

Determining adsorbate diffusion coefficients on surfaces from helium-3 spin-echo measurements of atomistic dynamics

Min Lin (林旻) ^{1,*} Sam M. Lambrick ^{1,2} and Andrew P. Jardine ¹

¹The Cavendish Laboratory, *University of Cambridge*, JJ Thomson Avenue, Cambridge, CB3 0US, United Kingdom

²ISIS Facility, *Rutherford Appleton Laboratory*, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom



(Received 29 April 2025; revised 8 December 2025; accepted 15 January 2026; published 12 February 2026)

Surface diffusion is typically described using tracer diffusion coefficients D_s , which provides a bridge between atomistic dynamics and macroscopic modeling. Here we introduce a new framework to convert helium-3 spin-echo (HeSE) coherent scattering information into tracer diffusion coefficients D_s , systematically distinguishing and treating three different diffusion regimes—Brownian, hopping, and correlated—within a single HeSE analysis framework. HeSE resolves adsorbate motion on both Å length scales and picosecond timescales and yields highly accurate hopping rates and dephasing rates data across a broad range of systems, yet results are seldom reported directly as D_s because a standard conversion from the coherent intermediate scattering function has been lacking. By combining analytical models with molecular dynamics simulations where interadsorbate forces are explicitly included, we establish a unified workflow to extract D_s , and produce an initial benchmark library of HeSE-derived D_s for surface-diffusion studies, providing an experimentally derived tracer diffusion coefficients for a set of adsorbate-substrate systems.

DOI: [10.1103/rys7-5t69](https://doi.org/10.1103/rys7-5t69)

I. INTRODUCTION

The diffusion of atoms and molecules on surfaces [1–4] is one of the most fundamental processes in science and engineering, underpinning processes as diverse as heterogeneous catalysis [5–7], material growth and device fabrication [8,9], and even environmental processes such as ice nucleation and astrochemistry [10,11]. Characterizing diffusion is therefore essential in order to understand and model complex behavior and to develop and improve processes for fabricating new materials and devices.

In many experimental and theoretical studies of surface diffusion, the microscopic details of atomic motion are ultimately summarized in a single effective parameter: the tracer diffusion coefficient D_s . This quantity provides a common currency for comparing diffusion processes across different materials, substrates, and measurement techniques. Helium-3 spin-echo (HeSE) spectroscopy offers unique capabilities to probe collective adsorbate dynamics at picosecond timescales; however, HeSE accesses the coherent intermediate scattering function and naturally yields jump rates or dephasing rates that characterize collective adsorbate dynamics, rather than the tracer diffusion coefficient itself. Since HeSE data encode not only the rate but also the underlying mechanism of motion,

the information they provide is inherently richer than can be captured by a single diffusion coefficient.

This mismatch of observables has limited direct comparison between HeSE results from more conventional probes of diffusion and has hindered the integration of helium scattering data into the broader surface diffusion literature. To bridge this gap, the aim of the present work is therefore to establish an analysis workflow that converts coherent HeSE spectra into tracer diffusion coefficients providing a reference framework and dataset for future surface-diffusion studies.

A wide range of experimental techniques have been used to study diffusion [2,12–14] with results often presented in the form of a diffusion coefficient. Some of the popular techniques include: scanning tunneling microscopy (STM) [2,15,16], which provides excellent sensitivity for slow surface dynamics; quasielastic neutron scattering (QENS), which measures single-particle and collective dynamics; x-ray photon correlation spectroscopy (XPCS) [17], which probes coherent density fluctuations over mesoscopic length scales; pulsed-field gradient NMR [18], which can yield tracer diffusion constants; dynamic light scattering (DLS) [19,20], which accesses diffusive relaxation in colloidal and other mesoscopic systems; and atomic resolution TEM [21]. However, the majority of these techniques are fundamentally bulk sensitive, rather than surface sensitive techniques, and while bulk techniques such as QENS can be used to measure surface diffusion [22] their sensitivity is severely limited and extraction of surface behavior from bulk behavior will always be an issue. Of the surface sensitive approaches STM is the premier technique, which is typically limited to diffusion coefficients below $10^{-15} \text{ cm}^2 \text{ s}^{-1}$, with experiments often performed at low temperatures, corresponding to motion on the scale of seconds or longer. Some alternative techniques, such

*Contact author: ml976@cam.ac.uk

as laser-induced thermal desorption have recovered much higher diffusion constants [23] but are limited in the types of systems, which can be studied and provide no atomistic information.

In contrast, HeSE spectroscopy can probe lateral dynamics on surfaces with picosecond time resolution over Å distance scales, allowing access to diffusion rates up to at least $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and enabling studies at elevated temperatures of greater technological relevance. HeSE measurements have elucidated a wide range of adsorbate dynamical mechanisms across many adsorbate-substrate pairings, including hopping [24–26], Brownian motion [27], rotation [28,29], confinement [30], correlations [31,32], and more.

In the present work, we develop a HeSE-based analysis that systematically distinguishes Brownian, hopping, and correlated regimes. While many previous HeSE studies have extracted jump rates or barrier heights from Chudley-Elliott fits, only a small subset explicitly reported tracer diffusion coefficients, often using system-specific conventions. Here, we bring these analyses together in a unified framework and make the conversion to D_s explicit in all three dynamical regimes, providing a practical route from HeSE observables to tracer diffusion coefficients. For Brownian motion we exploit the quadratic $\alpha(\Delta K)$ dependence; for well-defined hopping we use a Chudley-Elliott-type description; and for complex motion we employ Langevin molecular dynamics calibrated against HeSE data. These workflows are then applied to HeSE measurements to convert them into tracer diffusion coefficients D_s , thereby assembling a benchmark library for surface-diffusion studies. For the majority of the systems discussed here, and for all of those involving correlated motion, we report values for D_s measured using HeSE. The remainder of the paper is organized as follows: Sec. II defines the diffusion coefficients used, Sec. III summarizes the HeSE method, Sec. IV presents the three analysis routes, Sec. V discusses the resulting D_s values in the context of alternative approaches, and Sec. VI gives our conclusions.

II. DIFFUSION COEFFICIENT DEFINITIONS

Surface diffusion is a broad term that encompasses several distinct but closely related processes. It is therefore crucial to define exactly what we mean by surface diffusion, and within that context precisely what we mean by a diffusion coefficient. On macroscopic and mesoscopic scales, surface diffusion typically relates to the continuum flux of matter across a surface. On these length scales the relevant diffusion coefficient, known as the collective or chemical diffusion coefficient, D_c , is defined through either the decay in density fluctuations, or through the flux of material in proportion to a concentration gradient according to Fick's law [33,34],

$$\mathbf{J}(\mathbf{R}, t) = -D_c \nabla \rho(\mathbf{R}, t), \quad (1)$$

where $\mathbf{J}(\mathbf{R}, t)$ is the flux of material in the presence of the density profile $\rho(\mathbf{R}, t)$. Typically, measurements of D_c are obtained from macroscopic profile evolution measurements, often using optical or electron-based techniques [1,2]. While such measurements provide empirical characterization of the diffusive behavior under specific conditions, they are more

difficult to use to gain insight into underlying physical processes at an atomistic level.

On the microscopic scale, diffusion proceeds through the motion of individual atoms or molecules, which can occur in the form of jumps over a substrate lattice [35], continuous Brownian motion across a flat effective potential [27], or more complex processes such as exchange with substrate atoms [36]. These processes usually result in the mean-square displacement of an individual particle increasing linearly with time. The single-particle, self- or tracer-diffusion coefficient, D_s or D^* , can therefore be defined as [33,34]

$$D_s = \lim_{t \rightarrow \infty} \frac{\langle \Delta \mathbf{R}^2(t) \rangle}{2td}, \quad (2)$$

where $\langle \Delta \mathbf{R}^2(t) \rangle$ is the mean-square displacement and $d = 2$ is the dimensionality of the system. Tracer diffusion corresponds to the spontaneous thermal motion of atoms or molecules and can take place in the absence of a concentration (or chemical potential) gradient, proceeding continuously under equilibrium conditions. The experimental methods that have been applied often involve following the motion of individual atoms in STM or FIM micrographs [1,2]. The rate at which such micrographs can be acquired limits the tracer measurements to low rates of diffusion.

At low coverages, the collective diffusion coefficient can be approximated by the tracer diffusion coefficient, as the interactions between adatoms are weak and the influence of those interactions on the diffusion process is small. However, as coverage increases, the approximation gradually becomes invalid as interactions between adatoms affect the rate of diffusion. In general, the two diffusion coefficients represent different but closely related quantities and various models have been established to relate them together over a wider range of conditions [33]. Both diffusion coefficients are usually observed to follow an Arrhenius dependence with temperature, T ,

$$D = D_0 \exp \left[-\frac{E_a}{k_B T} \right]. \quad (3)$$

D_0 and E_a are a preexponential factor and activation energy, respectively, that are related to the other properties of the system [37] and k_B is the Boltzmann constant. The tracer diffusion coefficient, along with its activation energy and preexponential factor, characterize the atomic-scale dynamics on surfaces, capturing the combined influence of the effects of many different processes, including barrier crossing (and re-crossing), adsorbate-substrate energy exchange and the shape of the interaction potentials.

