

Thermal Roughness of a Close-Packed Metal Surface: Pt(001)

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An x-ray scattering study of the morphology of the Pt(001) surface reveals that below 1820 K it is atomically smooth on length scales exceeding 5000 Å. However, above 1820 K the Pt(001) surface is rough. Specifically, the scattering near the specular condition is diffuse, and may be modeled using a height-height correlation function which diverges logarithmically at large distances. Our data suggest that the average separation between thermally generated steps is many lattice constants.

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The equilibrium shape of a crystal of fixed volume is determined by the minimum of its surface free energy. In many cases, the equilibrium shape involves facets. For example, the (001) and (111) orientations of face-centered-cubic (fcc) metals are believed to be faceted at room temperature [1]. However, at high temperatures, there may also occur orientations which appear rounded, reminiscent of a liquid droplet [1]. Crystal surfaces which correspond to rounded orientations are expected to support capillary modes in a manner similar to liquid surfaces [2,3]. In both cases, liquid and solid, a surface with capillary modes is rough. A number of studies have characterized the roughness of vicinal, fcc (001) surfaces, including the (113), (115), and (117) orientations [4-6]. In these instances, the surface roughness arises microscopically from the meandering of preexisting steps. The roughening behavior of fcc (110) surfaces [7-10] may also be visualized in this way [7,11,12]. In this paper, we present an x-ray scattering study of the Pt(001) surface at 1850 K under ultrahigh vacuum conditions. Because of the fine reciprocal space resolution possible with x-ray scattering techniques, we have been able to investigate the surface morphology on length scales up to several thousand angstroms. Our results indicate that a clean, *close-packed* metal surface—in this case Pt(001)—may roughen below the bulk melting temperature ($T_m = 2045$ K for Pt). In addition, they yield new insight into the microscopic structure of a rough metal surface. Specifically, we find that the average separation between thermally generated steps on the rough Pt(001) surface is many lattice constants.

Measurements were performed on beam line X22C at the National Synchrotron Light Source. Our procedures yielded a clean surface which remained clean at elevated temperatures for extended periods [13]. The sample was a Pt disk with a mosaic of 0.01° full width at half maximum (FWHM) and surface orientation such that the macroscopic surface normal was inclined at an angle of 0.06° away from the crystallographic (001) direction to-

wards (010). The sample was aligned so that the (002) Bragg reflection lay within the scattering plane. X rays were incident at an angle θ_1 with respect to the surface, with a collimation in the scattering plane of $\Delta\theta_1 = 0.01^\circ$ FWHM and a wave number $k = 4.08 \text{ \AA}^{-1}$. The detector was set at an angle θ_2 with respect to the surface, so that x rays scattered through an angle $2\theta = \theta_1 + \theta_2$ were collected within an angular acceptance of $\Delta\theta_2 = 0.1^\circ$ FWHM, as set by slits. The angular acceptance normal to the scattering plane was $\Delta\psi_2 = 0.8^\circ$ FWHM. In the following, we employ a coordinate system for the wave-vector transfer (\mathbf{Q}) in which Q_z is along the surface normal, Q_x is parallel to the surface within the scattering plane, and Q_y is the out-of-plane wave-vector transfer. With this spectrometer configuration, the reciprocal space resolution along Q_x is $\Delta Q_x \cong k \sin(2\theta/2) \Delta\theta_2 = Q_z \Delta\theta_2/2$; along Q_y , the resolution width is $\Delta Q_y = k \Delta\psi_2$.

