



Lineshapes in quasi-elastic scattering from species hopping between non-equivalent surface sites

Fay E. Tuddenham^{a,*}, Holly Hedgeland^a, Andrew P. Jardine^a, Barbara A.J. Lechner^a, B.J. Hinch^b, William Allison^a

^a Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge, CB3 0HE, UK

^b Chemistry & Chemical Biology, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854, USA

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ABSTRACT

We present an analytic model applied to quasi-elastic scattering from an adsorbed surface species undergoing jump diffusion between adsorption sites described by a Bravais lattice combined with a basis of multiple points. The model allows for hops between adsorption sites which are both symmetrically and energetically inequivalent. We give results for 1-D hopping, which are applicable to a species jumping between the top and bridge sites along the $[1\bar{1}0]$ direction on an fcc-(110) surface or for jumps along a step edge. In 2-D, results for hopping between fcc and hcp hollow sites and between the bridge sites of an fcc-(111) surface are presented. These examples give characteristic signatures which will allow these forms of motion to be recognized in experimental data and will enable the underlying physical parameters to be extracted by comparison with the analytical forms derived here.

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1. Introduction

Quasi-elastic scattering experiments provide an important technique for studying fast diffusion of atoms and molecules adsorbed on surfaces [1–5]. The technique, which is typically applied to neutrons or helium atoms, relies on the fact that when probe particles scatter from moving atoms, small amounts of energy are exchanged, which are characteristic of the nature of the adsorbate motion. Such scattering experiments can yield information about both the rate and mechanism of the atomic scale dynamics. This paper describes a generalized method for evaluating the distribution of energy exchanges with the probe expected for scattering from an adsorbate undergoing different types of surface hopping motion.

The spectrum of energy exchanges is given by the dynamic structure factor for scattering¹, $S(\mathbf{Q}, \omega)$, which is related to the Van Hove pair

correlation function, $G(\mathbf{r}, t)$, by a Fourier transform in both space and time [6],

$$G(\mathbf{r}, t) \xrightarrow[FT]{\text{space}} I(\mathbf{Q}, t) \xrightarrow[FT]{\text{time}} S(\mathbf{Q}, \omega) \quad (1)$$

\mathbf{r} and t correspond to surface position and time, while \mathbf{Q} and ω are the momentum and energy transfer on scattering, respectively. $G(\mathbf{r}, t)$ provides a complete statistical description of the surface motion and can be interpreted classically as the probability of finding a particle at position (\mathbf{r}, t) , given that there was a particle at $(\mathbf{r} = 0, t = 0)$. In general, $G(\mathbf{r}, t)$ is the sum of a self part, $G_s(\mathbf{r}, t)$ (same particle) and a distinct part, $G_d(\mathbf{r}, t)$ (different particle). Note that in this paper, we consider systems in the low adsorbate concentration limit, so that the distinct part can be disregarded and $G(\mathbf{r}, t) = G_s(\mathbf{r}, t)$. $G(\mathbf{r}, t)$ can be obtained, in principle, from a suitable experimental measurement of $S(\mathbf{Q}, \omega)$. Quasi-elastic scattering measurements can also be carried out in the time domain, typically using spin-echo methods [7,8], which yield the intermediate scattering function (ISF), $I(\mathbf{Q}, t)$. $I(\mathbf{Q}, t)$ is the spatial Fourier transform of $G(\mathbf{r}, t)$ and the temporal Fourier transform of $S(\mathbf{Q}, \omega)$. It represents the time evolution of the correlation of

* Corresponding author.

E-mail address: fet22@cam.ac.uk (F.E. Tuddenham).

¹ The kinematic scattering approximation assumes that the scattered intensity is the product of the form factor of the scatterers and the dynamic structure factor. However, in many circumstances, the variation of the form factor may be neglected [2].

the atoms and molecules on the surface, as measured by the probe particles, in the direction of \mathbf{Q} and over the periodic repeat distance $2\pi/Q$. For a static system, $I(\mathbf{Q}, t)$ does not decay from its initial value of unity with increasing t . However, for a dynamical system, there will generally be a loss of surface correlation with time, resulting in $I(\mathbf{Q}, t)$ usually being a decaying function of t .

In practice, the Fourier transforms in Eq. (1) are difficult to perform [2], so measurements are not inverted to give $G(\mathbf{r}, t)$ directly. Instead, measurements of $S(\mathbf{Q}, \omega)$ or $I(\mathbf{Q}, t)$ are compared with the ‘signatures’ expected for various forms of diffusion. Both the ‘lineshape’ and the variation of parameters describing the lineshape with \mathbf{Q} are important. A discussion of the signatures expected for different forms of simple motion, such as Brownian or ballistic motion, can be found in Section 5.2 of ref. [7]. For random hopping between discrete adsorption sites that form a Bravais lattice (one adsorption site at each point on the Bravais lattice), the analytic form of the lineshape is also well established. It was originally derived to interpret incoherent neutron scattering from a lattice gas by Chudley & Elliott [9,10] and gives an exponential decay, with a decay parameter that varies sinusoidally with Q . The result has been used widely in the interpretation of experimental data [1,3,7]. Underlying the simple jump diffusion model is the assumption that the adsorbate performs only discrete jumps and remains stationary between them – there is no implicit inclusion of vibration or of a hopping ‘attempt frequency’. While this is a useful simplification for many systems, more sophisticated dynamical models include continuous motion to give a more complete description of adsorbate dynamics. For example, these can include the effects of intra-cell diffusive motion (i.e. vibrational dephasing) in the quasi-elastic lineshape [11,12]. Generally, such models lead to $I(\mathbf{Q}, t)$ undergoing a transition from an exponential to a Gaussian form in t , as the motion becomes ballistic on progressively smaller lengthscales (larger Q) [13]. More recently, quantum mechanical effects associated with the recoil of the probe particle from the diffusing species have also been shown to introduce a complex component into $I(\mathbf{Q}, t)$ (or equivalently an asymmetry into $S(\mathbf{Q}, \omega)$ with ω) [14]. However, all these effects are expected to appear on very short timescales, making them easily distinguishable from the diffusion signatures described in this work.

