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Temperature dependence in atom–surface scattering

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Abstract

It is shown that a straightforward measure of the temperature dependence of energy resolved atom–surface scattering spectra measured under classical conditions can be related to the strength of the surface corrugation. Using classical perturbation theory combined with a Langevin bath formalism for describing energy transfer, explicit expressions for the scattering probabilities are obtained for both two-dimensional, in-plane scattering and full three-dimensional scattering. For strong surface corrugations results expressed as analytic closed-form equations for the scattering probability are derived which demonstrate that the temperature dependence of the scattering probability weakens with increasing corrugation strength. The relationship to the inelastic rainbow is briefly discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The investigation of the structure and dynamical properties of surfaces using atomic probes as scattering projectiles has proven to be a useful experimental tool, in part because it is sensitive only to the outermost layers and, for incident translational energies in the thermal and hyperthermal regimes, it is non-destructive. The scattering of light mass atoms, especially helium at low energies, has become a major experimental tool of surface science. Typical experimental conditions are well within the quantum mechanical regime and prominent features observed when atoms are reflected from ordered surfaces are diffraction peaks and features associated with single quantum phonon excitation from which information about structure, interaction potentials and vibrational properties of the surface can be ascertained [1–4].

However, for decades there have also been a number of experimental studies of the scattering of atomic and molecular beams from surfaces carried out in the classical regime [5, 6]. Under conditions of higher translational energies, larger surface temperatures and particularly for heavier mass atomic projectiles, the well defined peaks associated with quantum mechanical features disappear from the scattered intensity spectra and the collision events are adequately described within the framework of classical scattering theory [7]. Under such classical conditions the scattered spectra tend to consist of broad peaks exhibiting significant energy transfer with the surface. However, even in the absence of detailed quantum mechanical features much information can be gleaned about the interaction forces. For example, under appropriate initial conditions energy resolved scattering intensities can exhibit separate features arising due to direct scattering over a short collision time or from trapping with subsequent desorption [6, 8–10], and analysis of these features leads to physical information about the interaction potential and its attractive physisorption well [11, 12]. Measurements of angular distributions scattered from ordered surfaces can exhibit rainbow patterns that reveal the structure and corrugation of the outermost surface layers [13].

The concept of surface corrugation is well defined for a surface represented by a hard repulsive wall interaction force where the position of the wall is described by a function of the two-dimensional displacement vectors parallel to the surface. For scattering in a more realistic interaction potential a corrugation function can be introduced as the reference from which the displacement perpendicular to the surface is measured, and it defines the locus of the classical turning points.

The purpose of this paper is to point out how the temperature dependence of energy resolved scattered intensity spectra can be related to the nature of the surface corrugation. We develop here theoretical models that show how temperature dependent measurements can be used to obtain physical information on the corrugation function. Typically, energy resolved spectra are measured using a monoenergetic atomic beam with both incident and final (detector) angles fixed. In a plot of scattered intensity as a function of final translational energy what is often observed is a single broad peak, although for corrugated surfaces multiple features can also be observed [14, 15]. As a function of increasing surface temperature this peak broadens while simultaneously the most probable intensity decreases. Such behavior is easily understandable as a consequence of overall unitarity of the scattering process, if the peak broadens the decrease in maximum intensity tends to preserve the integrated number This decrease in intensity as a of scattered particles. function of surface temperature can be directly related to the surface corrugation and provides a measure of the corrugation height [16].

The origin of this temperature effect can be most easily illustrated by comparing the well-known scattered intensity probabilities for an incident beam of atomic projectiles making a single collision with two quite different models of the surface, a highly corrugated surface and a smooth surface whose only corrugation is that due to thermal vibrations. A strongly corrugated surface would appear to resemble a collection of discrete scattering cores. For such a case the probability, calculated within the impulse approximation, for an incident projectile of mass *m* and momentum \mathbf{p}_i to be scattered into a final state of momentum $\mathbf{\bar{p}}$ after a single collision with a target consisting of a collection of discrete scattering centers of mass $M_{\rm S}$ initially moving with an equilibrium velocity distribution is given by [17–19]

$$P(\bar{\mathbf{p}}) \propto \left(\frac{1}{2\pi k_{\rm B} T_{\rm S} \Delta E_0}\right)^{1/2} \exp\left\{-\frac{(E_{\rm f} - E_{\rm i} + \Delta E_0)^2}{4k_{\rm B} T_{\rm S} \Delta E_0}\right\},\tag{1.1}$$

where $T_{\rm S}$ is the temperature, $k_{\rm B}$ is Boltzmann's constant, the initial and final projectile energies are $E_i = \mathbf{p}_i^2/2m$ and $E_{\rm f} = \bar{\mathbf{p}}^2/2m$, and the binary recoil energy is $\Delta E_0 = (\bar{\mathbf{p}} - \mathbf{p})^2/2m$ $(\mathbf{p}_i)^2/2M_{\rm S}$. Equation (1.1) has the appearance of a Gaussian when viewed as a function of final energy $E_{\rm f}$, but is actually a skewed function because of the momentum dependence of the recoil energy ΔE_0 and this asymmetry can be very pronounced, as for example under conditions of low incident energy. In equation (1.1) the most probable intensity occurs for the conditions where the argument of the exponential vanishes, $E_{\rm f} = E_{\rm i} - \Delta E_0$, an equation which is identical to that for energy transferred in a hard-core binary particle collision where the only conditions are conservation of translational energy and momentum. Thus the temperature dependence of the most probable intensity is governed by the envelope prefactor and decreases with increasing temperature as $1/\sqrt{T_s}$.