III. HELIUM-3 SPIN-ECHO METHOD

All measurements analysed in the present work were obtained with HeSE using the Cambridge instrument [38]. HeSE is a surface scattering technique that uses neutral helium atoms to perform a correlation measurement with a time sensitivity of between picoseconds and nanoseconds, a regime that is otherwise very difficult to access experimentally. Along with the completely nondestructive and chemically inert nature of the helium probe, the approach is ideal for measuring atomistic transport on surfaces. The HeSE technique has

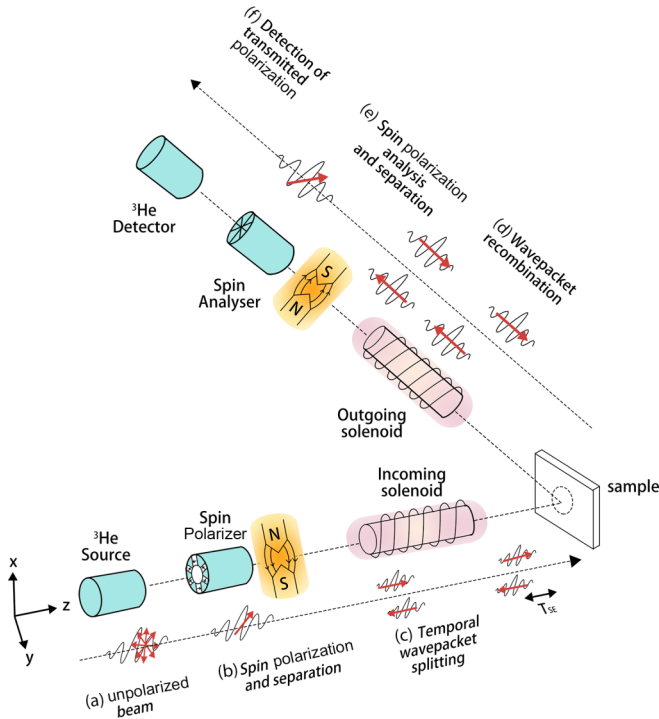


FIG. 1. Schematic representation of the spin-echo technique. An unpolarized helium-3 beam is first produced in the (a) beam source by expanding gas through a nozzle, towards towards the (b) nuclear-spin polarizer. (c) The polarized spins are transferred into solenoid field, where they are split into parallel and antiparallel components with different velocities. The components separate by spin-echo time, τ_{SE} , before scattering from the sample surface. (d) Scattered atoms then pass through an identical but reversed solenoid field, where the spin components are recombined. (e) The beam passes through a nuclear-spin analyzer before (f) individual atoms are counted in the detector, to provide a beam-averaged polarization measurement. A change in the surface correlation during τ_{SE} , due to adsorbate diffusion, shows up as a drop in the measured polarization.

already been described in detail elsewhere [39], so we only briefly outline the important concepts here.

Figure 1 shows a schematic representation of the HeSE spectrometer. First [Fig. 1(a)] a beam of helium-3 atoms is generated from a free jet expansion, then the atoms are nuclear-spin polarized [Fig. 1(b)] in a direction perpendicular to the beam axis. The polarized atoms are passed through a variable strength magnetic field parallel to the beam [Fig. 1(c)], where the helium wave packets are split into components parallel and antiparallel to the field. The two components propagate at different speeds, so arrive at the sample with a time separation, τ_{SE} , known as the spin-echo time. After scattering, the wave packet components are recombined in a reverse magnetic field [Fig. 1(d)], before finally measuring the beam polarization [Figs. 1(e)–1(f)]. In the Cambridge apparatus, τ_{SE} can be scanned within the subpicosecond to nanosecond range. If the surface changes during that interval, due to adsorbate motion or other dynamic processes, then the wave packet components cannot be recombined exactly. The result is a loss of spin polarization in the scattered beam, which can be measured to provide a

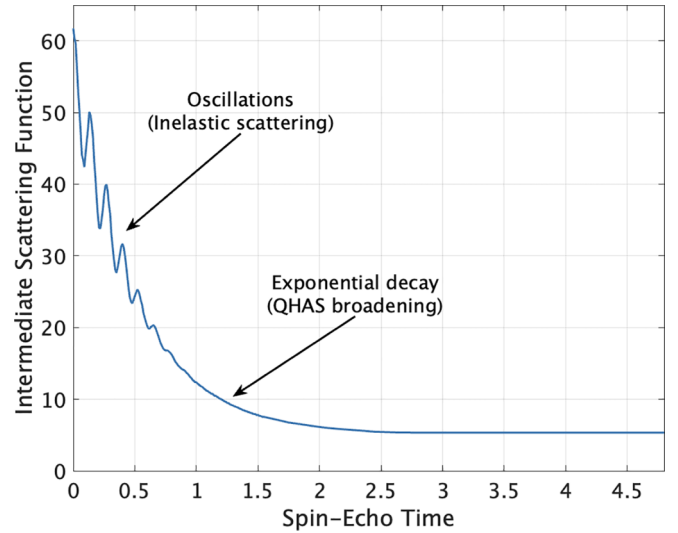


FIG. 2. Cartoon of an ISF measured using HeSE. The oscillatory part, which typically decays quickly, is usually associated with surface vibrations or phonons. The overall decay is associated with the aperiodic diffusion and corresponds to a quasielastic broadening in an energy domain measurement. The length scale of the observation are set by the scattering momentum transfer, $\Delta\mathbf{K}$.

temporal correlation measurement on the lengthscale and in the direction given by the scattering momentum transfer, $\Delta\mathbf{K}$. Within the kinematic approximation, the measured polarization corresponds to the normalized intermediate scattering function (ISF), $I(\Delta\mathbf{K}, t)$ [39], a typical form of which is shown in Fig. 2. On small timescales, the ISF typically oscillates due to periodic motion such as substrate phonons, while aperiodic adsorbate diffusion usually results in an exponential decay over longer times. More generally, the ISF is the spatial Fourier transform of the Van Hove pair correlation function, $G(\mathbf{R}, t)$,

$$I(\Delta\mathbf{K}, t) = \int G(\mathbf{R}, t) \exp(i\Delta\mathbf{K}t) dt, \quad (4)$$

where $G(\mathbf{R}, t)$ describes the probability of finding a particle at position $\mathbf{R}$ and time t , given the particle was located at $\mathbf{R} = 0$ at time $t = 0$ [40]. Thus, by measuring the ISF over a range of scattering conditions and times, a complete statistical description of the dynamical behavior of the surface can be constructed. We note that as helium spin echo measures only coherent scattering, methods developed to extract diffusion constants from the incoherent dynamic structure factor, $S_s(\Delta\mathbf{K}, \omega)$, which is the temporal Fourier transform of the ISF, for neutron scattering [34] must be applied with caution in the case of HeSE; a further discussion of the approaches used in HeSE and neutron scattering can be found in Sec. V.

The ISF encodes detailed information about surface dynamics, including jump frequencies, trajectories, and correlations, as well as information on other surface processes such as phonons. A common approach to extracting dynamical parameters is to characterize the decay of the ISF in terms of a dephasing rate, $\alpha(\Delta\mathbf{K})$, which quantifies the rate at which correlations are lost due to atomic motion. At sufficiently long time scales, the decay of the ISF is often well described by a

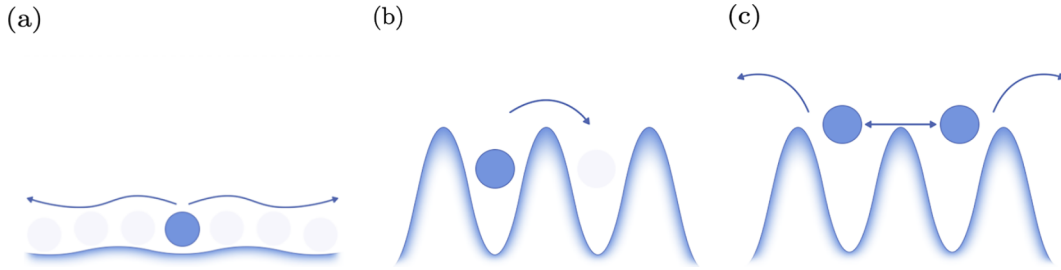


FIG. 3. Schematic representation of three types of diffusion models: (a) continuous Brownian motion, occurring when thermal energy is comparable to the activation energy; (b) single hop between adsorption sites when the activation energy is sufficiently high; and (c) more complex motion, including multiple jumping or correlated motion when the interaction energy between adsorbates is also strong.

single-exponential form,

$$I(\Delta\mathbf{K}, t) = A \exp[-\alpha(\Delta\mathbf{K})t] + C, \quad (5)$$

from which the dephasing rate can be determined through numerical fitting. The dependence of α on momentum transfer $\Delta\mathbf{K}$ provides the underlying mechanism of surface diffusion.

IV. OBTAINING DIFFUSION COEFFICIENTS FOR ADSORBATE-SUBSTRATE SYSTEMS

Despite surface diffusion typically being described by a single coefficient, the motion of an adsorbate on a pristine atomic surface is a surprisingly complex process. The rich and sophisticated range of behavior that can be exhibited arises from the adsorbate atom/molecule being coupled to every other particle in the system through interaction potentials, and whose exploration depends on temperature and the rate of energy transfer around the system. To date, to make diffusion analysis tractable various different levels of approximation have been applied [34]. Following standard approaches to surface diffusion modeling [41,42], we assume that the overall motion of an adsorbate particle can be split into slow degrees of freedom that can be represented by a frozen potential energy surface (PES) on which the adsorbate moves following classical dynamics. The fast degrees of motion are associated with the heat bath to which the adsorbate is coupled, as represented by a series of random impulses that are scaled according to the fluctuation-dissipation theorem. We also assume that interactions between adsorbates can normally be represented as pairwise interactions. While these assumptions generally work well, they can occasionally break down badly (for example Refs. [43] and [44]), but the model still provides a useful framework within which the different regimes of adsorbate motion can be understood and distinguished.

