. Consumption of quantum coherence is shown to produce work.

The deep physics behind the Second Law of thermodynamics, however, is not violated. The assumed atomic coherence itself causes energetic costs, as e. g. it must be generated by the passage of the atoms through a suitable microwave field. An explicit estimation of the necessary microwave field's energy to produce the assumed appreciable coherence between the atomic levels was shown to be greater than the extracted work in the above process. Consequently and in line with the Second Law of thermodynamics, the total entropy of the whole system is constantly increasing [19].

2.3. Del Rio et al. Model

Another theoretical result demonstrating certain dramatic consequences of quantum correlations is given by del Rio et al. [20], who showed that the standard formulation and implications of Landauer's principle [11, 12, cf. Introduction] are no longer valid in the presence of quantum information and/or correlations. Their main result is that the work cost of erasure of information is determined by the entropy of the system, conditioned on the quantum information an 'observer' (or Maxwell's demon) has about it: the more an observer knows about the system carrying the information, the less it costs to erase the information. Obviously this result gives a direct thermodynamic significance to *conditional entropy* [18], which plays a dominant role in the theory of quantumness of correlations.

The main result by del Rio et al. characterizes the work, $W(A|Q_M)$, that an observer (or demon) with access to a quantum memory Q_M correlated with the system A , needs to perform to erase system A . In the 'thermodynamic limit', where the observer erases many identical copies of A jointly, the authors have found

a specific erasure procedure [20] whose work cost does not exceed

$$W(A|Q_M) = S(A|Q_M)kT \ln(2) \quad (1)$$

per copy of A ; (k : Boltzmann constant, T : temperature). Here $S(A|Q_M)$ is the conditional von Neumann entropy,

$$S(A|Q_M) = S(AQ_M) - S(Q_M). \quad (2)$$

This work cost is shown to be optimal, under the assumption that Landauer's principle holds for a classical observer (or demon). In the quantum case, however, several novel features may arise. Especially, the last equation implies that the work required for erasure may be negative for an observer with a quantum memory Q_M : the process may result in a net *gain* of work. For instance, the combined system AQ_M may be closed and in a pure state, in which case its von Neumann entropy will be zero, $S(AQ_M) = 0$, whereas the reduced state of the memory Q_M is mixed and has positive entropy $S(Q_M) > 0$. This finally yields $S(A|Q_M) < 0$ and thus $W(A|Q_M) < 0$, i. e. negative work costs.

This surprising result provides a novel thermodynamic operational meaning for negative conditional entropies, which earlier only had information-theoretical interpretations [18, 20].

2.4. Schulman and Gaveau Model

The preceding theoretical result is certainly unexpected, since erasure of quantum phases and/or correlations – specifically in the absence of interactions – is not widely acknowledged as a source of energy, or equivalently, as having 'negative' energy costs. In order to further illustrate the above theoretical framework in the context of the specific INS experimental context considered in this paper, the theoretical model by Schulman and Gaveau [23] may be mentioned here. Consider a quantum system A , e. g. a quantum oscillator, with free Hamiltonian H_A , making an elastic collision with a second system B with free Hamiltonian H_B . Let the short-range interaction potential be V_{AB} . The total Hamiltonian is $H = H_A + H_B + V_{AB}$. Before the collision, the two systems are assumed to be not correlated and so the complete density matrix $\rho(0)$ is $\rho(0) = \rho_A(0) \otimes \rho_B(0)$. In general, subsequent to their collision the systems become quantum correlated (or even entangled) and the exact density operator

$$\rho(t) = U(t)\rho(0)U^\dagger(t)$$

($U(t)$: time evolution operator) is not a product of individual density operators $\rho_A(t) = \text{Tr}_B\rho(t)$ and $\rho_B(t) = \text{Tr}_A\rho(t)$.

It is widely believed that once the particles are separated the quantum correlations can be dropped (provided one does not perform an experiment of Einstein–Podolsky–Rosen type [2, 4, 6]), simply because measurements of physical quantities of each of the two particles cannot depend on their correlations. Thus the replacement

$$\rho(t) \rightarrow \rho_A(t) \otimes \rho_B(t), \quad (3)$$

i. e. the erasure of quantum correlations (which e. g. a quantum Maxwell's demon could perform!), is usually assumed to be 'innocuous' and does e. g. not affect the energies of the systems.