On the other hand, if the scattering is a single impulsive collision with a smooth surface that is flat and uncorrugated except for small thermal ripples caused by vibrations of the underlying atomic cores the classical scattering probability distribution is [19–21]

$$P(\bar{\mathbf{p}}) \propto \left(\frac{1}{2\pi k_{\rm B} T_{\rm S} \Delta E_0}\right)^{3/2} \times \exp\left\{-\frac{(E_{\rm f} - E_{\rm i} + \Delta E_0)^2 + 2v_R^2 \mathbf{P}^2}{4k_{\rm B} T_{\rm S} \Delta E_0}\right\},\tag{1.2}$$

where P is the parallel component of the scattering vector $\bar{\mathbf{p}} - \mathbf{p}_i$. The quantity v_R is defined as a weighted average of phonon velocities parallel to the surface, but in usual practice it is taken to be a constant [20, 21]. Although the temperature dependence appearing in the prefactor of equation (1.2) varies as $1/T_{\rm S}^{3/2}$, this does not necessarily dictate the temperature dependence of the most probable intensity. It is only under special circumstances that both the energy transfer and parallel momentum transfer terms in the argument of the exponential are simultaneously vanishing, thus this total argument rarely vanishes and the most probable intensity occurs when the argument of the exponential attains a minimum value. Consequently, the temperature dependence of the most probable intensity is only approximately given by the $1/T_s^{3/2}$ envelope prefactor of equation (1.2), but under conditions corresponding to that of available experiments at hyperthermal energies this dependence is a very good approximation.

The temperature dependence of the widths of the scattered intensity probabilities is largely driven by the appearance of the factor of $T_{\rm S}$ in the denominator of the argument of the exponentials in equations (1.1) and (1.2). Under conditions such as high incident energies in which the scattering appears as a single peak, and is approximately symmetric and nearly Gaussian-like in the final energy $E_{\rm f}$, the full width at half maximum increases very nearly as $\sqrt{T_{\rm S}}$. This $\sqrt{T_{\rm S}}$ temperature dependence of the widths of the scattered intensity is characteristic of classical scattering distributions regardless of the specific properties of the surface, as illustrated by the widely different surface corrugations that lead to equations (1.1) and (1.2). However, the effect of surface corrugation is manifest in the temperature dependence of the prefactors and with equation (1.2), showing that a weakly corrugated surface has a much stronger temperature dependence than that of a highly corrugated surface such as that illustrated by the discrete model of equation (1.1).

This analysis indicates that if one considers the thought experiment of starting with a smooth, non-corrugated surface and then gradually increasing the corrugation amplitude, the temperature dependence would gradually weaken from the strongly decreasing approximately $1/T_8^{3/2}$ behavior and would approach the $1/T_8^{1/2}$ behavior of the discrete surface model if the corrugation becomes strong, such that each atomic core of the surface appears as a nearly discrete scattering center. This strong difference in temperature behavior between the highly corrugated and flat surfaces described by equations (1.1) and (1.2) would indicate that comparison of experimental data with an appropriately developed theory for arbitrary corrugation should allow extraction of information on the average corrugation height of the surface by merely examining the temperature dependence of the most probable intensity.

It should also be noted that the temperature in both equations (1.1) and (1.2) always appears multiplied by the classical recoil energy ΔE_0 . Thus for both types of surface corrugation the behavior of the reflected intensity as a function of ΔE_0 for fixed T_S should be similar to that of the temperature dependence for fixed ΔE_0 (or equivalently for fixed initial and final momenta). However, there are circumstances for

which $\Delta E_0 \propto E_i$, notably the case in which the incident energy is large compared to the surface temperature [7]. In such conditions measurements of the scattered intensity as a function of incident energy E_i could be used to get the same information on the corrugation as could be obtained from a temperature dependent measurement at fixed energy. However, in view of the experimental observation that it is usually easier to obtain good relative scattering intensities as a function of T_S than as a function of beam energy E_i , it is expected that temperature dependent measurements would be the first method of choice.

Starting from a treatment of surface scattering using classical perturbation theory with energy transfer treated within the generalized Langevin formalism as developed by one of the authors [14, 15] we examine the temperature dependence of the state to state scattering probability. This model allows the general result for the scattering probability to be expressed in terms of a spatial integral over a unit cell of the surface. In the case of two-dimensional, in-plane scattering and relatively strong corrugation strengths the spatial integral can be evaluated approximately leading to a scattering probability expressed in terms of analytic closed-form expressions whose temperature dependence clearly exposes the different behaviors predicted for smooth versus highly corrugated surfaces.

The remainder of this paper is organized as follows. Section 2 presents a brief review of classical perturbation theory as applied to surface scattering. Explicit expressions for the scattering probabilities are developed for two-dimensional scattering, the approximate analytic forms are extracted under the conditions of large corrugation amplitudes, and some numerical examples are presented. Section 3 gives the development of the theory for full three-dimensional scattering. In section 4 some conclusions on the usefulness of these results are presented as well as a brief discussion of quantum mechanical implications.

2. Classical two degrees of freedom scattering probability

2.1. General theoretical considerations

The starting point of this study is the problem of an atomic projectile colliding inelastically with a surface, modeled by Langevin baths. Restricting the problem to two-dimensional scattering, including vibrational motion of the surface in both perpendicular and parallel directions, the final momentum distribution has been shown to be [14]

$$P(\bar{p}_x, \bar{p}_z) = \frac{1}{l} \int_0^l dx \, \langle \delta(\bar{p}_x - p_{x_f}) \delta(\bar{p}_z - p_{z_f}) \rangle_{x,z}, \quad (2.1)$$

where \bar{p}_z and \bar{p}_x are the final momenta perpendicular and parallel to the surface, l is the length of a unit cell of the surface, and the averaging is over the thermal baths in the vertical and horizontal z, x directions. From general considerations we assume that

$$p_{x_{\rm f}} = \langle p_{x_{\rm f}} \rangle + \delta p_{xx}, \qquad (2.2)$$

where δp_{xx} are the Gaussian stochastic fluctuations created by the horizontal bath. Similarly

$$p_{z_{\rm f}} = \langle p_{z_{\rm f}} \rangle + \delta p_{zz} + \delta p_{zx}, \qquad (2.3)$$

where in addition to the stochastic fluctuations contributed by the vertical bath (assumed independent of the horizontal bath) we have stochastic Gaussian fluctuations induced by the horizontal bath in the form of δp_{zx} . We note that all terms in equations (2.2) and (2.3) may depend on position, or impact parameter *x* within the surface unit cell.