Figure 3 shows a cartoon representation of the three different regimes of adsorbate motion on a surface that we consider here; Fig. 3(a) Brownian motion in a flat, or nearly flat, interaction potential, Fig. 3(b) single-jump discrete hopping in a corrugated potential, and Fig. 3(c) more complex motion, such as multiple jumping or strongly correlated motion. Each of these behaviors has been observed using HeSE, and can be distinguished clearly through the form of the dependence of the dephasing rate on momentum transfer, $\alpha(\Delta\mathbf{K})$. In the following sections, we examine each of these regimes in turn, and how tracer diffusion coefficients may be obtained in each case.

A. Brownian motion

When the corrugation of the PES is small enough to be ignored compared to the thermal energy of the adsorbate, as illustrated in Fig. 3(a), the periodic nature of the substrate becomes unimportant. Coupling to the substrate heat bath through random impulses is the dominant process, which results in the adsorbate performing continuous Brownian motion rather than discrete hopping between lattice sites. Under these circumstances, the relationship between the dephasing rate and parallel momentum transfer has been shown to be [45]

$$\alpha(\Delta\mathbf{K}) = D\Delta\mathbf{K}^2, \quad (6)$$

where D is the diffusion coefficient along $\Delta\mathbf{K}$.

Hedgeland *et al.* observed this situation in the benzene/graphite system [27], as illustrated in Fig. 4. The measured dephasing rate follows an almost perfect quadratic dependence and the energy barrier to diffusion was observed to be negligible. By fitting the observations to Eq. (6),

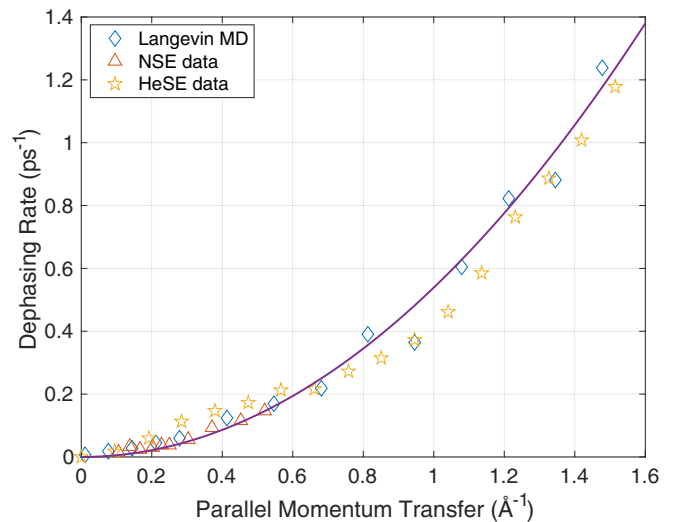


FIG. 4. The dephasing rate, α , obtained from HeSE ($\star$) and NSE (Δ) experiments of benzene on (azimuthally disordered) highly oriented pyrolytic graphite at 140 K for coverages of 0.5 ML. The dephasing rates follow a quadratic dependence, enabling the tracer diffusion to be obtained from the quadratic coefficient. Data reproduced from Ref. [27].

they readily obtained a diffusion coefficient of $D = (5.39 \pm 0.13) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 140 K.

Thus for systems exhibiting continuous Brownian motion, as opposed to hopping, the diffusion coefficient can be obtained trivially from the quadratic scaling of HeSE dephasing rates. However, HeSE measurements to date suggest that such Brownian behavior is quite rare; the majority of adsorbate-substrate surface systems exhibit some degree of hopping between adsorption sites [34,39], so require a more sophisticated model.

B. Hopping motion

When the adsorbate thermal energy, $k_B T$, is significantly smaller than the PES energy barrier between adsorption sites, E_b , adsorbate motion is strongly influenced by the periodic structure of the surface, leading to hopping motion. For ideal instantaneous jumps on a Bravais lattice, the relation between the dephasing rate, $\alpha(\Delta \mathbf{K})$, and the parallel momentum transfer, $\Delta \mathbf{K}$, is described by the Chudley-Elliot (CE) model [46],

$$\alpha(\Delta \mathbf{K}) = 2 \sum_j \Gamma_j \sin^2 \left(\frac{\Delta \mathbf{K} \cdot \mathbf{R}_j}{2} \right), \quad (7)$$

where the summation is over the different possible jump vectors, $\mathbf{R}_j$, and Γ_j is the corresponding hopping rate to a particular site.

When the rate of energy exchange between the adsorbate and substrate is sufficiently high, single jumps are the dominant transport mechanism between adjacent adsorption sites [34,37]. The exact sites depend on the nature of the bonding in any particular system, but often correspond to the hollow sites on f.c.c. {001} surfaces or a combination of hexagonal close-packed and face-centered-cubic hollow sites on f.c.c. {111} surfaces. By symmetry, the jump rate Γ_j to the j th site is equal for all j equivalent nearest-neighbor sites so Eq. (7) can be further simplified using a single value of Γ ,

$$\alpha(\Delta \mathbf{K}) = 2\Gamma \sum_j \sin^2 \left(\frac{\Delta \mathbf{K} \cdot \mathbf{R}_j}{2} \right). \quad (8)$$

Figure 5 shows an example of existing HeSE experimental data, for H diffusion on Pt(111) along the $\langle 11\bar{2} \rangle$ azimuth [25], overlaid with a single-jump Chudley-Elliot model. The model uses a best-fitted value of Γ with the known jump length, while the shaded region shows one standard deviation of uncertainty based on the standard error on Γ obtained from the fitting routine. The good agreement, with the majority of data points falling within the shaded band is consistent with single hops being the dominant form of motion for this system.

Having established that the motion is dominated by single hops, the established relationship analytically gives the two-dimensional (2D) tracer diffusion coefficient [2,34],

$$D = \frac{1}{4} \Gamma_T \langle l \rangle^2. \quad (9)$$

Here, $\langle l \rangle^2$ is the mean-square jump length, which in the single-jump model is typically equivalent to the surface lattice constant squared, a^2 . Γ_T is the total jump rate from a given site

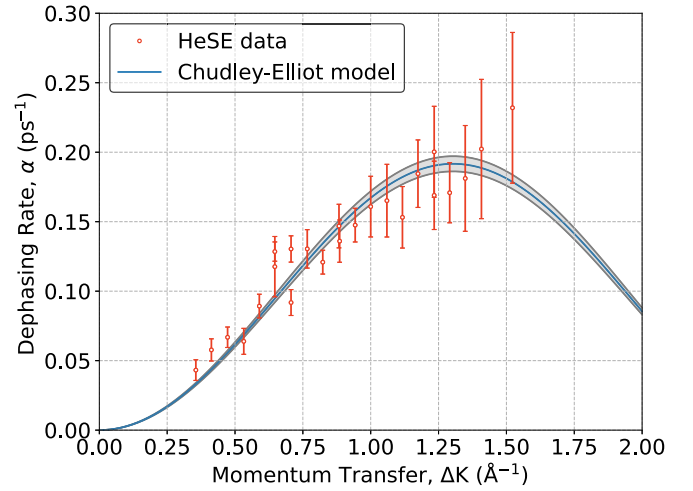


FIG. 5. Dephasing rates, α , from HeSE measurements of H on Pt(111) at 220 K, at a coverage of 0.1 ML (red points), reported in Ref. [25], for the $\langle 11\bar{2} \rangle$ azimuth. The results are in good agreement with a single-jump Chudley-Elliot model using a fitted value of the hopping rate (blue line and confidence interval). The majority of data points fall within one standard deviation of the fit line and there are no obvious systematic deviations, enabling a diffusion coefficient to be obtained using Eq. (9).

given by,

$$\Gamma_T = \sum_j \Gamma_j = N \cdot \Gamma, \quad (10)$$

where N is the number of the nearest neighbors, usually taking values of 3, 4, or 6, depending on adsorption site symmetry. For H on Pt(111), we therefore obtain a diffusion coefficient of $(2.77 \pm 0.08) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, using data measured along the $\langle 11\bar{2} \rangle$ azimuth at 220 K, which is consistent with the previous analysis.

A number of systems previously studied using HeSE conform to a single-jump model, so diffusion coefficients can be extracted using this approach, which can be summarized schematically as:

$$\begin{array}{c} I(\Delta \mathbf{K}, t) \\ \text{Spin-Echo Experiment} \end{array} \xRightarrow{\text{CE model}} \alpha(\Delta \mathbf{K}) \xRightarrow{\text{By Eq. (9)}} \Gamma \xRightarrow{} D. \quad (11)$$

Table I shows resulting values computed for a representative selection of these systems, including at different coverages and temperatures where data is available. The results span atoms and small molecules (H/Pt(111) [25], CO/Cu(111) [47], CO/Pt(111) [44]), then larger hydrocarbons (C_3H_8 /Pt(111) [48], C_6H_6 /Cu(001) [49]). Table I summarizes the D_s obtained from the Chudley-Elliot model for all the systems considered, with the exception of H/Pt(111) these diffusion constants have not previously been extracted from HeSE measurements. In these systems, the long-time two-dimensional tracer diffusion coefficient D_s is a scalar property of the surface and is therefore not expected to depend on the azimuth along which the HeSE measurement is performed. The small variations in the D_s values obtained for different azimuths are attributed to the combined statistical and systematic uncertainties of the fits. We have calculated the variation of D_s with coverage in the case of CO/Pt(111)

TABLE I. Diffusion coefficients for systems exhibiting single-jump motion over different azimuths, coverages, and temperatures. The values are based on a reanalysis of experimental HeSE data that was previously reported in the literature, using a single-jump Chudley and Elliot model. For all systems except H/Pt(111), these represent the first tracer diffusion coefficients explicitly extracted from HeSE measurements.

