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Communication: Semiclassical perturbation theory for the quantum diffractive scattering of atoms on thermal surfaces

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Inspired by the semiclassical perturbation theory of Hubbard and Miller [J. Chem. Phys. **80**, 5827 (1984)], we derive explicit expressions for the angular distribution of particles scattered from thermal surfaces. At very low surface temperature, the observed experimental background scattering is proportional to the spectral density of the phonons. The angular distribution is a sum of diffraction peaks and a broad background reflecting the spectral density. The theory is applied to measured angular distributions of Ne, Ar, and Kr scattered from a Cu(111) surface. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4768227>]

The first observations of quantum diffraction of He scattered from a LiF surface were reported 80 years ago.¹ Since then, many authors repeated such experiments with increasing sophistication.² It is now well understood that diffraction peaks found in surface scattering of atoms as heavy as Kr are due to the periodic corrugation of the surface.

Surface phonons tend to smear out the angular distribution and it then becomes difficult to distinguish between features arising from the corrugation or the interaction of the particle with the phonons.³ It is thus of special interest to have a reliable estimate of the phonon spectral density. The spectral density also provides information on the diffusional properties of the same atom on the surface. It also controls energy transfer to the surface as well as sticking probabilities. The spectral density is a fundamental building block in the theory of the dynamics of atoms in the presence of solid surfaces.

At very low surface temperatures, the angular distribution of a scattered particle will be dominated by two contributions. One is elastic scattering, which leads to sharp Bragg peaks in the angular distribution.² The second is the broad background, which results from imparting a single quantum of energy to one of the surface phonon modes of the surface.⁴ A central theme of this letter is to show how this broad background may be inverted to determine the phonon spectral density and predict the angular distribution as a function of surface temperature. The theory developed here provides a good description of the quantum dominated low energy and low surface temperature measurement of the scattering of Ne, Ar, and Kr on a Cu(111) surface.^{4,5}

The quantum theory of scattering from surfaces has been developed extensively by Manson using a distorted wave theory.⁶ Here, we provide a different route, based on the semiclassical perturbation (SCP) theory of Hubbard and Miller.⁷ This enables us to provide an analytic theory, which includes realistic force fields. The SCP theory provides a direct route between the spectral density and the observed measured

low surface temperature angular distribution. For the sake of brevity, we will make a few inessential simplifying assumptions. We limit the dynamics to two degrees of freedom for the scattered particle (with mass M), the vertical z and horizontal x directions. The particle phonon interaction will be limited to the vertical motion since it is the major route for the dissipation of energy from the particle to the surface.³

The starting point is a Hamiltonian (operators are denoted with a caret) with linear coupling to the phonon bath,³ whose (mass weighted) phase space variables are $x_j, p_j; j = 1, \dots, N$ and whose frequencies are ω_j :

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_z^2}{2M} + \bar{V}(\hat{z}) + \bar{V}'(\hat{z})h(\hat{x}) + \sum_{j=1}^N \left[\frac{\hat{p}_j^2}{2m_j} + \frac{m_j \omega_j^2}{2} \left(\hat{x}_j - \frac{\sqrt{M} c_j}{\omega_j^2} \bar{V}'(\hat{z}) \right)^2 \right]. \quad (1)$$

$\bar{V}(z)$ is the vertical interaction potential, $h(x)$ is the corrugation function with period l taken to be: $h(x) = h \sin(2\pi x/l)$ and h is the corrugation height. The prime in Eq. (1) denotes the derivative with respect to the argument. The c_j 's are the coupling coefficients of the vertical motion to the bath modes. The continuum limit is obtained by defining the spectral density

$$J_z(\omega) = \frac{\pi}{2} \sum_{j=1}^N \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j), \quad (2)$$

which is a central object of this Communication. In contrast to the surface phonon density of states,⁶ the spectral density depends on the specific coupling of the scattered particle to the surface through the coupling coefficients c_j .