The defining characteristic of a rough surface is succinctly expressed in the behavior of the height-height correlation function, $g(\mathbf{r})$. If $z(\mathbf{r})$ is the surface height at a given location (\mathbf{r}) within the plane of the interface, then $g(\mathbf{r})$ is defined to be $g(\mathbf{r}) = \langle [z(\mathbf{r}) - z(\mathbf{0})]^2 \rangle$. The surface is smooth if $g(\mathbf{r})$ tends to a finite limit as r grows; if $g(\mathbf{r})$ diverges with r , the surface is rough [12]. Measurements of the x-ray scattering cross section ($d\sigma/d\Omega$) can elucidate the behavior of $g(\mathbf{r})$. Assuming that $z(\mathbf{r}) - z(\mathbf{0})$ is a Gaussian random variable, it may be shown that the cross section for scattering from a surface near the condition for x-ray specular reflection and at small Q_z is related to $g(\mathbf{r})$ via

$$d\sigma/d\Omega = (A\rho_0^2 r_0^2 |F(\mathbf{Q})|^2 / Q_z^2) \times \int d^2r \exp[i\mathbf{Q}_t \cdot \mathbf{r} - Q_z^2 g(\mathbf{r})/2], \quad (1)$$

where $\mathbf{Q}_t = (Q_x, Q_y, 0)$, $\mathbf{r} = (x, y, 0)$, A is the illuminated area, $F(\mathbf{Q})$ is the atomic form factor, ρ_0 is the number density, and r_0 is the Thomson radius of the electron [14]. It may be seen from Eq. (1) that for a smooth surface there is a delta-function contribution to $d\sigma/d\Omega$.

This is the specular component. For a rough surface $d\sigma/d\Omega$ is entirely diffuse—there is no truly specular reflection.

To predict the diffuse intensity (I_s) corresponding to Eq. (1), $d\sigma/d\Omega$ must be integrated over the detector acceptance and multiplied by the incident flux (I_0/A_0). For the present measurements, the acceptance perpendicular to the scattering plane is sufficiently coarse that the entire spectrum of scattering in Q_y is collected. In addition, the acceptance within the scattering plane is quite well described by a Gaussian [as shown by the solid line in Fig. 1(b)]. It follows that I_s may be expressed as an integral involving $g(x,0)$:

$$\frac{I_s}{I_0} = R_F \left(\frac{\sin\theta}{\sin\theta_1} \right) \frac{\Delta Q_x}{2\pi} \int dx e^{iQ_x x} e^{-x^2 \Delta Q_z^2 / 4\pi} e^{-Q_z^2 g(x,0)/2}, \quad (2)$$

where R_F is the reflectivity of the corresponding ideally smooth surface. Equation (2) may be applied to a crystalline surface by replacing Q_z^2 with an appropriate periodic function of Q_z .

Below 1820 K, the Pt(001) surface exhibits an ordered, hexagonal reconstruction. Above 1820 K, however, the surface is unreconstructed and the surface shows the symmetry of the bulk (001) planes [13]. The Q_x dependence of the scattered x-ray intensity at fixed $Q_z = c^* = \pi/d$, where d is the interlayer spacing along the surface normal direction, is illustrated in the high-temperature phase at 1850 K in Fig. 1(a) and in the hexagonally reconstructed

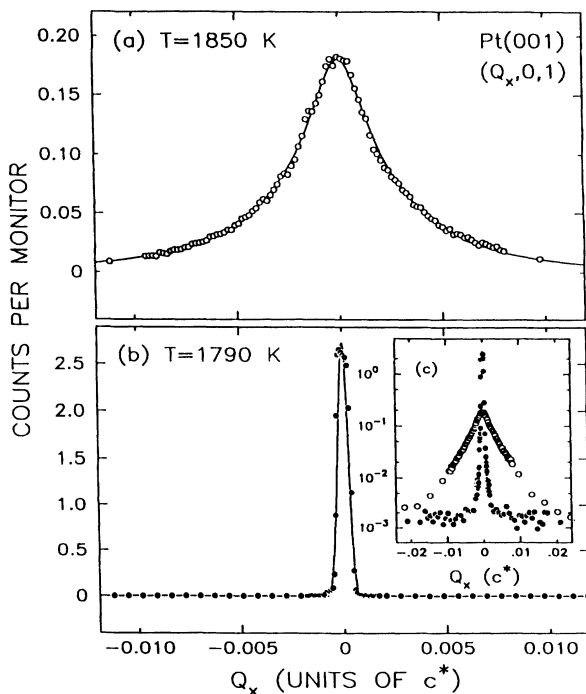


FIG. 1. Q_x scans obtained at $Q_z = c^*$ for (a) 1850 K and (b) 1790 K. (a) and (b) are replotted on a logarithmic intensity scale in (c).