System	Azimuth	Coverage/ Θ	Temperature/K	2D Diffusion Coefficient/ $m^2 s^{-1}$
H/Pt(111) [25]	$\langle 112 \rangle$	0.04	90	$(5.9 \pm 0.3) \times 10^{-11}$
		0.04	140	$(5.4 \pm 0.2) \times 10^{-10}$
		0.04	220	$(2.77 \pm 0.08) \times 10^{-9}$
CO/Cu(111) [47]	$\langle 110 \rangle$	0.04	190	$(6.6 \pm 0.3) \times 10^{-11}$
	$\langle 112 \rangle$	0.04	190	$(5.7 \pm 0.3) \times 10^{-11}$
CO/Pt(111) [44]	$\langle 112 \rangle$	0.065	340	$(1.68 \pm 0.08) \times 10^{-10}$
		0.165	340	$(2.5 \pm 0.3) \times 10^{-10}$
		0.220	340	$(3.8 \pm 0.2) \times 10^{-10}$
		0.300	340	$(6.5 \pm 0.5) \times 10^{-10}$
C ₃ H ₈ /Pt(111) [48]	$\langle 110 \rangle$	0.02	115	$(7.0 \pm 0.4) \times 10^{-10}$
	$\langle 112 \rangle$	0.02	115	$(5.8 \pm 0.2) \times 10^{-10}$
C ₆ H ₆ /Cu(001) [49]	$\langle 100 \rangle$	0.07	170	$(3.1 \pm 0.4) \times 10^{-9}$
	$\langle 110 \rangle$	0.07	170	$(3.6 \pm 0.3) \times 10^{-9}$

and temperature in the case of H/Pt(111) as shown in Table I; these are consistent with the mechanisms reported in Refs. [44] and [25], respectively.

In certain systems, HeSE experiments have revealed contributions from jumps beyond nearest neighbors [26,31,50], where a fraction of the adsorbed molecules jump further than the nearest-neighbor site in one activation event. In such cases, a single-jump Chudley-Elliott model cannot reproduce the data adequately, but additional multiple jump components can be added into Eq. (7). For reasons of uniqueness it is normally desirable to only add enough additional jump components to achieve an acceptable fit. The resulting diffusion coefficient may then be obtained by summing Eq. (9) over the different jump components. As an example, Fig. 6 shows a Chudley and Elliot model fit to HeSE measurements of CO on Cu(001) [50] with both single and double jumps included. Using single jumps to nearest neighbors is inadequate, but with the addition of a fraction of next-nearest-neighbor jumps the model accurately reproduces the data, to give a diffusion coefficient of $(2.5 \pm 0.4) \times 10^{-11} m^2 s^{-1}$ using the $\langle 110 \rangle$ azimuth data and $(1.8 \pm 0.3) \times 10^{-11} m^2 s^{-1}$ for the $\langle 001 \rangle$ direction. As before the small difference is attributed to minor differences in the fitting between azimuths.

C. Complex and correlated motion

While many of the systems studied using HeSE exhibit hopping diffusion that can be explained well using the Chudley and Elliott model, many more exhibit complex motion that cannot be reduced to simple discrete jumps. A particular example is the case of alkali metals adsorbed onto metal surfaces, where electron transfer leads to strong dipole-dipole repulsion between the alkali adatoms [33]. Under the influence of these strong dipole interactions, the adsorbates arrange themselves into a quasihexagonal pattern to maximise the mean interatomic spacing to give the most stable arrangement, as shown in Fig. 7. At the momentum transfer values corresponding to unstable spacings the dephasing rate is higher than at other values of $\Delta \mathbf{K}$, resulting in a peak and dip in $\alpha(\Delta \mathbf{K})$. The variation is characteristic of the corresponding

correlated adsorbate motion (i.e., each atom influences its neighbours) and the effect is known from neutron scattering as a de Gennes narrowing [51]. Such features are clearly visible in many HeSE measurements, including the K/Cu(001) data as shown in Fig. 8. In this case, the optimized single-jump model completely misses the correlation feature around $0.3 \text{ \AA}^{-1}$. A more sophisticated model is clearly needed to obtain diffusion coefficients accurately.

Here, we have taken a new approach to determining diffusion coefficients, using numerical simulations that are accurately calibrated against experimental HeSE data. The

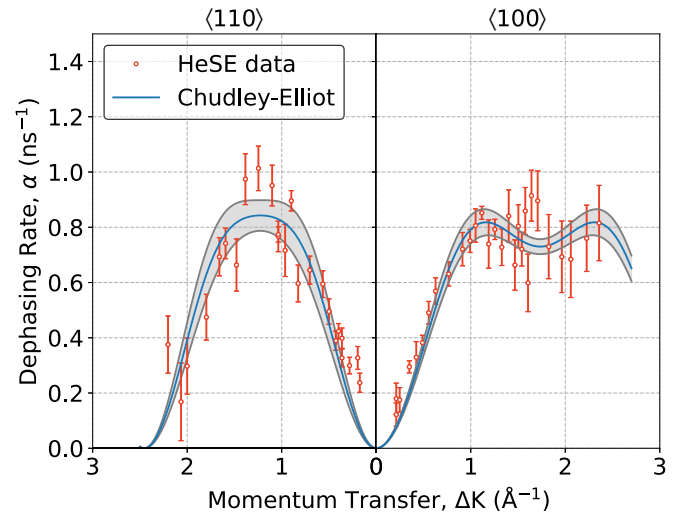


FIG. 6. Dephasing rates, α , from HeSE measurements of CO on Cu(001) at 155 K, for coverages of 0.04 ML (red points), reported in Ref. [50], for both the $\langle 110 \rangle$ (left) and $\langle 100 \rangle$ (right) azimuths. The solid line and one-standard deviation band shows a Chudley-Elliott jump model fitted with single- and double-jump rates of $(9.12 \pm 0.34) \times 10^7 s^{-1}$ and $(3.01 \pm 0.30) \times 10^7 s^{-1}$ along $\langle 100 \rangle$ direction, and $(1.29 \pm 0.39) \times 10^8 s^{-1}$ and $(4.07 \pm 0.14) \times 10^7 s^{-1}$ along $\langle 110 \rangle$ direction, respectively, giving good agreement with the data and enabling the corresponding tracer diffusion coefficient to be obtained.

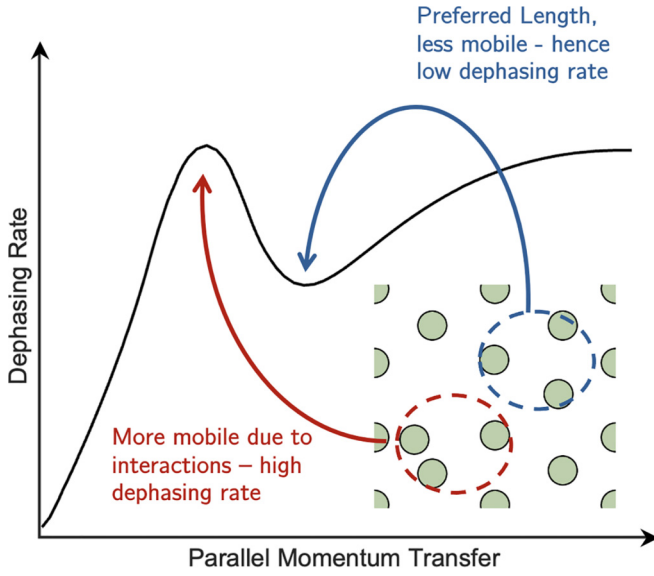


FIG. 7. Illustration of the signature of strong correlated motion where its dephasing rate exhibits the de Gennes feature. When the interatomic spacing reaches the preferred length, the system will be in its most stable state, resulting in the minimum dephasing rate. When the interatomic distance is too far or too close, the adsorbates become more mobile, resulting in a higher dephasing rate. These conditions manifest as a narrowing dip and a peak for small values of $\Delta\mathbf{K}$. Reproduced from Ref. [39].

simulations are used to generate adsorbate trajectories, which can then be used to compute the corresponding tracer diffusion coefficients. In principle any dynamic simulations may be used in this process, but here we have used Langevin molecular dynamics (MD), as they are already widely used in the interpretation of HeSE data [12].