The SCP theory is based on the observation that typically the corrugation and the coupling to the phonon bath is weak. The zero-th order motion is that of a conserved horizontal momentum, independent oscillator motion, and the vertical motion is governed by the potential $\bar{V}(z)$. When choosing the Morse potential form, with well depth V_0 and stiffness

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parameter α , the vertical motion is known analytically, thus allowing a fully analytical theory of the scattering. Due to the periodicity of the surface, one may show from the SCP theory that (as expected) the difference between the final p_{x_f} and initial p_{x_i} horizontal momentum is quantized according to Bragg's law $p_{x_f} = p_{x_i} + \frac{2\pi\hbar n}{l}$ with n taking integer values, whose range is limited by energy conservation. The S matrix element for scattering from the elastic ($n = 0$) channel and initial harmonic bath oscillator state defined by the vector $\mathbf{n} = (n_1, \dots, n_N)$, which gives the occupation number in each mode, to the n th Bragg peak and \mathbf{n}_f final bath state is given by the expression⁷

$$S_{n,\mathbf{n}_f;0,\mathbf{n}_i} = \frac{1}{2\pi} \int_0^{2\pi} dq_x \frac{1}{(2\pi)^N} \times \int_0^{2\pi} d\mathbf{q} e^{-iq_x} e^{-i\Delta\mathbf{n}\cdot\mathbf{q}} e^{2i\eta(q_x, \mathbf{q})}. \quad (3)$$

Here, $q_x = 2\pi x/l$ and \mathbf{q} denotes the vector of harmonic bath angle variables defined by the relationship $x_j = \sqrt{\frac{2\hbar(n_j + \frac{1}{2})}{\omega_j}} \cos(q_j + \omega_j t)$. The phase shift $2\eta(q_x, \mathbf{q})$ is determined by the unperturbed classical dynamics and has the form

$$2\eta(q_x, \mathbf{q}) = 2\eta_0 - \hbar A(\omega_x) \sin q_x - F(\omega_j; c_j) + \sum_{j=1}^N \bar{A}_j(n_j) \cos q_{jz}, \quad (4)$$

where η_0 is a phase shift due to the unperturbed potential $\bar{V}(z)$; the coefficient

$$A(\omega) = \frac{1}{\hbar} \int_{-\infty}^{+\infty} dt \bar{V}'(z_t) \cos \omega t, \quad (5)$$

where z_t denotes the unperturbed motion in the vertical direction; the frequency $\omega_x = 2\pi p_{x_i}/(Ml)$; $F(\omega_j; c_j)$ is a constant phase due to the bath and the phase amplitude for the j th oscillator is

$$\bar{A}_j(n_j) = \sqrt{M} c_j \sqrt{\frac{2\hbar(n_j + \frac{1}{2})}{\omega_j}} A(\omega_j). \quad (6)$$

One may now readily carry out the integrations in Eq. (3) to find that the S -matrix element squared is a product of Bessel functions⁷

$$|S_{n,\mathbf{n}_f;0,\mathbf{n}_i}|^2 = J_n^2(\hbar A(\omega_x)) \prod_{j=1}^N J_{n_{j_f}-n_{j_i}}^2(\bar{A}_j(n_{j_{if}})), \quad (7)$$

with $\omega_x = 2\pi p_{x_i}/(Ml)$. In principle, the S matrix must be symmetrical with respect to inversion of the initial and final bath states. In Eq. (7), we have imposed this symmetry by replacing the argument of $\bar{A}_j(n_j)$ with its symmetrized version $\bar{A}_j(n_{j_{if}} = \frac{n_{j_i} + n_{j_f}}{2})$. This symmetrization also guarantees unitarity when expanding to order $\bar{A}_j(n_{j_{if}})^2$. Energy conservation implies