Averaging over the vertical bath gives

$$P(\bar{p}_x, \bar{p}_z) = \frac{1}{l} \int_0^l dx \, \frac{1}{\sqrt{2\pi \langle \delta p_{zz}^2 \rangle}} \\ \times \left\langle \delta(\bar{p}_x - p_{x_f}) \exp\left(-\frac{(\bar{p}_z - \langle p_{zf} \rangle - \delta p_{zx})^2}{2 \langle \delta p_{zz}^2 \rangle}\right) \right\rangle_x. \quad (2.4)$$

Because the averaging over the Langevin bath for parallel motion in equation (2.4) introduces correlations in the vertical direction, this second average becomes somewhat more complicated. One way to carry out the averaging is by first introducing a dummy variable *W* so that

$$P(\bar{p}_x, \bar{p}_z) = \int_{-\infty}^{\infty} dW \frac{1}{l} \int_0^l dx \frac{1}{\sqrt{2\pi \langle \delta p_{zz}^2 \rangle}} \\ \times \exp\left(-\frac{(\bar{p}_z - \langle p_{z_f} \rangle - W)^2}{2 \langle \delta p_{zz}^2 \rangle}\right) \\ \times \langle \delta(\bar{p}_x - p_{x_f}) \delta(\delta p_{zx} - W) \rangle_x.$$
(2.5)

Then denoting the following variances

$$H_{xx} = \langle \delta p_{xx}^2 \rangle_x, \tag{2.6}$$

$$H_{zx} = \langle \delta p_{zx} \delta p_{xx} \rangle_x, \qquad (2.7)$$

$$H_{zz} = \langle \delta p_{zx}^2 \rangle_x, \qquad (2.8)$$

it is straightforward to show that for example

$$\langle \delta(\bar{p}_x - p_{x_{\rm f}}) \delta(\delta p_{zx} - W_x) \rangle_x = \frac{1}{2\pi \sqrt{H_{xx}H_{zz} - H_{zx}^2}} \times \exp(\{-H_{zz}(\bar{p}_x - \langle p_{x_{\rm f}} \rangle)^2 - 2W_x H_{zx}(\bar{p}_x - \langle p_{x_{\rm f}} \rangle) + H_{xx} W_x^2 \} \{2(H_{xx}H_{zz} - H_{zx}^2)\}^{-1}).$$
(2.9)

Integrating over the dummy variable W gives the expression for the final momentum distribution as

$$P(\bar{p}_{x}, \bar{p}_{z}) = \frac{1}{l} \int_{0}^{l} dx \frac{1}{2\pi\sqrt{\Sigma^{2}}} \exp(\{-H_{xx}(\bar{p}_{z} - \langle p_{z_{f}} \rangle)^{2} + 2H_{xz}(\bar{p}_{z} - \langle p_{z_{f}} \rangle)(\bar{p}_{x} - \langle p_{x_{f}} \rangle) + (H_{zz} + \langle \delta p_{zz}^{2} \rangle)(\bar{p}_{x} - \langle p_{x_{f}} \rangle)^{2} \{2\Sigma^{2}\}^{-1}), \qquad (2.10)$$

with

$$\Sigma^{2} = H_{xx}(H_{zz} + \langle \delta p_{zz}^{2} \rangle) - H_{zx}^{2}.$$
 (2.11)

Typically, the second moments of classical thermal fluctuations will be proportional to $\beta^{-1} = k_{\rm B}T_{\rm S}$, thus $\Sigma^2 \propto T_{\rm S}^2$. To understand the temperature dependence of the scattered particle it remains for us to analyze this expression under different conditions.

2.2. Scattering in the absence of corrugation

If the surface is smooth with no static corrugation, one may assume that the various momentum averages and variances are independent of the impact parameter. The averaging over the impact parameter is then trivial and the final momentum distribution is

$$P(\bar{p}_x, \bar{p}_z; \text{ no corrugation})$$

$$= \frac{1}{2\pi\sqrt{\Sigma^2}} \exp(\{-H_{xx}(\bar{p}_z - \langle p_{z_f} \rangle)^2 + 2H_{xz}(\bar{p}_z - \langle p_{z_f} \rangle)(\bar{p}_x - \langle p_{x_f} \rangle) + (H_{zz} + \langle \delta p_{zz}^2 \rangle)(\bar{p}_x - \langle p_{x_f} \rangle)^2 \} \{2\Sigma^2\}^{-1}).$$
(2.12)

In this zero-corrugation limit the temperature dependence of the probability is determined largely by the prefactor $1/\sqrt{\Sigma^2} \propto 1/T_S$. Near the maximum of the final momentum distribution, where the argument of the exponential vanishes the prefactor dominates the temperature dependence. This $1/T_S$ dependence is the expected result for two-dimensional scattering from a corrugationless surface, and as shall also be shown in section 2.3, corresponds to the full three-dimensional scattering probability of equation (1.2) whose temperature dependent prefactor varies as $1/T_S^{3/2}$.