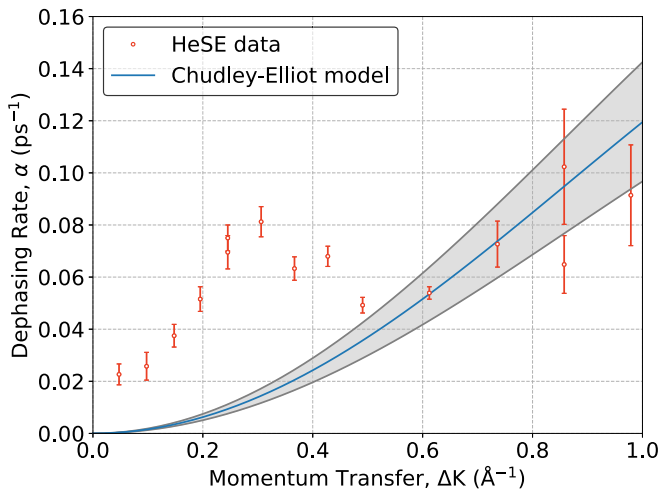


FIG. 8. The dephasing rate, α , obtained from $^3\text{HeSE}$ experiment of K on Cu(001) at 155 K for coverages of 0.032 ML, measured along (100) azimuths. The results cannot be fit to a Chudley-Elliot model, suggesting more complicated diffusion behavior.

Within the Langevin model, adsorbate motion is described by

$$m\ddot{\mathbf{R}} = -\nabla V(\mathbf{R}) - \eta m\dot{\mathbf{R}} + \xi(t) + \sum_{i \neq j} \mathbf{F}(\mathbf{R}_j - \mathbf{R}_i), \quad (12)$$

where $\mathbf{R}$ is the position of the adsorbate and $V(\mathbf{R})$ is the adsorbate-surface PES. The second and third terms describe coupling to the substrate heat bath via viscous drag and a stochastic force. By the fluctuation-dissipation theorem, $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = 2k_B T \eta \delta(t - t')$. Finally, the last term represents pairwise interaction forces between adsorbates.

We used the PIGLE code (Particles Interacting in Generalized Langevin Equation) [52] to perform our Langevin MD simulations. A series of parameters need to be defined to run a simulation according to Eq. (12), these are the PES, the friction, η , the temperature, the interparticle forces $\mathbf{F}$, and the coverage of adsorbates, Θ . The coverage and the temperature are defined by the experiment. For the adsorbate-substrate PES, we used the previously optimized empirical potential of the form

$$V(x, y) = \frac{E_T}{4} + \frac{E_B}{2} + \frac{E_T}{4} \left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) \right] + \frac{1}{4}(E_T - 2E_B) \cos\left(\frac{2\pi x}{a}\right) \cos\left(\frac{2\pi y}{a}\right), \quad (13)$$

written in terms of the bridge site energy, E_B , and the atop site energy, E_T , with respect to the lowest-energy hollow site. For our systems Na/Cu(001) and K/Cu(001) systems we adopt literature parameter sets for the two PES parameters [24,53]. For Na/Cu(001) values of $E_B = 75$ meV and $E_T = 85$ meV were used, which have been acquired via fitting to the experimental ISFs. For K/Cu(001) values [24] and $E_B = 35$ meV and $E_T = 64$ meV were used, which are calculated using density functional theory [53].

For the interparticle forces we apply the Kohn-Lau dipole interaction potential [24,53,54] to incorporate the dipole-dipole interactions between the alkali-metal adsorbates,

$$E_{ij} = \frac{1}{4\pi\epsilon_0} \frac{2\mu^2}{|\mathbf{R}_i - \mathbf{R}_j|^3}, \quad (14)$$

where E_{ij} is the interaction energy between the adsorbates pair i and j . The coverage-dependent dipole moment, μ , was deduced from the work-function measurements of Aruga *et al.* [55] and Mizuno *et al.* [56]. 200 interacting adsorbates were used in each simulation.

The final parameter is the frictional, η , which is the only parameter in our approach that must be fitted to the experimental ISF—for cases where an *ab initio* calculation of the PES is not present E_B and E_T may also be fitted, resulting in three empirical parameters. In principle more of the parameters could be fitted using the Langevin simulation, however, where possible independent values have been and should be used to reduce parameter degeneracy and maintain physical realism. In our simulations we adhere to the values used by Hedgeland *et al.* [53] and Alexandrowicz *et al.* [24] with values of 0.5 ps^{-1} for Na/Cu(001) and 0.2 ps^{-1} for K/Cu(001).

For both systems the size of the Cu(001) supercell was automatically adjusted to accommodate the total number

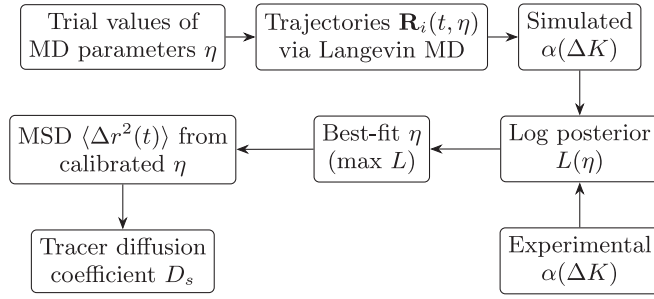
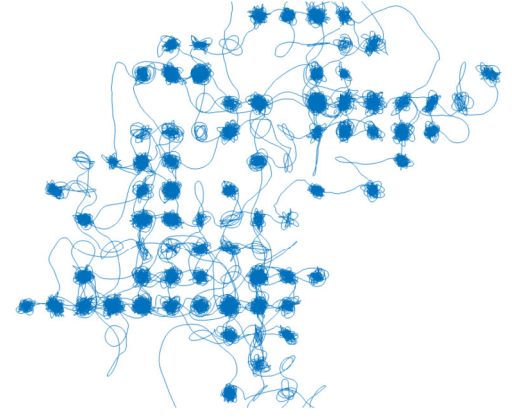


FIG. 9. Flow chart for obtaining tracer diffusion coefficients from Langevin molecular dynamics constrained by experimental data. Trial values of MD parameter(s) are used to generate trajectories and simulated $\alpha(\Delta K; \eta)$; in the present work the parameter is the friction η , but it could also include other MD parameters. Comparison with the experimental $\alpha(\Delta K)$ defines the log posterior $L(\eta)$ and yields the best fit η . The MSD $\langle \Delta r^2(t) \rangle$ from MD with this calibrated parameter is then used to obtain the tracer diffusion coefficient D_s .

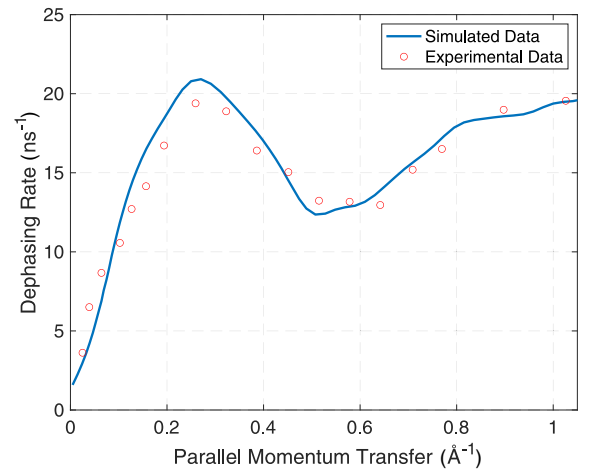
of adsorbates and the coverage. The total simulation time was 20 ns with a time step of 1 fs, at coverages of $\Theta = 0.02, 0.04, 0.065$, and 0.08 ML and a temperature of 155 K.

The Langevin based workflow is summarized in Fig. 9. For each trial η a PIGLE Langevin-MD trajectory $\mathbf{R}_i(t)$ is generated, from which the coherent ISF and the corresponding dephasing rate $\alpha(\Delta K)$ is computed under the same ΔK as the experiment. For each candidate η , a joint log posterior that measures the mismatch between simulated and experimental $\alpha(\Delta K, t)$ is calculated, following the Supplemental Material of Ref. [57]. The optimal value is taken to be $\eta = \arg \max_{\eta} \ln P(\eta)$. Once the calibrated η is determined, its corresponding simulated trajectories can be used for subsequent computation. For Na/Cu(001) and K/Cu(001) literature parameter sets are already established [24,53], for new systems that have not yet been parameterized the workflow in Fig. 9 must be followed afresh.

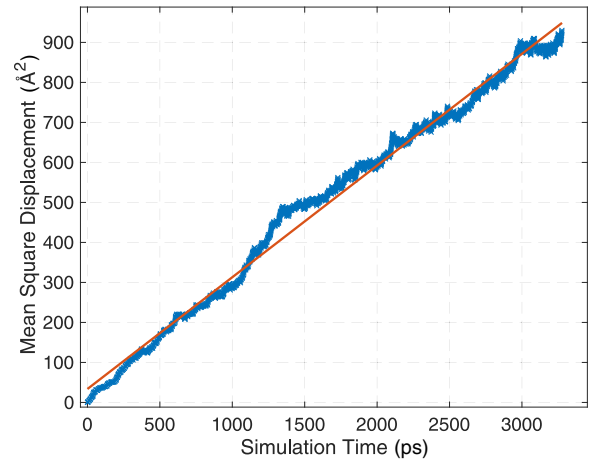
Once calibrated parameters, in particular the friction η , have been established a final set of Langevin simulations can be performed. Figure 10 illustrates the result of this process for the case of Na/Cu(001). Figure 10(a) shows the trajectory of an individual adsorbate. While the atom predominantly resides near the PES minimum at the adsorption site, there is a substantial level of fluctuation and the motion shows substantial deviations from idealised jumping. Close inspection reveals a mixture of long jumps and deflection due to repulsion from neighboring adsorbates. Figure 10(b) shows a simulated dephasing rates, $\alpha(\Delta K)$, compared with the experimental data from Ref. [24]; as expected the previously optimised simulation reproduces the experimental data closely. Both the de Gennes feature (a peak and a dip) at $\Delta K \approx 0.3\text{--}0.6 \text{ \AA}^{-1}$ and the sinusoidal jump diffusion characteristic at larger momentum transfers are reproduced. Figure 10(c) shows the relationship between the mean-square displacement, $\langle \Delta r^2(t) \rangle$, and t , which was computed by av-



(a)



(b)



(c)

FIG. 10. (a) Simulated trajectory of a Na atom on Cu(001) at 155 K and coverages of 0.04 ML obtained from PIGLE. (b) Experimental (red circles) and simulated (PIGLE, blue curve) dephasing rates under the same conditions. (c) Plot of mean-square displacement versus simulation time; the red line is the best-fitted linear regression line used to obtain the 2D diffusion coefficient.