$$p_{z_f}^2 = |p_{z_i}|^2 \left[\frac{\cos(|\theta_i| + 2\theta(n))}{\cos|\theta_i| \cos^2\theta(n)} - \frac{2M\hbar\Delta\mathbf{n} \cdot \boldsymbol{\omega}}{|p_{z_i}|^2} \right] \equiv |p_{z_i}|^2 \zeta^2, \quad (8)$$

where the vector $\boldsymbol{\omega} = (\omega_1, \dots, \omega_N)$; $\Delta\mathbf{n} = \mathbf{n}_f - \mathbf{n}_i$; $\tan\theta(n) = \frac{2\pi\hbar n}{|p_{z_i}|}$, and $\tan\theta_i = p_{x_i}/p_{z_i}$. For an initial choice of the bath oscillator states, the final momentum and angular distributions are then by definition:

$$P(p_{x_f}, p_{z_f}; \mathbf{n}_i) = \sum_n \sum_{\mathbf{n}_f} |S_{n,\mathbf{n}_f;0,\mathbf{n}_i}|^2 \delta(p_{z_f} - |p_{z_i}| \zeta) \times \delta\left(p_{x_f} - p_{x_i} - \frac{2\pi\hbar n}{l}\right), \quad (9)$$

$$P(\theta; \mathbf{n}_i) = \int_{-\infty}^{\infty} dp_{x_f} \int_0^{\infty} dp_{z_f} \delta\left(\theta - \tan^{-1} \frac{p_{x_f}}{p_{z_f}}\right) P(p_{x_f}, p_{z_f}; \mathbf{n}_i) = \sum_n \sum_{\mathbf{n}_f} |S_{n,\mathbf{n}_f;0,\mathbf{n}_i}|^2 \frac{2E_i \sin^2(|\theta_i| + \theta(n))}{\hbar |\sin^2\theta \tan\theta| \cos^2\theta(n)} \delta(\Delta\mathbf{n} \cdot \boldsymbol{\omega} - \bar{\Omega}). \quad (10)$$

Here, $E_i = (p_{x_i}^2 + p_{z_i}^2)/(2M)$ and the “phonon frequency” $\bar{\Omega}$ is defined as

$$\bar{\Omega}(\theta, \theta_i, n) = \frac{E_i}{\hbar} \left[1 - \frac{\sin^2(|\theta_i| + \theta(n))}{\cos^2\theta(n) \sin^2\theta} \right]. \quad (11)$$

The surface is in thermal equilibrium prior to the collision. The final angular distribution is obtained by thermal averaging over the initial phonon states. We first consider zero-phonon transitions ($n_{j_f} - n_{j_i} = 0$). Within the SCP theory, the phase amplitudes $\bar{A}_j(n_{j_{if}})$ are small, due to the weak coupling to the phonon bath, so that we approximate the Bessel function $J_0^2(x) \simeq \exp(-x^2/2)$. Within the same order, we approximate the thermal average $\langle \exp(-\gamma_j(n_j + 1/2)) \rangle \simeq \exp(-\gamma_j \langle n_j + 1/2 \rangle)$ with $\langle n_j + \frac{1}{2} \rangle = \frac{1}{2} \coth(\frac{\hbar\beta\omega_j}{2})$. One then readily finds that the zero phonon contribution to the angular distribution is (the arguments of $\bar{\Omega}$ are henceforth suppressed)

$$\langle P(\theta; \Delta n=0) \rangle \simeq \sum_n J_n^2(\hbar A(\omega_x)) \frac{2E_i \sin^2(|\theta_i| + \theta(n))}{\hbar |\sin^2\theta \tan\theta| \cos^2\theta(n)} \times \delta(\bar{\Omega}) \exp(-2W), \quad (12)$$

and we identify the Debye-Waller factor⁸ as

$$2W \equiv \sum_{j=1}^N \frac{M\hbar c_j^2 A^2(\omega_j)}{2\omega_j} \coth\left(\frac{\hbar\beta\omega_j}{2}\right) = \frac{M}{2\pi\hbar} \int_{-\infty}^{+\infty} dt'' \int_{-\infty}^{+\infty} dt' \bar{V}'(z_{t'}) \bar{V}'(z_{t''}) \times \int_0^{\infty} d\omega J_z(\omega) \coth\left(\frac{\hbar\beta\omega}{2}\right) \cos(\omega(t' - t'')). \quad (13)$$