The striking result [23] contradicts this intuitive expectation. Putting

$$\Delta\rho(t) = \rho_A(t) \otimes \rho_B(t) - \rho(t)$$

and for a particular form of the interaction Hamiltonian, they show that for sufficiently *short* times the following relation holds:

$$\Delta E \equiv \text{Tr}(\Delta\rho(t)H) = \text{Tr}(\Delta\rho(t)V_{AB}) > 0. \quad (4)$$

In simple terms, the 'replacement' of the entangled $\rho(t)$ by the non-entangled state $\rho_A(t) \otimes \rho_B(t)$ necessarily increases the system's energy [23]. In other terms, as also mentioned above, consumption or erasure of quantum correlations may have 'negative' energetic costs. This appears highly paradoxical – as the authors put it: '... losing quantum correlations should not heat the gas. You do not burn your fingers because of a partial trace over a density matrix' [23].

One may object here that this result is unphysical since it seems to violate energy conservation. However this is not the case. It was stressed that, in the situation contemplated, the coupling short-range Hamiltonian must be considered as time dependent, because the physical approach and separation (i. e. the collision) of the particles A and B should be described by a time-dependent coupling $g(t)V_{AB}$, and thus, energy conservation need not apply. Moreover, it was clarified that this additional energy $\Delta E > 0$, which may be called 'quantum heating', is supplied by the *translational* degrees of freedom of A and/or B [23]. These do

not appear explicitly in the above model Hamiltonian and thus should represent an 'effective environment' or 'bath', say $\mathcal{E}_{\text{trans}}$. A quantum Maxwell's demon \mathcal{D} observes and manipulates (here: erases) the quantum correlations after each $A - B$ collision, thus transferring energy unidirectionally from $\mathcal{E}_{\text{trans}}$ to oscillators A and B .

The quantum-theoretical concepts under consideration are rather unknown in the field of neutron scattering (and other scattering disciplines). Therefore the aforementioned works were chosen for the purpose of introducing concepts and/or illustration, and by no means cover the whole relevant literature. For further investigations, see [10, 18, 24, 25, and references therein].

3. Incoherent Inelastic Neutron Scattering (INS) – Vibrational Spectroscopy

Vibrational spectroscopy with incoherent inelastic neutron scattering can provide spectra that are more detailed and easier to interpret than optical spectra. The measured intensity depends on energy transfer and kinetic momentum transfer, allowing determination of the potential function (see e. g. the textbook [26] and [27, 28]). The focus will be the *stretching vibrational* modes of H_2O .

The INS experiments reported below were carried out with modern time-of-flight (TOF) spectrometers. For a TOF t measured by a detected neutron holds

$$t = \frac{L_0}{v_0} + \frac{L_1^\theta}{v_1} + t_0. \quad (5)$$

Here L_0 is the source–sample distance, L_1^θ is the sample–detector distance; the detector is positioned at the scattering angles θ . v_0 and v_1 are the velocities of the incident and scattered neutron, respectively. t_0 is a small time offset due largely to electronic delays. In direct geometry spectrometers, the energy of the incident neutrons is well determined, $E_0 = \text{constant}$. For each value of t , the associated transfers of momentum ($\hbar Q$) and energy ($E = \hbar\omega$) from the neutron to the struck particle are uniquely determined.

In a general INS experiment, the scattering intensity is measured as a function of the neutron energy transfer (or: energy loss)

$$E = E_0 - E_1 = \hbar\omega = \frac{(\hbar k_0)^2}{2m_n} - \frac{(\hbar k_1)^2}{2m_n} \quad (6)$$

(m_n : neutron mass) due to the neutron–atom collision, and the corresponding neutron momentum transfer is given as

$$\hbar Q = \hbar k_0 - \hbar k_1, \quad (7)$$

where

$$|Q| = Q = \sqrt{k_0^2 + k_1^2 - 2k_0k_1 \cos \theta}, \quad (8)$$

and θ being the scattering angle (sometimes also denoted as 2θ). The subscripts ‘0’ and ‘1’ refer to quantities before and after the collision. Since the scattering is incoherent, it is due to the collision of a neutron with the nucleus of an atom.