More generally, where more complex forms of motion are present, surface experiments have been interpreted by comparison with numerical simulations that combine molecular dynamics simulations of the adsorbate motion and scattering calculations [15–18]. These enable, for example, interactions between adsorbates and frictional coupling between the substrate and adsorbates to be included. However, such simulations are time consuming. The analytic approach is highly beneficial as it allows results from a wide range of scattering geometries to be understood quickly, in terms of a small number of parameters, while also providing insight into the underlying physical behaviour.

Recently, the helium-3 spin-echo method (HeSE) has begun to yield a wide range of high quality quasi-elastic scattering data, describing adsorbate diffusion in a variety of surface systems [7]. The new data enables subtle effects to be studied and so new and improved analysis tools are also required to interpret the data effectively. An important set of surface systems now being studied are those in which the adsorbed species undergoes jump diffusion between inequivalent sites. Surface diffusion between inequivalent sites has already been investigated using analytic models and kinetic Monte-Carlo simulations and a range of theoretical results have been derived for coverage dependent thermodynamic properties and diffusion coefficients (for example, [19–22] and references therein). However, in order to interpret experimental data and determine the applicability of these models to real systems, we are specifically interested in obtaining the corresponding quasi-elastic lineshapes.

A model for quasi-elastic scattering of neutrons from an adsorbate undergoing jump diffusion between multiple, but degenerate, adsorption sites in the basis of a Bravais lattice was developed by Rowe et al [23] and later extended to hopping between energetically inequivalent sites [24–27]. The models have been used to interpret quasi-elastic neutron scattering (QNS) measurements of bulk diffusion between interstitial sites for hydrogen [10], heavier atoms and ions [28–32] and molecular species [33]. The models have also been applied to bulk diffusion measurements using Mössbauer and nuclear resonant spectroscopy [27,32,34]. In addition, the theory for hopping between non-degenerate sites has been applied to diffusion amongst sites with periodic defects [25,35]. More recently, bulk diffusion between inequivalent sites has been observed using neutron spin-echo spectroscopy (NSE) [31]. However, to our knowledge these models have not been applied to diffusion on surfaces.

The current paper is the first time that these theories for quasi-elastic scattering from species diffusing between non-equivalent adsorption sites have been rigorously applied to surface, rather than bulk, diffusion. We aim to set out a framework in which scattering experiments involving such diffusion may be analyzed. More specifically, we consider analytical models for idealized jump diffusion over non-Bravais lattices (adsorbate lattices which require a basis containing two or more distinct sites per Bravais lattice point) and obtain analytic forms for the quasi-elastic lineshape. This work offers a compendium of the key results expected for the most commonly encountered surface diffusion problems of this type and identifies the signatures that will enable experimental data to be related to different models.

Following a brief outline of the relevant theory in Section 2, in Section 3, we demonstrate the general behaviour expected in 1-D, such as for hopping between top and bridge sites on an fcc-(110) surface or for hopping along a stepped surface. Since the adsorption energies at these sites may differ, we illustrate the effect of hopping between both symmetrically and energetically inequivalent sites. In Section 4, we consider the 2-D case of adsorption on an fcc-(111) surface, where the three-fold hollow sites have either hcp or fcc coordination, and the case of hopping between two-fold bridge sites on an fcc-(111) surface. In all cases, the analytic results given below were validated against Monte-Carlo simulations. The results are directly analogous to the Chudley & Elliott form [9], but correspond to lattices which have more than one adsorption site in the basis.

2. Theory

We start by briefly reviewing the derivation of the Chudley & Elliott model for jump diffusion [9], in a form suitable for comparison with the later work in this paper. We closely follow the approach set out in [3]. The model considers a particle, with a site residence time τ , which can jump to n sites, which are vectorially \mathbf{l}_k away. The sites are assumed to be energetically identical and form a Bravais lattice with a single site basis (i.e. each site is a lattice point), so are referred to as equivalent. Successive jumps are uncorrelated and assumed to take negligible time. The probability, $P(\mathbf{r}, t)$, of finding the particle at (\mathbf{r}, t) evolves with time as

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = \frac{1}{n\tau} \sum_k (P(\mathbf{r} + \mathbf{l}_k, t) - P(\mathbf{r}, t)), \quad (2)$$

where the index k runs over the n vectors, \mathbf{l}_k , between the site and its nearest neighbours. $G_s(\mathbf{r}, t)$ is the probability of finding the atom at position (\mathbf{r}, t) , averaged over all possible starting sites. Since all the

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