In the last line, we used the definition of the spectral density (Eq. (2)). The zero phonon contribution is thus a series of delta function peaks whose intensity is temperature dependent, via the Debye-Waller factor. The expression (13) has been derived for neutron scattering through surfaces⁹ and for surface scattering.⁸ What is new here is the derivation of the same result, based on the SCP theory of Hubbard and Miller.⁷

This derivation is valid also for very low temperatures, justifying its usage by Andersson *et al.*¹⁰

The one phonon contribution follows similar lines. Any oscillator is allowed to add or lose one phonon, so that $n_{j_f} - n_{j_i} = \pm 1$. Keeping terms only up to order $\bar{A}_j(n_{j_{if}})^2$, we approximate $J_1^2(x)/J_0^2(x) \simeq x^2/4$ to find that

$$\begin{aligned} & \langle P(\theta; \Delta n = 1) \rangle + \langle P(\theta; \Delta n = -1) \rangle \\ & \simeq \sum_n J_n^2(hA(\omega_x)) \exp(-2W) J_z(|\bar{\Omega}|) A(\bar{\Omega})^2 \\ & \cdot \frac{ME_i \cos \theta \sin^2(|\theta_i| + \theta(n))}{\pi |\sin^3 \theta| \cos^2 \theta(n)} \\ & \times \left[\coth \left(\frac{\hbar \beta |\bar{\Omega}|}{2} \right) + H(\bar{\Omega}) - H(-\bar{\Omega}) \right], \quad (14) \end{aligned}$$

where $H(x)$ is the unit step function. This result, central to this Communication, shows explicitly that in the continuum bath limit, the contribution from one phonon transitions to the angular distribution, is a smooth background contribution, proportional to the spectral density. This smooth background has contributions from all Bragg peaks since the effective phonon frequency $\bar{\Omega}$ depends on the Bragg diffraction number n . When the temperature is sufficiently low, the angular distribution is composed of “delta” function peaks at the Bragg angles (Eq. (12)) and a broad background (Eq. (14)) that reflects the spectral density of the surface phonons. When $T = 0$ K, the phonon frequency $\bar{\Omega}$ must be positive as the oscillators can only gain a phonon. This causes a decrease in the vertical energy so that the dominant background scattering for $n = 0$ will appear only for angles greater than specular. This is indeed observed in the measured low temperature angular distributions.⁴

For the two phonon contribution, one has to consider five possibilities: a single mode absorbing two phonons; two different modes, each absorbing a single phonon; two different modes, one absorbing and one emitting a phonon; two different modes, each emitting a phonon; one mode, emitting two phonons. The thermal averaging follows the same reasoning as before. We approximate $J_2^2(x)/J_0^2(x) \simeq x^4/64$ and ignore contributions of the form $\sum_j g_j c_j^4$ since they vanish in the continuum limit. One then finds that the two phonon contribution to the angular distribution is

$$\begin{aligned} \langle P(\theta; 2) \rangle &= \sum_n J_n^2(hA(\omega_x)) \exp(-2W) \\ &\times \frac{\hbar M^2 E_i \sin^2(|\theta_i| + \theta(n))}{4\pi^2 |\sin^2 \theta \tan \theta| \cos^2 \theta(n)} [S_2 + S_0 + S_{-2}], \quad (15) \end{aligned}$$

$$\begin{aligned} S_2 &= H(\bar{\Omega}) \int_0^{\bar{\Omega}} d\omega J_z(\omega) J_z(\bar{\Omega} - \omega) A^2(\omega) A^2(\bar{\Omega} - \omega) \\ &\cdot \left[\coth \left(\frac{\hbar \beta \omega}{2} \right) + 1 \right] \left[\coth \left(\frac{\hbar \beta (\bar{\Omega} - \omega)}{2} \right) + 1 \right], \quad (16) \end{aligned}$$

TABLE I. Parameters used for Ne, Ar, and Kr scattered on a Cu(111) surface.