For scattering from free atoms with mass M at rest holds the kinematic relation

$$\frac{v_1}{v_0} = \frac{k_1}{k_0} = \frac{\cos \theta + \sqrt{\left(\frac{M}{m_n}\right)^2 - \sin^2 \theta}}{\frac{M}{m_n} + 1}. \quad (9)$$

M is the mass of the struck nucleus (atom). In practice, this equation corresponds to neutrons measured at the center of the measured recoil peak.

In this paper we consider only incoherent scattering (which is usually the case in INS), which means that the elementary scattering happens between the neutron and a single atom (nucleus); cf. the textbooks [29, 30].

Modern neutron detector systems incorporate a large number (of the order 10^5) of detector pixels, which provide a large and dense area of E and Q transfers for the measured INS intensity map $S(Q, E)$. (More precisely, this quantity represents the experimental dynamic structure factor.) A key difference between vibrational neutron spectroscopy and infrared and Raman spectroscopies is that the neutron has mass, and thus an INS event results in a significant transfer of both energy and momentum. Both the Q and E dimensions are accessible in certain limits (depending on the specific instrumental setup). Hence INS spectroscopy is intrinsically a two-dimensional form of spectroscopy, thus being capable of providing potentially more (and sometimes qualitatively new) information than Raman scattering or infrared absorption.

According to the harmonic approximation of conventional neutron scattering theory, each vibrational transition appearing in the measured INS intensity map $S(Q, E)$ is expected to be an ‘island’ due to broadening in energy caused by the Doppler effect and various interactions with the environment. Maxima of intensity

should occur at specific Q -values along the recoil line for the oscillator mass M_{vibr} :

$$E_r = \frac{\hbar^2 Q^2}{2M_{\text{vibr}}}. \quad (10)$$

In general, however, since the neutron has a non-negligible mass m_n there must be a recoil effect in a neutron–molecule INS event. The effect of this recoil on the INS vibrational spectra has been investigated by Tomkinson [31]. For the excitation of a molecular vibration with energy E_{vibr} , energy conservation implies

$$E = E_{\text{vibr}} + E_r. \quad (11)$$

E is given by the energy loss of the scattered neutron (6). Remembering that we deal with incoherent scattering (i.e. the neutron scatters off one nucleus only), it follows that as the mass of the scattering particle falls the magnitude of the recoil energy increases.

The last equation (11) which expresses energy conservation, has a straightforward consequence. Consider INS from protons (hydrogen atoms; with mass M_H) of a molecule. Due to the similarity of neutron and proton masses, one may put $m_n = M_H$, and then the kinetic equations (8) and (9) yield the simple result $k_0^2 - k_1^2 = Q^2$. Thus one obtains for the neutron energy transfer (6) for n–H scattering:

$$E = E_0 - E_1 = \frac{\hbar^2 Q^2}{2m_n}. \quad (12)$$

It should be emphasized that this simple form for the energy transferred from a neutron to a scatterer in a collision holds only for scattering from protons (hydrogen atoms).

4. INS Results from H₂O Vibrational Modes

Here are considered two independent experiments. The first can be interpreted within conventional theory. The second experiment reveals novel features which contradict every conventional interpretation.