2.3. Scattering in the presence of corrugation

The analysis becomes slightly more involved in the presence of corrugation. To simplify, and since typically conditions justify this simplification, we assume that the thermal fluctuations are all independent of the impact parameter. Only the final average momenta are assumed to be affected by the corrugation. Energy conservation implies that

$$\langle p_{z_{\rm f}} \rangle = \frac{2ME_{\rm i} - M\langle \Delta E_{\rm B} \rangle}{|p_{z_{\rm i}}|} - |\tan(\theta_i)|\langle p_{x_{\rm f}} \rangle \qquad (2.13)$$

where $\langle \Delta E_{\rm B} \rangle$ is the average energy lost by the particle to the surface during the collision. We also assume that this average energy is independent of the corrugation.

To estimate the integration over the impact parameter, we use a steepest descent approximation. Writing the exponent of equation (2.10) as $\exp(-f(x))$ we have that

$$\Sigma^{2} \frac{\partial f(x)}{\partial x} = \frac{\partial \langle p_{x_{f}} \rangle}{\partial x} [(\bar{p}_{z} - \langle p_{z_{f}} \rangle)(H_{xx} | \tan(\theta_{i})| - H_{xz}) + (\bar{p}_{x} - \langle p_{x_{f}} \rangle)(H_{xz} | \tan(\theta_{i})| - H_{zz} - \langle \delta p_{zz}^{2} \rangle)].$$
(2.14)

The stationary points require that $\partial f(x)/\partial x = 0$ and occur either when $\partial \langle p_{x_t} \rangle / \partial x = 0$ or when the term in the square bracket vanishes. If the term in the bracket vanishes, we denote the corresponding stationary point as x_1 and find that the second derivative at the stationary point is positive

$$\Sigma^{2} \frac{\partial^{2} f(x)}{\partial x^{2}}_{x=x_{1}} = \left(\frac{\partial \langle p_{x_{f}} \rangle}{\partial x}\right)_{x=x_{1}}^{2} \times [\langle \delta p_{zz}^{2} \rangle + \langle (|\tan(\theta_{i})|\delta p_{xx} - \delta p_{zx})^{2} \rangle_{x}].$$
(2.15)

The stationary phase approximation will be valid if the magnitude of the second derivative is sufficiently large, that

is the term on the right-hand side must be larger than the variance Σ^2 . Since the impact parameters which lead to rainbow scattering are points at which $\partial \langle p_{x_f} \rangle / \partial x = 0$ it is clear that the main contributions to the integral will come from the 'inner' regions of the distribution where there are no rainbows. It is also clear that if the corrugation is too weak, then the final average momentum will hardly vary with the impact parameter and the steepest descent estimate is not valid. For very weak corrugation, one can assume that *f* is independent of the impact parameter and one reverts to the regime of section 2.2.

If the steepest descent estimate is valid, then one can now readily perform the Gaussian integration over the impact parameter to find that

$$P(\bar{p}_{x}, \bar{p}_{z})$$

$$\simeq \frac{1}{l} \frac{1}{\sqrt{2\pi [\langle \delta p_{zz}^{2} \rangle + \langle (|\tan(\theta_{i})|\delta p_{xx} - \delta p_{zx})^{2} \rangle_{x}]} |(\frac{\partial \langle p_{x_{t}} \rangle}{\partial x})_{x=x_{1}}|}}{\times \exp \left(-\frac{(\bar{p}_{x} - \langle p_{x_{t}} \rangle)^{2}}{2(H_{xx}|\tan(\theta_{i})| - H_{xz})^{2}} (\langle \delta p_{zz}^{2} \rangle + H_{zz} - 2H_{xz}|\tan(\theta_{i})| + H_{xx}|\tan^{2}(\theta_{i})|)\right)}.$$
(2.16)

Assuming as before that the second moments of the fluctuations are proportional to $\beta^{-1} = k_{\rm B}T_{\rm S}$, we find that in this region the maximum of the distribution is found when $\bar{p}_x = \langle p_{x_{\rm f}} \rangle$ which also implies that $\bar{p}_z = \langle p_{z_{\rm f}} \rangle$ and its dependence on the temperature goes as $\beta^{1/2}$. This is a significant reduction in the strength of the temperature dependence as compared to the direct proportionality to β noted for the zero-corrugation case discussed above just after equation (2.10) and demonstrates that the corrugation weakens the surface temperature dependence of the scattered distribution. If the corrugation is sufficiently strong, it may be considered as overcoming the thermal fluctuations in one degree of freedom and therefore one remains with only a $\beta^{1/2}$ temperature dependence.

For rainbow scattering, that is if the derivative of the final averaged horizontal momentum with respect to the impact parameter vanishes, we denote the stationary point as x_2 if the second derivative $\partial^2 \langle p_{x_f} \rangle / \partial x^2$ is positive, and x_3 if it is negative (but the full second derivative remains positive). In this second scenario, the second derivative of the function is

$$\Sigma^{2} \frac{\partial^{2} f(x)}{\partial x^{2}}_{x=x_{2},x_{3}} = \left(\frac{\partial^{2} \langle p_{x_{t}} \rangle}{\partial x^{2}}\right)_{x=x_{2},x_{3}} \times \left[(\bar{p}_{z} - \langle p_{z_{t}} \rangle)(H_{xx} | \tan(\theta_{i})| - H_{xz}) + (\bar{p}_{x} - \langle p_{x_{t}} \rangle)(H_{xz} | \tan(\theta_{i})| - H_{zz} - \langle \delta p_{zz}^{2} \rangle)\right].$$
(2.17)