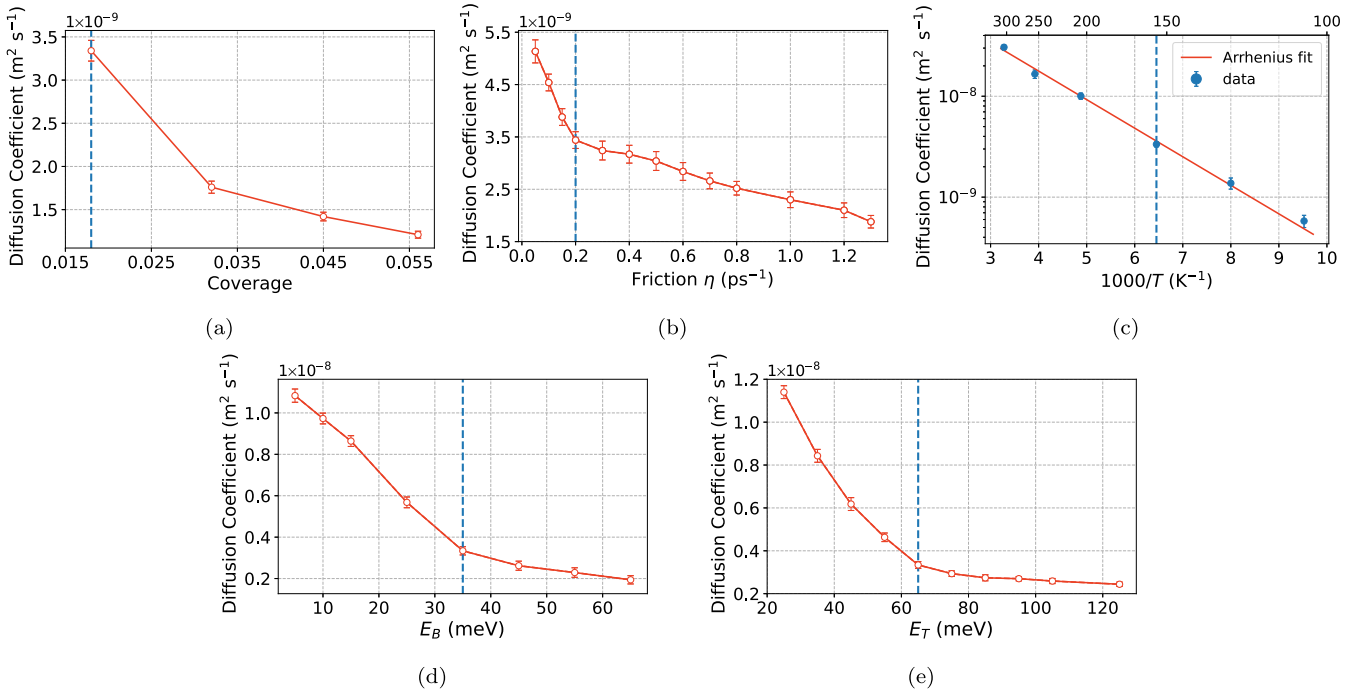


FIG. 11. Sensitivity of the simulated 2D tracer diffusivity D_s to Langevin-MD parameters for K/Cu(001). The blue vertical dashed lines mark the calibrated baseline values: $\Theta = 0.018$ ML, $\eta = 0.2$ ps^{-1} , $T = 155$ K, $E_B = 35$ meV (bridge), and $E_T = 65$ meV (top). (a) D_s vs coverage Θ . (b) D_s vs friction η . (c) Arrhenius plot $\ln D_s$ vs $1/T$; the line is a linear fit (activation slope noted in the text). (d) D_s vs lower barrier E_B . (e) D_s vs upper barrier E_T . Error bars are 95% confidence intervals; lines are guides to the eye. Across physically reasonable ranges the trends are monotonic and changes are modest, indicating that the extracted D_s is not overly sensitive to fine tuning of the MD parameters.

eraging the square of the displacement of all the atoms at t . Linear regression was used to determine the gradient, from which the tracer diffusion coefficient was obtained; uncertainties are estimated with the approximate Bayesian procedure of McCluskey *et al.* [58], as implemented in the open-source package KINISI [59].

To demonstrate that the resulting tracer diffusivities D_s are predictive rather than tuning dependent, we quantify parameter sensitivity via one-parameter-at-a-time scans about a calibrated baseline (K/Cu(001), coverage $\theta = 0.018$ ML, temperature $T = 155$ K, lower barriers $E_B = 35$ meV, upper barriers $E_T = 65$ meV and friction $\eta = 0.2$ ps^{-1} ; see Fig. 11. For each scan over coverage θ , friction η , lower/upper barriers E_B/E_T , and temperature T , D_s and their uncertainties were extracted using the same procedure. The trends are monotonic and physically expected: D_s decreases with increasing θ , η , and E_B ; its dependence on E_T weakens and approaches a plateau, indicating transport governed by the lower-barrier direction; and $\ln D_s$ versus $1/T$ is approximately linear. Within these physically reasonable ranges, D_s does not change dramatically and follows a monotonic trend with all the parameters. These figures show that the diffusion coefficients are not overly sensitive to small variations in the Langevin-MD parameters.

Table II shows diffusion coefficients for Na/Cu(001) and K/Cu(001) at several different conditions, obtained using our Langevin simulations. As expected, the diffusion coefficients decrease with increasing coverage. The decrease is most rapid at low coverages, with the values stabilising as the coverage

increases, showing similar behavior to the observations in Ref. [60]. For comparable coverages, the diffusion coefficient of K is always higher than that of Na, which we attribute to the lower PES and rate limiting energy barrier. Therefore, K adsorbates have greater mobility on the Cu(001) surface, despite their larger mass.

V. DISCUSSION

In the present work we have systematically distinguished and treated three qualitatively different diffusion regimes within a single HeSE analysis framework. For Brownian and jump diffusion we apply established analytic models to a wide range of systems, while for complex correlated motion we present a Langevin molecular dynamics approach, which allows the extraction of D_s from a simulation that is accurately validated against HeSE measurements in conjunction with Eq. (2). On this basis we have presented a unified workflow that converts the coherent HeSE observables into the tracer diffusion coefficient D_s , thereby making both the workflow and the resulting tracer diffusion coefficients accessible to the wider diffusion community. Applying this workflow to a range of canonical HeSE systems, we assemble the first internally consistent set of HeSE-derived tracer diffusion coefficients, which are summarized in Tables I and II. For the majority of the systems listed in Tables I and all in Table II, tracer diffusion coefficients have not previously been tabulated in the literature. Even for cases when D_s values from HeSE have appeared, they are often based on system-specific conventions or implicit assumptions that are not stated in a reproducible

TABLE II. Diffusion coefficients for strongly correlated motion systems under various conditions. These values are computed based on the simulation package PIGLE combined with $^3\text{HeSE}$ experimental data. The computation procedure is shown in Fig. 9. Uncertainties in the diffusion coefficient values were obtained using approximate Bayesian regression method [58].

System	Azimuth	Coverage/ Θ	Temperature/K	2D Diffusion Coefficient/ $\text{m}^2 \text{s}^{-1}$
Na/Cu(001) [24]	$\langle 110 \rangle$	0.020	155	$(1.38 \pm 0.05) \times 10^{-9}$
		0.040	155	$(6.74 \pm 0.49) \times 10^{-10}$
		0.065	155	$(5.36 \pm 0.33) \times 10^{-10}$
		0.080	155	$(5.11 \pm 0.18) \times 10^{-10}$
K/Cu(001) [53]	$\langle 100 \rangle$	0.018	155	$(3.34 \pm 0.12) \times 10^{-9}$
		0.032	155	$(1.76 \pm 0.07) \times 10^{-9}$
		0.045	155	$(1.42 \pm 0.05) \times 10^{-9}$
		0.056	155	$(1.20 \pm 0.04) \times 10^{-9}$

way. With the aid of our Langevin simulations we not only test the sensitivity of the 2D tracer diffusion coefficients, but also explore how D_s depends on the Langevin-MD parameters.