4.1. INS Results from Bulk Ice

INS results from water and ice are well known in the scientific literature. Figure 1 shows the observed INS intensity $S(Q, E)$ of microcrystalline ice (ice Ih) at $T = 20$ K and $p = 1$ bar, measure with $E_0 = 750$ meV with the TOF-spectrometer MARI (ISIS spallation source,

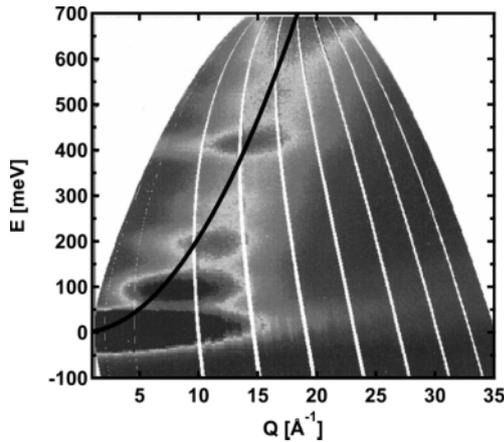


Fig. 1. Measured $S(Q, E)$ intensity map of ice Ih at 20 K and 1 bar, recorded on MARI. Neutron incident energy $E_0 = 750$ meV. The calculated black line (parabola) shows the recoil trajectory of a free proton. The strong intensity contribution centered around zero E -transfer (for low Q 's) is mainly scattering from the aluminium cell.

Rutherford Appleton Laboratory, UK) [32]. The inserted black (parabola) line is the calculated recoil line of a free hydrogen atom (being at rest before collision)

$$E_r^{\text{free}} = \frac{\hbar^2 Q^2}{2M_H}, \quad (13)$$

(M_H : hydrogen atom mass) shown as a guide to the eye. The formal similarity of this equation with the special case (12) should be noticed.

The intensity peak around $E = 420$ meV and 14 \AA^{-1} is due to the well-known stretching vibrational modes of H_2O in water or ice [26]. It should be observed that the free hydrogen atom recoil line intersects the center of this intensity peak (within experimental accuracy). In view of (13) and (12), and the fact that $m_h \approx M_H$, this experimental result tells us that there is no significant recoil in this case; in other terms, the energy loss of the neutron equals the energy of the stretching hydroxide vibrational mode. This is expected in the frame of standard theory, for the following reasons:

- (i) The INS intensity depends on the ratio (inelastic cross-section/atomic mass) [26, 29] which for hydrogen atoms is at least 100 times larger than that of other atoms (here: oxygen). Thus the observed stretching vibrational excitation by incoherent INS is overwhelmingly due to neutron-proton collision.

- (ii) The H_2O molecule is H-bonded with adjacent molecules and thus cannot recoil freely as a whole; additionally, the O–H bond is not broken by the collision.
- (iii) The very short (of the order of 1 fs) characteristic vibrational time, and the spectral separation of the stretching from other modes, ‘decouples’ the H-vibrational motion from the other, slower atomic motions (and/or modes) in the molecule and/or ice. It may be noted that a similar decoupling of H-dynamics has also been observed in many biomolecules [28], appearing even in the quantum tunnelling of protons in H-bonds.

Let us now compare the above result with results obtained from the intensity peak due to the so-called water scissors (or bending) vibrational mode around $E = 200$ meV. One finds that this peak does not lie on the calculated free H-recoil line, but is centered around *higher* Q -values. This experimental finding has a natural explanation within conventional theory, for the following reasons. As the H-motion in this H-bonded system should be hindered by adjacent particles, the hydrogen atom may become ‘dressed’ by environmental degrees of freedom, and hence its effective mass for the neutron–hydrogen collision should become *larger* than 1 a.m.u. (atomic mass unit). Indeed, a rough estimate (derived from the peak position shown in Fig. 1) of the effective H-mass for the scissors mode turns out to be $M_H^{\text{eff}} \approx 1.35$ a.m.u.

This physical situation can also be rationalized by considering that E_{vibr} is smaller than the energy transfer E at the Q of the peak maximum. (Recall that the black parabola curve represents also the E -transfer for neutron–hydrogen collision.) The preceding point (i) remains valid here too. Thus a part of the neutron’s E -loss is transferred to, or dissipated by, environmental degrees of freedom of the struck hydrogen atom. Obviously, the scissors vibrational mode is not ‘decoupled’ from the other dynamical modes (i. e. librations, phonons, etc.) of the complex molecule-ice system.

Summarizing, the presented results show no anomalous or unexpected feature in the light of standard theory.