phase at 1790 K in Fig. 1(b). There is a dramatic difference between the two profiles. At the lower temperature, there is a narrow peak, the width of which (0.001 \AA^{-1} FWHM) corresponds to the spectrometer resolution, indicating that the surface is atomically smooth on length scales exceeding 5000 \AA . In contrast, at 1850 K, the profile is diffuse. The difference between the two profiles appears equally striking using a logarithmic intensity scale, as in the inset of Fig. 1. From our preceding discussion, we infer that above 1850 K the surface is rough. The absence of significant diffuse surface scattering at 1790 K suggests that consideration of surface phonons is not required for an understanding of the scattering line shape. Further measurements have revealed that the observed line shape is independent of azimuth about the (001) direction, ruling out the possibility that the misalignment of the surface from the (001) direction (miscut) introduces additional complexities, such as faceting, on length scales less than 2000 \AA [7,9]. For a miscut of 0.06° , one expects an average step separation of 2000 \AA on Pt(001).

The intensity of the scattering versus Q_x for different values of Q_z is shown in Fig. 2. The data were obtained at 1850 K in the rough phase and are plotted using a logarithmic ordinate. In each scan, the location of a peak at $Q_x = 0$ coincides with the condition for x-ray specular reflection. On this basis, we identify those peaks with scattering from the crystal surface. Evidently, the profiles obtained in the range $0.5 < Q_z/c^* < 1.5$ display significant diffuse intensity away from the specular condition ($Q_x = 0$). Analysis of the profiles about $Q_x = 0$ (see below) leads to a detailed description of the surface morphology. In this regard, we note that there is an increase in the apparent width of the surface scattering with Q_z , which is the result of the coarser reciprocal space resolution at larger Q_z . For $Q_z < 0.5c^*$ the macroscopic surface finish affects the scattering profile and prevents quantitative analysis. The scattering far removed from the specular condition in Fig. 2 is thermal diffuse scattering from the bulk. The thermal diffuse intensity shows an overall increase with increasing wave vector. Moreover, it increases near bulk Bragg reflections, where intensity maxima located symmetrically about $Q_x = 0$ are apparent (Fig. 2). Such peaks occur if the energies of transverse phonons are smaller than those of longitudinal phonons of the same wave vector [15].

For a liquid surface, roughness results from a thermal population of propagating capillary waves [16]. A rough, solid surface also supports capillary modes. In this case, the modes in question are expected to be diffusive [3]. However, because our experiments probe the instantaneous surface configuration, we are unable to characterize the dynamics of the rough Pt(001) surface. For a liquid surface Sanyal *et al.* [2] give