The tracer diffusion coefficient D_s serves as a compact and transferable measure of long-time adsorbate mobility: it averages over step lengths, back-and-forth motion, and multiple pathways, enabling meaningful comparison across different surfaces and probes. By contrast, microscopic hopping rates are strongly model dependent and much less comparable across systems. A system may exhibit a high jump rate but very short step lengths, frequent back-forth jumps or multiple competing pathways, so that its long-time spreading is not necessarily faster than that of a system with a smaller jump rate but longer or more directed jumps. While hopping rates therefore remain essential for understanding the mechanism of motion, they do not by themselves provide a simple, system-independent measure of how fast the adsorbate diffuses. Thus, while hopping rates are convenient local quantities within a given model, the tracer diffusion coefficient provides a system-independent measure of the net rate of adsorbate transport, and hence serves as a common currency between systems.

Examining Fig. 11, the simulated tracer diffusivity D_s shows physically sensible and simple trends with the Langevin-MD parameters. D_s decreases monotonically with friction η in the high-friction (overdamped) regime, and with coverage as adsorbates become more crowded and increasingly block one another's motion. It also decreases with increasing lower barrier E_B ; D_s shows a weakening dependence and approach to a plateau as the upper barrier E_T is raised, indicating that transport is governed primarily by the lower-barrier direction. Within the ranges explored here, temperature has the strongest apparent influence on D_s , consistent with Arrhenius behavior as Eq. (3), whereas variations in η , coverage and barrier heights all lead to relatively modest, monotonic changes.

Also, in the case of CO/Pt(111), Alexandrowicz *et al.* [44] established the remarkable result that pairwise forces between adsorbates do not drive the changes in the diffusion rate, but that there must be a mean-field-driven change in the PES corrugation with increasing coverage [44]. As the corrugation reduces, the overall rate of diffusion increases in that system. Our results, shown in Table I, quantify

those changes in the form of diffusion coefficients; the increase in D_s with coverage reflects the mechanism previously identified. We note this is in contrast to the normal expectation that diffusion coefficients reduce with increasing coverage [33,34].

Unlike incoherent neutron scattering, which is often used to isolate single-particle dynamics via the incoherent scattering, our coherent HeSE analysis explicitly captures collective, interaction-induced correlations in adsorbate motion. In neutron experiments the tracer diffusion coefficients are extracted from the low- q , low- ω limit of the incoherent dynamic structure factor [34], and the scattering geometry can often be chosen such that correlations between different atoms are largely removed at the level of the measurement, yielding an effective single-particle diffusion coefficient. In contrast, helium spin echo is inherently coherent, so that correlations between adsorbates are always present in the measured signal. The tracer diffusion coefficients reported here therefore complement bulk neutron measurements by providing surface-specific diffusion data that explicitly include the effects of lateral interactions at finite coverage.

An alternative strategy to remove the effect of correlations from HeSE data has been proposed by Ward *et al.* [61], who separate the incoherent contribution from the coherent scattering signal in order to obtain an effective zero-coverage diffusion coefficient. Such methods are highly complementary to our approach where diffusion coefficients are determined at finite coverage, inherently including correlated motion. Together these two approaches provided frameworks for standardizing the analysis of the uncorrelated and correlated motion in HeSE studies.

VI. SUMMARY & CONCLUSIONS

In this paper, we develop a framework to extract tracer diffusion coefficients from HeSE experimental data for three different types of system. For systems that exhibit continuous Brownian motion on the atomic scale, the tracer diffusion coefficient can be straightforwardly extracted from the quadratic variation in the measured dephasing rate, $\alpha(\Delta K)$. Similarly, for systems exhibiting well-defined hopping motion, experiments can be fitted using the Chudley-Elliott model, which

gives a hopping rate, Γ , that can be used to determine the diffusion coefficient as shown in Eq. (11).

For more complex motion, numerical simulations allow us to reproduce the experiments, then to arrive at the tracer diffusion coefficient, as illustrated in Fig. 9. Within the Langevin framework, that process involves developing a model for the PES, friction and interadsorbate forces, which can then be compared with experimental HeSE data and refined. Once a sufficient level of agreement is established the simulated trajectories, $R(t)$, can be used to obtain the relevant diffusion coefficients. Tables I and II give a summary of diffusion coefficients calculated using these methods, obtained from a reanalysis of existing HeSE data in the scientific literature, and which have not been readily available before. While these coefficients wrap up much of the mechanistic detail of diffusion into a single quantity, such values are of importance to the wider academic community where the overall rates of

motion are most important. As such, we hope this work will enable the progress made using HeSE methods to be exploited more generally.

ACKNOWLEDGMENTS

S.M.L. acknowledges support from Engineering and Physical Sciences Research Council (EPSRC) Impact Acceleration Account (IAA), Award No. EP/X525686/1. The authors thank Boyao Liu, William Allison, and David Ward for invaluable discussions; we are especially grateful to William Allison for insightful comments and suggestions.

DATA AVAILABILITY

The data that support the findings of this article are openly available [62].

- [1] R. Gomer, Diffusion of adsorbates on metal surfaces, *Rep. Prog. Phys.* **53**, 917 (1990).
- [2] J. V. Barth, Transport of adsorbates at metal surfaces: From thermal migration to hot precursors, *Surf. Sci. Rep.* **40**, 75 (2000).
- [3] R. Villarreal, C. J. Kirkham, A. Scarfato, D. R. Bowler, and C. Renner, Towards surface diffusion potential mapping on atomic length scale, *J. Appl. Phys.* **125**, 184301 (2019).
- [4] S. P. Rittmeyer, V. J. Bukas, and K. Reuter, Energy dissipation at metal surfaces, *Adv. Phys. X* **3**, 1381574 (2018).
- [5] L. Bonati, D. Polino, C. Pizzolitto, P. Biasi, R. Eckert, S. Reitmeyer, R. Schlögl, and M. Parrinello, The role of dynamics in heterogeneous catalysis: Surface diffusivity and N^2 decomposition on Fe(111), *Proc. Natl. Acad. Sci. USA* **120**, e2313023120 (2023).
- [6] D. Chen, C. Shang, and Z.-P. Liu, Machine-learning atomic simulation for heterogeneous catalysis, *npj Comput. Mater.* **9**, 2 (2023).
- [7] C. Vogt and B. M. Weckhuysen, The concept of active site in heterogeneous catalysis, *Nature Rev. Chem.* **6**, 89 (2022).
- [8] X. Zhang, J. Lai, and T. Gray, Recent progress in low-temperature CVD growth of 2D materials, *Oxford Open Mater. Sci.* **3**, itad010 (2023).
- [9] T. Nishinaga, T. Shitara, K. Mochizuki, and K. Cho, Surface diffusion and related phenomena in MBE growth of III–V compounds, *J. Cryst. Growth* **99**, 482 (1990).
- [10] T. Bartels-Rausch, Ten things we need to know about ice and snow, *Nature (London)* **494**, 27 (2013).
- [11] T. Hama and N. Watanabe, Surface processes on interstellar amorphous solid water: Adsorption, diffusion, tunneling reactions, and nuclear-spin conversion, *Chem. Rev.* **113**, 8783 (2013).
- [12] A. Jardine, G. Alexandrowicz, H. Hedgeland, W. Allison, and J. Ellis, Studying the microscopic nature of diffusion with helium-3 spin-echo, *Phys. Chem. Chem. Phys.* **11**, 3355 (2009).
- [13] M. Dürr and U. Höfer, Hydrogen diffusion on silicon surfaces, *Prog. Surf. Sci.* **88**, 61 (2013).
- [14] Y. Suchorski and G. Rupprechter, Surface science studies of the diffusion of adsorbed and intercalated lithium, *Solid State Ionics* **316**, 143 (2018).
- [15] L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, and G. Ertl, Dynamics of electron-induced manipulation of individual CO molecules on Cu (111), *Phys. Rev. Lett.* **80**, 2004 (1998).
- [16] A. Bera, S. Henkel, J. Mieres-Perez, Y. Andargie Tsegaw, E. Sanchez-Garcia, W. Sander, and K. Morgenstern, Surface Diffusion Aided by a Chirality Change of Self-Assembled Oligomers under 2D Confinement, *Angew. Chem. Int. Ed.* **61**, e202212245 (2022).
- [17] F. van der Veen and F. Pfeiffer, Coherent x-ray scattering, *J. Phys.: Condens. Matter* **16**, 5003 (2004).
- [18] J. Kärger, M. Avramovska, D. Freude, J. Haase, S. Hwang, and R. Valiullin, Pulsed field gradient NMR diffusion measurement in nanoporous materials, *Adsorption* **27**, 453 (2021).
- [19] B. J. Berne and R. Pecora, *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics* (Courier Corporation, New York, 2000).
- [20] J. Stetefeld, S. A. McKenna, and T. R. Patel, Dynamic light scattering: A practical guide and applications in biomedical sciences, *Biophys. Rev.* **8**, 409 (2016).
- [21] J. C. Spence, *High-Resolution Electron Microscopy* (Oxford University Press, Oxford, 2013).
- [22] M. Bée, *Quasielastic Neutron Scattering* (IOP, Bristol, 1988).
- [23] E. G. Seebauer, A. C. F. Kong, and L. D. Schmidt, Surface diffusion of hydrogen and CO on Rh(111): Laser-induced thermal desorption studies, *J. Chem. Phys.* **88**, 6597 (1988).
- [24] G. Alexandrowicz, A. P. Jardine, H. Hedgeland, W. Allison, and J. Ellis, Onset of 3D collective surface diffusion in the presence of lateral interactions: Na/Cu(001), *Phys. Rev. Lett.* **97**, 156103 (2006).
- [25] A. P. Jardine, Y. M. E. Lee, D. J. Ward, G. Alexandrowicz, H. Hedgeland, W. Allison, J. Ellis, and E. Pollak, Determination of the quantum contribution to the activated motion of hydrogen on a metal surface: H/Pt(111), *Phys. Rev. Lett.* **105**, 136101 (2010).
- [26] A. Sabik, J. Ellis, H. Hedgeland, D. J. Ward, A. P. Jardine, W. Allison, G. Antczak, and A. Tamtögl, Single-molecular diffusivity and long jumps of large organic molecules: CoPc on Ag(100), *Front. Chem.* **12**, 1355350 (2024).