4.2. INS Results from Ultra-Confined and Oriented H_2O Molecules

The second example under consideration concerns a very recent experiment by Anovitz et al. [33] car-

ried out with the TOF-spectrometer SEQUOIA (SNS spallation neutron source, Oak Ridge National Laboratory, USA) [34]. (This paper contains numerous results obtained with different spectroscopic techniques, most of which are not discussed here.) The INS spectra, measured at $T = 7$ K, are from single H_2O molecules ultra-confined in channels of single crystals of beryl (chemical formula: $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) with diameter about 4.86 \AA . The molecules are oriented with their H–H direction parallel to the c -axis of the crystal [33].

In this elegant INS experiment, spectra with Q parallel, and also Q perpendicular, to the c -axis were measured separately, thus allowing to quantify directional variations in the dynamics (and the associated effective potential) of the confined molecules. Various interesting new results were obtained. E. g. it was found that, counter-intuitively, vibrations parallel to the c -axis channels are significantly more hindered than those perpendicular to the channels. Equivalently, in view of standard theory, one must conclude that the effective potential for vibrations in the c -direction is harder than the potential in directions perpendicular to it [33]. Additionally, it seems to be no H-bonding constraining vibrations between the channel water and the beryl structure [33].

Let us now compare certain INS results of [33] from single H_2O molecules with the corresponding ones from ice as presented above. This comparison will demonstrate a new effect of stretching vibrations.

First, we consider the spectral intensity in the range $150\text{--}400$ meV, in which lies the scissors vibration mode of H_2O . Also in this experiment, the INS data exhibit qualitatively the same positive Q -shift as for the scissors mode in ice. As discussed above, such a Q -shift (or deviation from the ideal recoil line of the free hydrogen [33]) is by no means surprising. Additionally, note that this effect is equally present in the INS spectra measured with Q -perpendicular-to- c as well as with Q -parallel-to- c orientation. However, the intensity for the Q -perpendicular-to- c orientation appears to be *higher* than that of the other one.

Second, in clear contrast to the above finding, INS from the *stretching* modes reveals quite the opposite Q -shift, that is, the peak maximum (in fact, the whole peak) is now strongly shifted to *lower* Q 's than the theoretically expected free hydrogen-atom recoil peak (the comparison being at the same energy)! Moreover, both crystal orientations (Q -parallel-to- c and the sec-

ond one; see above) exhibit this striking effect (cf. [33, Figure 5]).

To visualize this finding, we refer to [33, Figure 7], from which our Figure 2 is adapted. Here the *difference* between two INS intensity maps is shown, both measured with incident neutron energy $E_0 = 800$ meV: the Q -parallel-to- c -orientation map is subtracted from that of the Q -perpendicular-to- c -orientation. This is sufficient for our purposes. Due to this subtraction and the fact that the Q -parallel-to- c peak is much stronger than the other one (see e. g. [33, Figure 5]), the intensity of the stretching vibrational peak in Figure 2 appears as being ‘negative’. Similarly to Figure 1, the black (parabola) curve represents the calculated conventional neutron recoil scattering from free protons.

Figure 2 shows that this momentum-transfer ‘deficit’ is remarkably large, i. e. the measured peak with $E \approx 470$ meV is centered around $Q \approx 10\text{--}12 \text{ \AA}^{-1}$, although the free H-recoil is expected to be at $Q_r \approx 15 \text{ \AA}^{-1}$.

The corresponding effective H-mass for the stretching vibrational modes, extracted from (13), is then $M_{\text{H}}^{\text{eff}} \approx 0.55 \pm 0.1$ a.m.u. Thus, in illustrative terms, one could say that the struck proton appears to be ‘more mobile’ than a free proton.