If the second derivative of the momentum with respect to the impact parameter is positive, this constrains the valid values of the final momenta such that

$$(\bar{p}_{z} - \langle p_{z_{t}} \rangle)(H_{xx} | \tan(\theta_{i})| - H_{xz}) + (\bar{p}_{x} - \langle p_{x_{t}} \rangle) \times (H_{xz} | \tan(\theta_{i})| - H_{zz} - \langle \delta p_{zz}^{2} \rangle) \ge 0.$$
(2.18)

If the second derivative is negative then the term in the square brackets of equation (2.17) must be negative, i.e. equation (2.18) must be negative. The corresponding

scattering probabilities are expressed as

$$P(\bar{p}_{x}, \bar{p}_{z}) \simeq \frac{1}{2\pi} \frac{1}{l} \exp(-f(x_{2,3}))$$

$$\times \left\{ \frac{\partial^{2} \langle p_{x_{f}} \rangle}{\partial x_{2,3}^{2}} [(\bar{p}_{z} - \langle p_{z_{f}} \rangle)(H_{xx} | \tan(\theta_{i})| - H_{xz}) + (\bar{p}_{x} - \langle p_{x_{f}} \rangle)(H_{xz} | \tan(\theta_{i})| - H_{zz} - \langle \delta p_{zz}^{2} \rangle)] \right\}^{-1/2}.$$

$$(2.19)$$

This in turn implies that these steepest descent points lead to contributions to the scattering probability of equation (2.19) that are exponentially small, since the conditions imposed by equation (2.18) imply that the exponent $f(x_{2,3})$ may not vanish. Similarly to the case of equation (2.16) the temperature dependence of the prefactor varies as $1/\sqrt{T_s}$, again indicating that the strength of the temperature dependence for the corrugated surface is decreased relative to that of a surface with no corrugation.

2.4. A numerical example

To understand in somewhat more detail the effect of the corrugation it is useful to consider a simplified model of the scattering. We will assume as before that all variances are independent of the impact parameter. It has been shown elsewhere, that if there is only vertical friction and the potential takes the form

$$V(x,z) = \bar{V}(z) + \bar{V}'(z)h\sin\left(\frac{2\pi x}{l}\right)$$
(2.20)

where $\overline{V}(z)$ is the vertical interaction potential (typically a Morse potential) and *h* is the corrugation height then

$$\langle p_{x_i} \rangle = p_{x_i} - p_{z_i} K \cos\left(\frac{2\pi x_0}{l}\right) + \Delta p_{x,1}$$
(2.21)

where p_{z_i} is the incident (negative) momentum in the vertical direction, *K* is the 'rainbow angle shift parameter', which is dimensionless, proportional to the corrugation height *h* (and thus typically much smaller than unity) and independent of the temperature [22, 23]. x_0 is the value of the horizontal coordinate as the particle reaches the turning point in the vertical direction and $\Delta p_{x,1}$ is a friction induced momentum shift, which is temperature independent. Within first order classical perturbation theory the Jacobian from the horizontal coordinate *x* to x_0 is unity, so that one may simply replace the integration in equation (2.4) with an integration over x_0 and there is no further need to carry the subscript 0. The final averaged momentum in the vertical direction is obtained from energy conservation (see equation (2.13)) and is thus also dependent on the impact parameter.

To further simplify, we will assume that only the 'direct' variances are important, that is we can neglect H_{zz} and H_{xz} . The final momentum distribution now takes the form

$$P(\bar{p}_{x}, \bar{p}_{z}) = \frac{1}{l} \int_{0}^{l} dx \frac{1}{2\pi \sqrt{H_{xx} \langle \delta p_{zz}^{2} \rangle}} \\ \times \exp\left(-\frac{H_{xx}(\bar{p}_{z} - \langle p_{z_{f}} \rangle)^{2} + \langle \delta p_{zz}^{2} \rangle(\bar{p}_{x} - \langle p_{x_{f}} \rangle)^{2}}{2H_{xx} \langle \delta p_{zz}^{2} \rangle}\right).$$

$$(2.22)$$

In the absence of corrugation, the averaging over the impact parameter is trivial, the distribution maximizes when $\bar{p}_z = \langle p_{z_f} \rangle$ and $\bar{p}_x = \langle p_{x_f} \rangle$. The dependence of the maximum on the (inverse) temperature goes as β .

In the presence of corrugation, one may write down the distribution (by substituting the variable $cos(2\pi r)$ with the variable u) as

$$P(\rho_x, \rho_z) = \int_{-K}^{K} du \frac{1}{2\pi^2 \sqrt{K^2 - u^2} \sqrt{\sigma_{xx}^2 \sigma_{zz}^2}}$$

$$\times \exp\left(\left\{-\sigma_{xx}^2 \left(\rho_z - 1 + \frac{\Delta\varepsilon}{2} + |\tan(\theta_i)|\Delta\eta_x + |\tan(\theta_i)|u\right)^2 + \sigma_{zz}^2 (\rho_x - |\tan(\theta_i)| + u + \Delta\eta_x)^2\right\} \{2\sigma_{xx}^2 \sigma_{zz}^2\}^{-1}\right), \quad (2.23)$$

using the following reduced variables

$$r = \frac{x}{l}, \qquad \rho_z = \frac{\bar{p}_z}{|p_{z_i}|}, \qquad \rho_x = \frac{\bar{p}_x}{|p_{z_i}|},$$
$$\Delta \varepsilon = \frac{2M \langle \Delta E_{\rm B} \rangle}{p_{z_i}^2}, \qquad \sigma_{xx}^2 = \frac{H_{xx}}{|p_{z_i}|^2}, \qquad (2.24)$$
$$\sigma_{zz}^2 = \frac{\langle \delta p_{zz}^2 \rangle}{|p_{z_i}|^2}, \qquad \Delta \eta_x = \frac{\Delta p_{x,1}}{|p_{z_i}|}.$$