	$\alpha \cdot l$	V_0 [meV]	$\bar{\gamma}$ [dimensionless]	h [a.u.]
Kr	4.2	134.0	0.1205	2.82×10^{-3}
Ar	3.3	70.0	0.05782	1.98×10^{-3}
Ne	3.0	31.6	0.01234	1.10×10^{-3}

$$\begin{aligned} S_0 &= \int_0^\infty d\omega J_z(\omega) J_z(\bar{\Omega} + \omega) A^2(\omega) A^2(\bar{\Omega} + \omega) H(\bar{\Omega} + \omega) \\ &\cdot \left[\coth \left(\frac{\hbar \beta \omega}{2} \right) - 1 \right] \left[\coth \left(\frac{\hbar \beta (\bar{\Omega} + \omega)}{2} \right) + 1 \right], \quad (17) \end{aligned}$$

$$\begin{aligned} S_{-2} &= H(-\bar{\Omega}) \int_0^{|\bar{\Omega}|} d\omega J_z(\omega) J_z(|\bar{\Omega}| - \omega) A^2(\omega) A^2(|\bar{\Omega}| - \omega) \\ &\cdot \left[\coth \left(\frac{\hbar \beta \omega}{2} \right) - 1 \right] \left[\coth \left(\frac{\hbar \beta (|\bar{\Omega}| - \omega)}{2} \right) - 1 \right]. \quad (18) \end{aligned}$$

In the following, we use the SCP theory to analyze the measured low temperature angular distribution of Ne, Ar, and Kr scattered from a Cu(111) surface.^{4,5} The vertical potential is taken to be a Morse potential. The well depths are taken from recent *ab initio* computations.¹¹ The lattice length is 3.61 Å.¹² The “corrugation height” is determined from the measured ratio of the $n = 0$ to $n = -1$ Bragg peaks, which determines the magnitude of the phase amplitude $hA(\omega_x)$ appearing in the argument of the respective Bessel functions. The spectral density is chosen to be Ohmic (for a theoretical justification see Ref. 13) with an exponential cutoff $J(\omega) = \gamma \omega \exp(-\omega/\omega_c)$. The cutoff frequency is considered here to be a property of the surface and is the same for all the atoms. The friction coefficient γ is fit separately for each atom. The theory thus involves only two parameters for each atom (γ, α) and the cutoff frequency ω_c , common to all cases. The parameters are given in Table I ($\bar{\gamma} = M^2 \omega_0^3 \gamma$ where $\omega_0^2 = 2V_0 \alpha^2/M$). The results for the temperature dependence of the Debye-Waller factor are shown in Fig. 1. These fits are substantially improved as compared to those given previously in Refs. 5 and 10. The Morse potential provides an adequate description and there is no need to use more elaborate functional forms.⁵

The Debye-Waller factors leave very little freedom in the fitting procedure, except for the cutoff frequency $\hbar \omega_c$ chosen to be 6 meV. The results for Ne, Ar, and Kr are shown in Fig. 2 (the plots were scaled by 0.02412 and 0.1150 for Kr, 0.01441 and 0.06670 for Ar, 0.01410 and 0.01896 for Ne, for the low and high temperatures, respectively, so as to fit the maxima of the reported experimental unnormalized distributions). In all cases, the elastic peaks were Gaussian broadened ($\Delta\theta = 0.4^\circ$), to agree with the experimental broadening, as also detailed in Ref. 5. For Ne scattering at 10 K, the two phonon contribution is negligible. This provides an objective criterion