Expressed in terms of energies involved in this INS process, the experimental finding appears even more

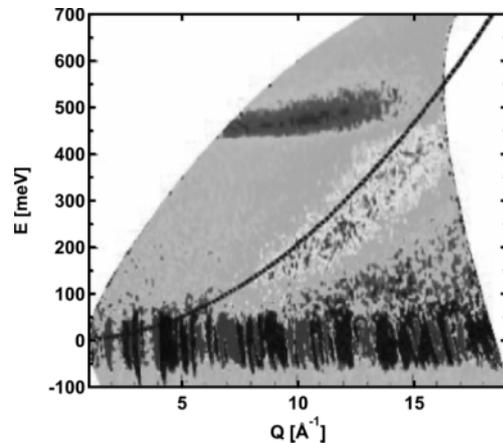


Fig. 2. Difference of the measured $S(Q, E)$ maps of oriented single H_2O molecules in sub-nano-channels of beryl at 7 K, for Q -perpendicular-to- c and Q -parallel-to- c orientations (see the text), recorded on SEQUOIA. Neutron incident energy $E_0 = 800$ meV. The black line (parabola) shows the calculated recoil trajectory of a free proton. (Adapted from [33, Figure 7].)

striking. Here, E_{vibr} comes out to be considerably larger (roughly 50%; see Fig. 2) than the energy transfer E at $Q \approx 11 \text{ \AA}^{-1}$ of the stretching-vibrational peak maximum – and this holds even for both crystal orientations. As explained in the preceding discussion of the MARI-experiment, the black parabola curve represents also the E -transfer for neutron–hydrogen collision. Also here the preceding point (i) remains valid. Thus, in the frame of conventional theory, we arrive at the highly surprising conclusion that the neutron's E -loss (even in the whole Q -range of the peak) is *smaller* than the energy E_{vibr} of the vibration being excited by the collision – which seems physically impossible.

It should be observed that, as the data of Figure 2 show, this ‘anomalous’ Q -deficit, or equivalently ‘anomalous’ E -surplus, is clearly far larger than any conceivable experimental error. The aforementioned discussions of the preceding section also show that this experimental finding is in blatant contradiction of conventional expectations.

4.3. Quantum Maxwell's Demon in Action

The result under consideration, however, loses its strangeness if it is considered in the light of the modern theory of quantumness of correlations and decoherence, shortly mentioned in Section 2. This theoretical frame provides the following qualitative theoretical scheme and/or interpretation.

Since H_2O and the sub-nano-channels (i. e. its environment) interact, it may be assumed as a working hypothesis that quantum correlations of the aforementioned kind (Section 2) may exist. Then, in the light of modern theory, these correlations can become a source of work gain, which, as discussed above, has no conventional theoretical analogue.

In bulk ice (see MARI experiment), these correlations seem to be ‘washed out’ in the characteristic time-window of the elementary INS process (of the order of 1 fs). I. e., during the scattering (which is short-time, but not instantaneous) the environment is strong enough to effectively achieve this goal. Note that ice, like water, represents a strongly H-bonded system.

In the single-molecule case (of SEQUOIA experiment) these correlations seem to survive and the ‘environment’ \mathcal{E} (parts of the wall of a sub-nano-channel) participates in the dynamics of the elementary

neutron–hydrogen scattering process. In other terms one may say that although the neutron scatters from a single proton, the composed system ‘proton + \mathcal{E} ’ participates essentially to the dynamics of scattering. The fully details of this dynamical process – the participation of Maxwell's demon – may be unknown (as they are in most theoretical models of Section 2).

But applying e. g. the Schulman–Gaveau model (Section 2.4), it becomes physically feasible that the consumption of quantum correlations in ‘neutron + proton + \mathcal{E} ’ can cause an enhanced E -transfer – a quantum energy-transfer surplus – from the neutron's translational degrees of freedom (the ‘bath’ $\mathcal{E}_{\text{trans}}$) to the energy of the vibrational mode. This dynamical process, when ‘interpreted’ in conventional terms, leads to the appearance of the ‘anomalously’ small effective mass $M_{\text{H}}^{\text{eff}} \approx 0.55$ a.m.u. of the recoiling proton.

Similar physical pictures can be given within the other theoretical models of Section 2 too.

In other words, the Maxwell's demon observing the actual INS process from a single H_2O which leads to the creation of a stretching vibrational mode, is a quantum one – and, as concerns E -transfer, by far more efficient than any classical demon!