To further simplify, we note that for weak dissipation $\Delta \varepsilon$, $\Delta \eta_x \ll 1$ so they can be ignored and for simplicity we choose $\sigma_{xx}^2 = \sigma_{zz}^2 = \sigma^2$. Taking the incident angle as $\pi/4$ and noting that by symmetry, the maximum of the final momentum distribution lies on the line $\rho_x = \rho_z \equiv \rho$ implies that it suffices to discuss

$$P\left(\rho_{x} = \rho_{z} \equiv \rho; \theta_{i} = \frac{\pi}{4}\right)$$

= $\int_{-K}^{K} du \frac{1}{2\pi^{2}\sigma^{2}\sqrt{K^{2} - u^{2}}} \exp\left(-\frac{(\rho - 1 + u)^{2}}{\sigma^{2}}\right).$ (2.25)

Now the temperature dependence becomes quite clear. If the width σ is much smaller than *K* then the distribution goes as

$$P\left(\rho; \theta_i = \frac{\pi}{4}, \sigma \ll K\right) \sim \frac{1}{2\pi^{3/2}\sigma\sqrt{K^2 - (1-\rho)^2}}$$
 (2.26)

while if the width σ is much larger than K then

$$P\left(\rho; \theta_i = \frac{\pi}{4}, \sigma \gg K\right) \sim \frac{K}{\pi\sigma^2} \exp\left(-\frac{(\rho-1)^2}{\sigma^2}\right). \quad (2.27)$$

The transition between the two regimes is readily noticeable in the plots shown in figure 1.

3. Three-dimensional considerations

The full three-dimensional case is qualitatively the same as the in-plane two-dimensional case. The added horizontal degree of freedom implies that in the absence of corrugation, or equivalently when the temperature is sufficiently high such



Figure 1. Temperature dependence for the maximal intensity of the final momentum distribution for two-dimensional dynamics. The top left panel shows the probability distribution (equation (2.25)) multiplied by (the square root of the variance) σ as a function of the symmetric (reduced) momentum (ρ) and temperature (σ) when the corrugation (K) is much larger than the noise (σ). The top right panel shows the variance σ^2 multiplied by the probability distribution when the temperature is high, that is when σ is larger then K. Note the approximate constancy of the two figures respectively about the maximal ridge. The bottom left panel shows the actual probability distribution in the strong corrugation regime, while the bottom right-hand panel is in the weak corrugation regime. Note the rainbow structure in the strong corrugation regime and the single peaked Gaussian structure in the weak corrugation regime. In all plots K = 0.2. For further details, see the text.

that the broadening wipes out the effects of the corrugation, the maximum of the final momentum distribution will go as $\beta^{3/2}$. When the corrugation is important then the scaling goes as $\beta^{1/2}$. The derivation is outlined below.

We consider scattering in three dimensions of a particle of mass M with initial momenta p_{j_i} , j = x, y, z in the vertical z and horizontal x and y directions. The surface is characterized by the lattice lengths l_x and l_y . The final momentum distribution is by definition

$$P(\bar{p}_{x}, \bar{p}_{y}, \bar{p}_{z}) = \frac{1}{l_{x}l_{y}} \int_{0}^{l_{x}} dx \int_{0}^{l_{y}} dy \, \langle \delta(\bar{p}_{x} - p_{x_{f}}) \\ \times \, \delta(\bar{p}_{y} - p_{y_{f}}) \delta(\bar{p}_{z} - p_{z_{f}}) \rangle_{x,y,z}.$$
(3.1)

The averaging is over thermal baths in the vertical and horizontal directions. Following the derivation in the twodimensional case, and from the same general considerations we assume that the final momenta in the horizontal directions may be described as the sum of an averaged and a fluctuational term

$$p_{j_{\rm f}} = \langle p_{j_{\rm f}} \rangle + \delta p_{jj}, \qquad j = x, y \tag{3.2}$$

where δp_{jj} are assumed to be Gaussian stochastic fluctuations created by the respective horizontal bath. For simplicity we assume that the two horizontal baths are uncorrelated, although this assumption is not essential. By definition, the fluctuations have zero mean. As before, the vertical motion is also coupled to the horizontal baths so that the final vertical momentum has the form

$$p_{z_{\rm f}} = \langle p_{z_{\rm f}} \rangle + \delta p_{zz} + \delta p_{zx} + \delta p_{zy} \tag{3.3}$$

where in addition to the stochastic fluctuations contributed by the vertical bath (assumed independent of the horizontal baths) we have stochastic Gaussian fluctuations induced by the horizontal baths in the form of δp_{zx} and δp_{zy} . Here too, we assume that these horizontal induced fluctuations are uncorrelated.

Deriving the final momentum distribution follows the same lines as in the two-dimensional case. One first averages over the vertical bath, then introduces two dummy variables W_x and W_y using identities similar to that given in equation (2.9) to find that the final momentum distribution is