$$g(\mathbf{r}) = (k_B T / \pi \alpha) (\ln Q_u r + 0.57 - \ln 2), \quad (3)$$

where Q_u is a maximum wave vector for capillary modes,

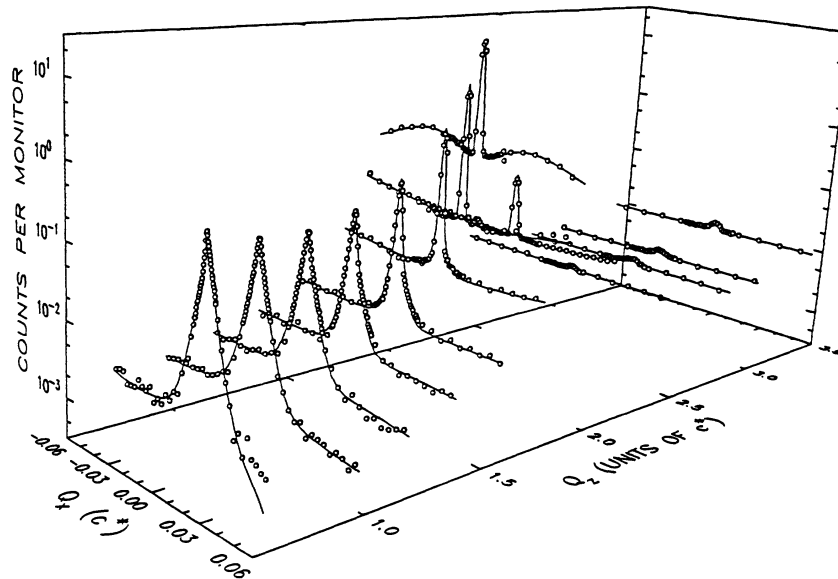


FIG. 2. Measured scattering function of Pt(001) at 1850 K as a function of Q_x and Q_z .

and α is the surface tension. However, Eq. (3) is appropriate only for $r \gg Q_u^{-1}$ [17]. To quantify the surface morphology in the rough phase of the Pt(001) surface, we have chosen a specific form for the height-height correlation function $g(r)$ and have performed least mean-squares fits of the resultant model profiles [Eq. (2) evaluated numerically] to the data of Fig. 2. We have found it necessary to approximate $g(r)$ in a manner which preserves both the large and small distance limits [$g(0) = 0$]. Specifically, we have taken [18]

$$g(r) = (k_B T / 2\pi\bar{\alpha}) \ln(Q_u^2 r^2 + 1). \tag{4}$$

To account for the difference between the height-height correlation function of a liquid surface and that of a rough solid surface, we have replaced the surface tension (α) by the surface stiffness ($\bar{\alpha}$) [3].

The predicted line shape [Eq. (2) combined with Eq. (4)] depends on three parameters: $\eta = k_B T Q_z^2 / 2\pi\bar{\alpha}$, Q_u , and ΔQ_x . To compare the observed scattering to the model, we employed the following fitting procedures. ΔQ_x was determined by fits of a Gaussian line shape to data obtained in the smooth phase of the Pt(001) surface at 1790 K. The values of ΔQ_x so obtained were then fixed for calculations of the model line shape in the rough phase. Since Q_u is expected to be independent of Q_z , its value was determined by fitting the profile obtained at $Q_z = c^*$ (Fig. 1). For fits to all of the other experimental profiles, Q_u was held fixed at that value. The parameters which were varied were the roughness exponent (η), the integrated intensity of the surface scattering, and the thermal diffuse intensity. As may be seen in Fig. 2, the model line shape (solid line) provides a good description of the data throughout the range of Q_z and Q_x studied.

The best-fit values of the roughness exponent are shown in Fig. 3(a). Its Q_z dependence appears periodic, with η being approximately zero at $Q_z = 2c^*$ and $4c^*$ and