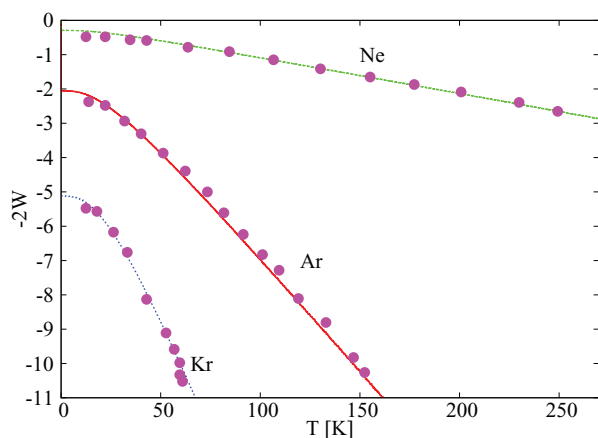


FIG. 1. The SCP fit to the measured temperature dependence of the Debye-Waller factor for Ne, Ar, and Kr scattered from Cu(111). The solid circles represent the experimental results of Ref. 4 while solid lines are the fits obtained with Eq. (13) and the parameters given in Table I.

for determining that at this temperature, only single phonon scattering takes place. The fit to experiment indicates that the chosen Ohmic spectral density provides a good description for the coupling of the Ne atom to the surface phonons. The minuscule Bragg peak at $n = -1$, which cannot be seen on the scale of the figure, implies that the corrugation is very weak. It is remarkable that at the elevated temperature of 300 K,

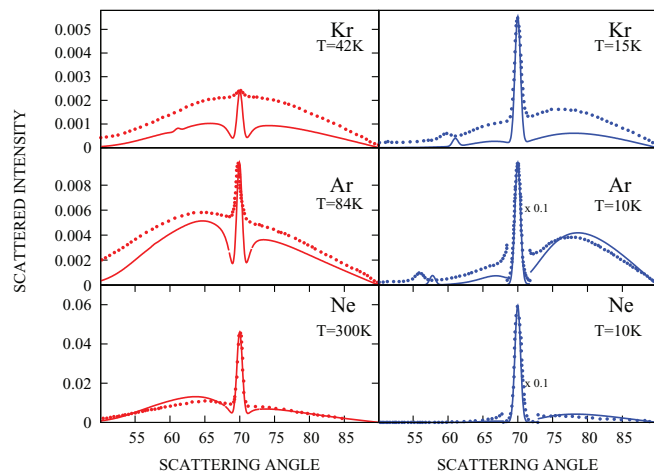


FIG. 2. Comparison of the SCP theoretically generated (solid lines) angular distributions using Eqs. (12)–(18) and the experimental measurements (dotted lines)⁵ for low (right panel) and high (left panel) surface temperatures. The low temperature experimental and theoretical specular peaks for Ne and Ar are multiplied by 0.1 to fit them into the scale of the plots.

the complete angular distribution is well described by adding only the two phonon contribution. This is a reflection of the weak friction coefficient, which effectively disallows higher order phonon transitions. Even at this elevated surface temperature, the angular distribution is dominated by the elastic quantum diffraction peak. The results for Ar are similar in quality, though here the reduced friction coefficient is larger so that at the higher temperature three or more phonons may be excited. Finally, for Kr even at a surface temperature of 15 K, multiphonon transitions cannot be neglected and the theoretical distribution remains somewhat lower than the measured one. To correctly describe the high temperature Kr results one may derive a classical bath “infinite phonon” limit of the present theory.¹⁴

In summary, we demonstrated by application of the semi-classical perturbation theory to experimentally measured data that the low temperature scattering of atoms from surfaces provides direct information on the spectral density of the phonons. The same theory can now be used to describe many other surface phenomena, such as quantum energy transfer to the surface, quantum sticking probabilities, diffusion, selective adsorption resonances, and more. It may be generalized to include the full three dimensions of the scattered particle as well as coupling to horizontal phonons.

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