$$P(\bar{p}_{x}, \bar{p}_{y}, \bar{p}_{z}) = \frac{1}{l_{x}l_{y}} \int_{0}^{l_{x}} dx \int_{0}^{l_{y}} dy \frac{1}{2\pi\sqrt{2\pi}} \frac{1}{\sqrt{\Sigma^{2}}} \\ \times \exp\left(-\frac{H_{xx}H_{yy}(\bar{p}_{z} - \langle p_{z_{f}} \rangle)^{2}}{2\Sigma^{2}}\right) \\ \times \exp\left(\{H_{zy}H_{xx}(\bar{p}_{y} - \langle p_{y_{f}} \rangle)(\bar{p}_{z} - \langle p_{z_{f}} \rangle) \\ + H_{zx}H_{yy}(\bar{p}_{x} - \langle p_{x_{f}} \rangle)(\bar{p}_{z} - \langle p_{z_{f}} \rangle)\{\Sigma^{2}\}^{-1}\right) \\ \times \exp\left(-\frac{H_{zx}H_{zy}(\bar{p}_{x} - \langle p_{x_{f}} \rangle)(\bar{p}_{y} - \langle p_{y_{f}} \rangle)}{\Sigma^{2}}\right) \\ \times \exp\left(\{-(\bar{p}_{x} - \langle p_{x_{f}} \rangle)^{2}(H_{yy}\langle \delta p_{zz}^{2} \rangle + H_{yy}H_{zyy} \\ + H_{yy}H_{zxx} - H_{zy}^{2})\}\{2\Sigma^{2}\}^{-1}\right) \\ \times \exp\left(\{-(\bar{p}_{y} - \langle p_{y_{f}} \rangle)^{2}[(H_{xx}\langle \delta p_{zz}^{2} \rangle + H_{xx}H_{zxx} \\ + H_{xx}H_{zyy} - H_{zx}^{2})]\}\{2\Sigma^{2}\}^{-1}\right),$$
(3.4)

and we used the following notation for the variances

$$H_{jj} = \langle \delta p_{jj}^2 \rangle_j, \qquad j = x, y, z \tag{3.5}$$

$$H_{zj} = \langle \delta p_{zj} \delta p_{jj} \rangle_j, \qquad j = x, y$$
 (3.6)

$$H_{zjj} = \langle \delta p_{zj}^2 \rangle_j, \qquad j = x, y \qquad (3.7)$$

and

$$\Sigma^{2} = H_{xx}H_{yy}\langle\delta p_{zz}^{2}\rangle + H_{xx}(H_{yy}H_{zyy} - H_{zy}^{2}) + H_{yy}(H_{xx}H_{zxx} - H_{zx}^{2}).$$
(3.8)

If all the bath fluctuations and energy losses are independent of the surface corrugation or, equivalently, the surface temperature is sufficiently high such that the fluctuations 'wash out' the effect of the corrugation, then one can effectively assume that the exponents become independent of the corrugation, as also noted in the previous section for the two-dimensional case. It is then evident that the maximum of the final momentum distribution will go as $1/\sqrt{\Sigma^2}$. Since the variance in this three-dimensional case goes as β^{-3} one will have recovered the 'free particle' $\beta^{3/2}$ temperature dependence.

Conversely, if the corrugation is large, or equivalently the variances are sufficiently small, then one cannot ignore the corrugation dependence of the exponent. However, one can carry out the integration over the impact parameters as before using a steepest descent estimate. Corrugation appears as a temperature independent contribution to the averaged final momentum in the horizontal directions, and through energy conservation in the final averaged momentum in the vertical direction

$$\{\langle p_{z_f} \rangle^2 + \langle \delta p_{zz}^2 \rangle + H_{zxx} + H_{zyy} + 2H_{zx} + 2H_{zy} + \langle p_{x_f} \rangle^2 + H_{xx} + \langle p_{y_f} \rangle^2 + H_{yy} \} \{2M\}^{-1} = E_i - \langle \Delta E_B \rangle.$$
(3.9)

To facilitate the integration over the impact parameters, we change variables from x, y to $\langle p_{x_{\rm f}} \rangle$, $\langle p_{y_{\rm f}} \rangle$. The Jacobian of the transformation is

$$J(\langle p_{x_{\rm f}}\rangle, \langle p_{y_{\rm f}}\rangle; x, y) = \frac{\partial \langle p_{x_{\rm f}}\rangle}{\partial x} \frac{\partial \langle p_{y_{\rm f}}\rangle}{\partial y} - \frac{\partial \langle p_{x_{\rm f}}\rangle}{\partial y} \frac{\partial \langle p_{y_{\rm f}}\rangle}{\partial x}.$$
(3.10)

The classical rainbow lines are the result of the vanishing of the Jacobian. We then estimate the integral using steepest descent. From the energy conservation relation we have that

$$\frac{\partial \langle p_{z_f} \rangle}{\partial \langle p_{x_f} \rangle} = -\frac{\langle p_{x_f} \rangle}{\langle p_{z_f} \rangle}, \qquad \frac{\partial \langle p_{z_f} \rangle}{\partial \langle p_{y_f} \rangle} = -\frac{\langle p_{y_f} \rangle}{\langle p_{z_f} \rangle}.$$
(3.11)

Denoting the Gaussian exponent in the expression for the final momenta distribution of equation (3.4) as $-f(\langle p_{x_f} \rangle, \langle p_{y_f} \rangle)$ one readily finds that the first derivatives of the exponent are

$$\Sigma^{2} \frac{\partial f(\langle p_{x_{t}} \rangle, \langle p_{y_{t}} \rangle)}{\partial \langle p_{x_{t}} \rangle} = A \left(\frac{\langle p_{x_{t}} \rangle}{\langle p_{z_{t}} \rangle} + \frac{H_{zx}}{H_{xx}} \right) - \frac{\Sigma^{2}}{H_{xx}} (\bar{p}_{x} - \langle p_{x_{t}} \rangle), \qquad (3.12)$$

 $\Sigma^{2} \frac{\partial f(\langle p_{x_{f}} \rangle, \langle p_{y_{f}} \rangle)}{\partial \langle p_{y_{f}} \rangle} = A\left(\frac{\langle p_{y_{f}} \rangle}{\partial \langle p_{y_{f}} \rangle} + \frac{H_{zy}}{\partial z}\right) - -$

$$=A\left(\frac{\langle p_{y_{f}}\rangle}{\langle p_{z_{f}}\rangle}+\frac{H_{zy}}{H_{yy}}\right)-\frac{\Sigma^{2}}{H_{yy}}(\bar{p}_{y}-\langle p_{y_{f}}\rangle),$$
(3.13)

with

$$A = H_{xx}H_{yy}(\bar{p}_z - \langle p_{z_t} \rangle) - H_{zy}H_{xx}(\bar{p}_y - \langle p_{y_t} \rangle) - H_{zx}H_{yy}(\bar{p}_x - \langle p_{x_t} \rangle).$$
(3.14)