- [27] H. Hedgeland, P. Fouquet, A. Jardine, G. Alexandrowicz, W. Allison, and J. Ellis, Measurement of single-molecule frictional dissipation in a prototypical nanoscale system, *Nat. Phys.* **5**, 561 (2009).
- [28] S. Paterson, W. Allison, H. Hedgeland, J. Ellis, and A. P. Jardine, Rotation and Translational Motion prior to Self-Assembly: Dynamics of Ethanethiolate on Cu(111), *Phys. Rev. Lett.* **106**, 256101 (2011).
- [29] B. A. Lechner, M. Sacchi, A. P. Jardine, H. Hedgeland, W. Allison, J. Ellis, S. J. Jenkins, P. C. Dastoor, and B. Hinch, Jumping, rotating, and flapping: The atomic-scale motion of thiophene on Cu(111), *J. Phys. Chem. Lett.* **4**, 1953 (2013).
- [30] O. Godsi, G. Corem, T. Kravchuk, C. Bertram, K. Morgenstern, H. Hedgeland, A. Jardine, W. Allison, J. Ellis, and G. Alexandrowicz, How atomic steps modify diffusion and inter-adsorbate forces: Empirical evidence from hopping dynamics in Na/Cu(115), *J. Phys. Chem. Lett.* **6**, 4165 (2015).
- [31] A. Tamtögl, E. Bahn, M. Sacchi, J. Zhu, D. J. Ward, A. P. Jardine, S. J. Jenkins, P. Fouquet, J. Ellis, and W. Allison, Motion of water monomers reveals a kinetic barrier to ice nucleation on graphene, *Nature Commun.* **12**, 3120 (2021).
- [32] A. Jardine, G. Alexandrowicz, H. Hedgeland, R. Diehl, W. Allison, and J. Ellis, Vibration and diffusion of Cs atoms on Cu(001), *J. Phys.: Condens. Matter* **19**, 305010 (2007).
- [33] R. Ferrando and A. P. Jardine, *Springer Handbook of Surface Science* (Springer Nature, Berlin, 2020), Chap. 2.
- [34] T. Ala-Nissila, R. Ferrando, and S. C. Ying, Collective and single particle diffusion on surfaces, *Adv. Phys.* **51**, 949 (2002).
- [35] G. Antczak and G. Ehrlich, Jump processes in surface diffusion, *Surf. Sci. Rep.* **62**, 39 (2007).
- [36] R. Ferrando, Correlated jump-exchange processes in the diffusion of Ag on Ag (110), *Phys. Rev. Lett.* **76**, 4195 (1996).
- [37] P. Hänggi, P. Talkner, and M. Borkovec, Reaction-rate theory: Fifty years after Kramers, *Rev. Mod. Phys.* **62**, 251 (1990).
- [38] P. Fouquet, A. Jardine, S. Dworski, G. Alexandrowicz, W. Allison, and J. Ellis, Thermal energy ^3He spin-echo spectrometer for ultrahigh resolution surface dynamics measurements, *Rev. Sci. Instrum.* **76**, 053109 (2005).
- [39] A. Jardine, H. Hedgeland, G. Alexandrowicz, W. Allison, and J. Ellis, Helium-3 spin-echo: Principles and application to dynamics at surfaces, *Prog. Surf. Sci.* **84**, 323 (2009).
- [40] L. Van Hove, Correlations in space and time and Born approximation scattering in systems of interacting particles, *Phys. Rev.* **95**, 249 (1954).
- [41] R. Martínez-Casado, A. Sanz, G. Rojas-Lorenzo, and S. Miret-Artés, Two-bath model for activated surface diffusion of interacting adsorbates, *J. Chem. Phys.* **132**, 054704 (2010).
- [42] T. L. Einstein, Interactions between adsorbate particles, in *Handbook of Surface Science* (Elsevier, Amsterdam, 1996), Vol. 1, pp. 577–650.
- [43] J. Zhu, Ph.D. thesis, University of Cambridge, Cambridge, 2015.
- [44] G. Alexandrowicz, P. R. Kole, E. Y. Lee, H. Hedgeland, R. Ferrando, A. P. Jardine, W. Allison, and J. Ellis, Observation of uncorrelated microscopic motion in a strongly interacting adsorbate system, *J. Am. Chem. Soc.* **130**, 6789 (2008).
- [45] J. Frenken and B. Hinch, Quasielastic helium scattering studies of adatom diffusion on surfaces, in *Helium Atom Scattering from Surfaces* (Springer, Berlin, 1992), pp. 287–313.
- [46] C. Chudley and R. Elliott, Neutron scattering from a liquid on a jump diffusion model, *Proc. Phys. Soc.* **77**, 353 (1961).
- [47] P. R. Kole, H. Hedgeland, A. P. Jardine, W. Allison, J. Ellis, and G. Alexandrowicz, Probing the non-pairwise interactions between CO molecules moving on a Cu(111) surface, *J. Phys.: Condens. Matter* **24**, 104016 (2012).
- [48] A. Jardine, H. Hedgeland, D. Ward, Y. Xiaoqing, W. Allison, J. Ellis, and G. Alexandrowicz, Probing molecule–surface interactions through ultra-fast adsorbate dynamics: Propane/Pt(111), *New J. Phys.* **10**, 125026 (2008).
- [49] H. Hedgeland, M. Sacchi, P. Singh, A. J. McIntosh, A. P. Jardine, G. Alexandrowicz, D. J. Ward, S. J. Jenkins, W. Allison, and J. Ellis, Mass transport in surface diffusion of van der Waals bonded systems: Boosted by rotations? *J. Phys. Chem. Lett.* **7**, 4819 (2016).
- [50] G. Alexandrowicz, A. P. Jardine, P. Fouquet, S. Dworski, W. Allison, and J. Ellis, Observation of microscopic CO dynamics on Cu(001) using ^3He spin-echo spectroscopy, *Phys. Rev. Lett.* **93**, 156103 (2004).
- [51] P. De Gennes, Liquid dynamics and inelastic scattering of neutrons, *Physica* **25**, 825 (1959).
- [52] N. Avidor, P. S. Townsend, D. Ward, A. Jardine, J. Ellis, and W. Allison, PIGLE—particles interacting in generalized Langevin equation simulator, *Comput. Phys. Commun.* **242**, 145 (2019).
- [53] H. Hedgeland, P. Kole, H. Davies, A. Jardine, G. Alexandrowicz, W. Allison, J. Ellis, G. Fratesi, and e. G. Brivio, Surface dynamics and friction of K/Cu(001) characterized by helium-3 spin-echo and density functional theory, *Phys. Rev. B* **80**, 125426 (2009).
- [54] W. Kohn and K.-H. Lau, Adatom dipole moments on metals and their interactions, *Solid State Commun.* **18**, 553 (1976).
- [55] T. Aruga, H. Tochiwara, and Y. Murata, Valence-electronic structure of potassium adsorbed on Cu(001) deduced from work-function change and electron-energy-loss spectroscopy, *Phys. Rev. B* **34**, 8237 (1986).
- [56] S. Mizuno, H. Tochiwara, and T. Kawamura, Alkali-metal adsorption on dissimilar alkali-metal monolayers preadsorbed on Cu(001): Li on Na and Na on Li, *Phys. Rev. B* **50**, 17540 (1994).
- [57] A. Raghavan, L. Slocumbe, A. Spreinat, D. J. Ward, W. Allison, J. Ellis, A. P. Jardine, M. Sacchi, and N. Avidor, Alkali metal adsorption on metal surfaces: New insights from new tools, *Phys. Chem. Chem. Phys.* **23**, 7822 (2021).
- [58] A. R. McCluskey, S. W. Coles, and B. J. Morgan, Accurate estimation of diffusion coefficients and their uncertainties from computer simulation, *J. Chem. Theory Comput.* **21**, 79 (2025).
- [59] A. R. McCluskey, A. G. Squires, J. Dunn, S. W. Coles, and B. J. Morgan, Kinisi: Bayesian analysis of mass transport from molecular dynamics simulations, *J. Open Source Software* **9**, 5984 (2024).
- [60] A. Cucchetti and S. Ying, Diffusion of Na atoms on a Cu(001) surface, *Phys. Rev. B* **60**, 11110 (1999).
- [61] D. J. Ward, A. Raghavan, A. Tamtögl, A. P. Jardine, E. Bahn, J. Ellis, S. Miret-Artés, and W. Allison, Inter-adsorbate forces and coherent scattering in helium spin-echo experiments, *Phys. Chem. Chem. Phys.* **23**, 7799 (2021).
- [62] M. Lin, Representative molecular dynamics trajectory data used in the extraction of diffusion coefficients for Na/Cu(001) at a coverage of $\theta = 0.020$ and temperature $T = 155$ K, University of Cambridge, Apollo Repository (2025), <https://doi.org/10.17863/CAM.125010>.