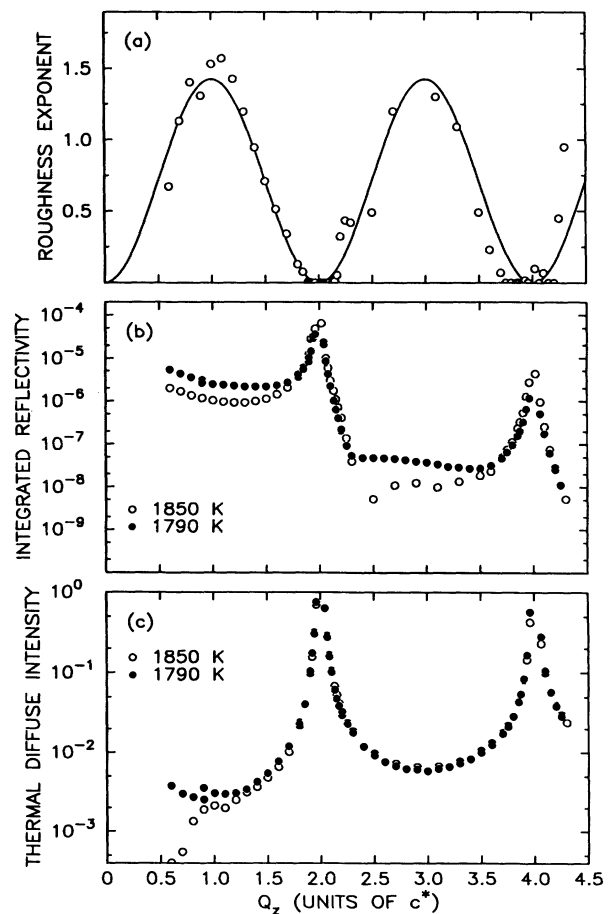


FIG. 3. (a) Roughness exponent at 1850 K vs Q_z . (b) Integrated reflectivity of Pt(001) vs Q_z at 1790 K (solid circles) and 1850 K (open circles). (c) Thermal diffuse scattering at $Q_x = 0$ vs Q_z at 1790 K (solid circles) and 1850 K (open circles).

taking its largest values at $Q_z = c^*$ and $3c^*$. For the longest length scales, Conrad *et al.* [5] have shown that $\eta = k_B T (Q_z \text{ mod } \pi/d)^2 / 2\pi\bar{a}$. However, they also show that, at shorter distances, this expression must be modified [5]. Villain, Gempel, and Lapujoulade [4] have suggested that a form which is satisfactory over a wide range of length scales is $\eta = k_B T (1 - \cos Q_z d) / 4\pi\bar{a}d^2$. The solid line in Fig. 3(a) illustrates the best fit of this expression, from which we deduce $k_B T / 2\pi\bar{a}d^2 = 1.4$. There is a theoretical criterion [3] for the existence of a rough, solid surface: If the surface stiffness (\bar{a}) is less than $k_B T / 2\pi d^2$, then a rough surface may exist. If, on the other hand, $\bar{a} > k_B T / 2\pi d^2$, the supposedly rough surface is unstable and is replaced by a smooth surface. This condition may be rewritten as $k_B T / 2\pi\bar{a}d^2 > 1$, which is consistent with our fitted value.

A surprising result is that the value of Q_u is rather small— $Q_u = 0.006 \pm 0.001 \text{ \AA}^{-1}$ —implying that the logarithmic divergence of $g(r)$ displayed in Eq. (4) occurs for length scales greater than $Q_u^{-1} \cong 170 \text{ \AA}$. This stands in contrast to what is observed in simulations of rough solid surfaces using lattice models and in exact calculations, where logarithmic behavior is obtained whenever r exceeds the nearest-neighbor separation [3,19]. For liquid surfaces, Q_u^{-1} is expected to be of the order of $(k_B T / \alpha)^{1/2}$, which is also of the order of an intermolecular distance [16] [$(k_B T / \bar{a})^{1/2} \cong 6 \text{ \AA}$ for $Q_z = c^*$ and $\eta = 1.4$]. We may speculate that for the Pt(001) surface the value of Q_u^{-1} represents the separation of thermally generated steps. To our knowledge, there are currently no realistic calculations of the step densities expected for close-packed metal surfaces at high temperatures. However, we further speculate that the discrepancy with theory originates with long-ranged elastic interactions between steps. Elastic interactions are absent both in simple lattice models and for liquid surfaces, but are important for understanding the phase behavior of Pt and Au surfaces [13,15,20].

Figures 3(b) and 3(c) show the integrated intensity of the surface scattering (reflectivity) and the thermal diffuse scattering intensity at $Q_x = 0$, respectively, versus Q_z , for both the rough (1850 K) and the smooth (1790 K) phases. The thermal-diffuse-scattering intensities at the two temperatures are indistinguishable. The specular reflectivities in the rough and reconstructed phases of Pt(001) [Fig. 3(b)] are comparable to those of the disordered and reconstructed phases, respectively, of Au(001) [20]. In this regard, it is noteworthy that the disordered phase of the Au(001) surface does not appear to be rough

[20]. This seems particularly intriguing in view of the otherwise similar structures and phase behaviors of Pt(001) and Au(001) [13].

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