Denoting the stationary point as $\langle p_{x_f} \rangle_1$, $\langle p_{y_f} \rangle_1$ it is clear that the steepest descent integration brings down to the denominator the square root of the determinant of the second derivative matrix of f with respect to $\langle p_{x_f} \rangle$ and $\langle p_{y_f} \rangle$. Some algebra then leads to the result

$$\Sigma^{4} \left[\frac{\partial^{2} f\left(\langle p_{x_{f}} \rangle, \langle p_{y_{f}} \rangle\right)}{\partial \langle p_{x_{f}} \rangle^{2}} \frac{\partial^{2} f\left(\langle p_{x_{f}} \rangle, \langle p_{y_{f}} \rangle\right)}{\partial \langle p_{y_{f}} \rangle^{2}} - \left(\frac{\partial^{2} f\left(\langle p_{x_{f}} \rangle, \langle p_{y_{f}} \rangle\right)}{\partial \langle p_{x_{f}} \rangle \partial \langle p_{y_{f}} \rangle} \right)^{2} \right] \\ = \frac{1}{H_{xx}} \left[\Sigma^{2} + \frac{AH_{yy}}{\langle p_{z_{f}} \rangle} \right] \frac{1}{H_{yy}} \left[\Sigma^{2} + \frac{AH_{xx}}{\langle p_{z_{f}} \rangle} \right] \\ + \frac{A}{\langle p_{z_{f}} \rangle} H_{yy} H_{xx} \left[\frac{\langle p_{y_{f}} \rangle}{\langle p_{z_{f}} \rangle} \frac{H_{zx}}{H_{xx}} - \frac{\langle p_{x_{f}} \rangle}{\langle p_{z_{f}} \rangle} \frac{H_{zy}}{H_{yy}} \right]^{2} \\ + \frac{1}{H_{xx}} \left[\Sigma^{2} + \frac{AH_{yy}}{\langle p_{z_{f}} \rangle} \right] \left(\left(H_{xx} \frac{\langle p_{x_{f}} \rangle}{\langle p_{z_{f}} \rangle} + H_{zx} \right)^{2} \\ + \frac{A}{\langle p_{z_{f}} \rangle} \frac{\langle p_{x_{f}} \rangle^{2}}{\langle p_{z_{f}} \rangle^{2}} \frac{H_{xy}}{H_{yy}} \right) + \frac{1}{H_{yy}} \left[\Sigma^{2} + \frac{AH_{xx}}{\langle p_{z_{f}} \rangle} \right] \\ \times \left(\left(H_{yy} \frac{\langle p_{y_{f}} \rangle}{\langle p_{z_{f}} \rangle} + H_{zy} \right)^{2} + \frac{A}{\langle p_{z_{f}} \rangle} \frac{\langle p_{y_{f}} \rangle^{2}}{\langle p_{z_{f}} \rangle^{2}} \frac{H_{yy}}{H_{xx}} \right), \quad (3.15)$$

from which it is evident that the determinant has a β^2 dependence on the (inverse) temperature. It thus follows that after the steepest descent integration, the prefactor goes as $\beta^{1/2}$. Strong corrugation decreases the temperature dependence of the maximum of the distribution.

4. Discussion

In atom–surface scattering experiments carried out in the domain of classical physics it has been shown both theoretically [16] and experimentally [24–26] that very different temperature dependence is expected in the scattered intensity spectra depending on whether the surface is smooth or highly corrugated. In this paper we demonstrate this

temperature dependence effect within the formalism of classical perturbation theory with the vibrational dynamics of the surface treated within a stochastic formalism.

The general expression for the scattering probability is presented as an integral over the impact parameters within a single unit cell. One then distinguishes between two regimes. When the noise is small so that the corrugations dominate the scattering (rainbow scattering) then one may well estimate the averaging over the impact parameters by the steepest descent method and the temperature dependence of the maximum of the final momenta distribution will go as $\beta^{1/2}$. If the corrugation is much weaker than the noise, in the sense that the noise term 'wipes out' all structure due to the corrugation, then the effective dependence on the impact parameters is negligible and the maximum of the distribution goes as $\beta^{3/2}$. If one limits the dynamics to two degrees of freedom, then the two limits go as $\beta^{1/2}$ when corrugation is important and as β when it may be ignored.

To derive these results we have presented a rather general stochastic theory of scattering from surfaces. Using the general properties of this theory we were able to understand how corrugation affects the temperature dependence of the intensity of the scattered particles. Elsewhere, this same approach has been used to formulate a theory of sticking to surfaces [27]. This formalism may be readily employed within a Langevin description of the dynamics to obtain analytical formulas for all aspects of the scattering.

The analysis presented in this paper was purely classical. It is evident that the quantum temperature dependence will differ from the classical. Only in classical mechanics does one expect the variances to be linearly dependent on the surface temperature. In quantum mechanics, at very low temperatures, the variances become temperature independent and so the intensity should become independent of the temperature, with and without corrugation. In many respects classical dynamics is more sensitive to surface corrugation than quantum dynamics. This is not unique to the temperature dependence, especially when scattering light atoms such as He from surfaces, the separation between diffraction peaks may become larger than the separation between the classical rainbow peaks and the quantum dynamics will not observe the rainbow structure at all. Such behavior has been observed in the scattering of He from surfaces.

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