5. Additional Remarks

The above results show that the advanced ‘two-dimensional’ INS spectroscopic technique, as applied e. g. with the instruments MARI (ISIS, RAL) and SEQUOIA (SNS, ORNL) represents a powerful method that may provide novel insights into the quantum dynamics of molecules and condensed matter. This is related with the fact that Q and E represent two independent physical variables, and this makes INS in principle superior to other spectroscopic methods (like Raman scattering and infrared absorption).

Obviously, the novel quantum effect revealed in the spectral stretching vibrational modes of single H_2O molecules cannot be detected with the standard (or, more conventional) ‘one-dimensional’ INS spectrometers, in which the detectors follow a specific, single trajectory in the (Q - E) plane, and the measured intensities are given as a function of energy; cf. the numerous examples given in [26, 27]. Measured with the latter, the stretching vibrational mode of oriented H_2O molecules reported in [33, see Section 4.3] would erroneously appear as being ‘very weak’, with obvious consequences for its theoretical interpretation.

The INS experimental results discussed in this paper provide first evidence that quantumness of correlations in molecules, when interacting with specific environments (here: sub-nano channels), has energetic costs that affect their dynamics and that of neutron scattering on ultrafast timescales. Similar indications of this effect (although with a much weaker E -shift) have been recently observed in neutron Compton scattering from molecular H_2 [35] and D_2 [36].

To our knowledge, the ‘anomalous’ Q -deficit (or equivalently ‘anomalous’ E -surplus, or quantum heating) considered in Section 2.4 has no conventional interpretation. In contrast to conventional neutron scattering theory, and based on the aforementioned theoretical understanding of quantumness of correlations and their dynamics accompanying elementary scattering processes, we attribute the experimentally observed ‘anomalous’ effect to theoretically predicted negative energetic costs of correlations mentioned in Section 2. In particular we refer to the qualitatively similar results following from the result of the Schulman–Gaveau analysis [23, Section 2.4], and the negative work costs of negative conditional entropy by del Rio et al. [20, Section 2.3]. Note that in all these cases the quantumness of correlations leads to higher work-values as compared to the associated processes in the absence of genuine quantum correlations. The same holds for quantum Maxwell's demons, which can extract more work from quantum correlations than classical demons can do; cf. [10, 18, 24]. A quantitative theoretical treatment of the ‘anomalous’ effect under consideration is still unknown.

In view of these remarks and considerations, the new INS scattering effect discussed above offers new physical insights into discord and related measures of quantumness of correlations, as well as on their operational meaning [18]. Moreover, the general character (i. e. which does not presume any specific interaction Hamiltonian) of its causes suggests that similar effects could probably be observed in related subfields of molecular spectroscopy (e. g. rotational spectroscopy of molecules, proton-transfer reactions in biological molecules, proton dynamics in fuel cells, H_2

uptake in hydrogen storage materials, etc.), and other experimental areas involving different scattering techniques (e. g. inelastic X-ray scattering, electron–atom Compton scattering).

At last, the following general remarks may be in order. Experimental investigations of the behaviour of quantumness of correlations have been started only very recently, and they are usually carried out with photons or nuclear spins (which are rather well isolated from the environment); see e. g. the review article [18], and references therein. Much more need to be done in order to lead us to a better test and comprehension about the quantum nature of correlations in composed and/or strongly interacting systems. Applications of these genuine quantum correlations to other areas like condensed matter physics and biological systems do not exist yet, and a long way is still to be traversed in order to give them a broader operational meaning and appreciate the true role of these correlations in these different fields of knowledge.

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Note added in proof

After submission of this paper, we learned about the very recent publication by E. C. Spencer, B. Huang, S. F. Parker, A. I. Kolesnikov, N. L. Ross, and B. F. Woodfield, *J. Chem. Phys.* **139**, 244705 (2013), which provides INS data from water molecules adsorbed on Al_2O_3 nanoparticles measured with SEQUOIA.

Interestingly, visual inspection of the data presented in Fig. 6a–c reveals the presence of the aforementioned ‘anomalous’ quantum Maxwell's demon effect also in the bending vibrational mode centered roughly at $E \approx 205$ meV and $Q \approx 8 \text{ \AA}^{-1}$.

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