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Statistical properties of local work function on stepped surfaces

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Local electrostatic potential of dipole rows along the steps on a solid surface, generated by the Smoluchowski electron smoothing effect, exhibits large fluctuations in the directions parallel to the surface. We analyze statistical properties of this potential for the distances above the surface, ranging from several atomic units to the macroscopic lengths. Complete probability density of the potential is evaluated for regularly spaced steps and for randomly distributed steps. Moreover, correlation function of the potential, probed at two different points, is analyzed in terms of the probability density for the terrace lengths between two consecutive steps. Several models for the latter quantity have been tested, giving rise to various forms of the distance dependence of the potential fluctuation above the surface. [S0163-1829(99)04927-9]

I. INTRODUCTION

It is well documented that atomic-scale defects on surfaces, such as steps, kinks, adatoms, vacancies, etc., have dramatic influence on many surface processes, including particle and light scattering, sticking, chemical reactions, heterogeneous catalysis, or film growth.[1,2] Structural and electronic properties of such defects have been studied by numerous surface analytical techniques, involving various ranges of sensitivity to distances across the surface and perpendicular to it. Ordinary work function measurements[3,4] provide information on averages of surface electronic properties on a macroscopic scale, covering large surface areas and large distances from the surface. Already at this level, the influence of surface defects shows up as a linear change of the work function with increasing density of defects. For example, the work function of a metal surface may be lowered by as much as several eV due to adsorption of alkali-metal atoms at submonolayer coverages.[3] On the other hand, the work function of vicinal surfaces may be lowered by as much as several tenths of eV with increasing step density, when compared to the work function of the corresponding low-index plane.[4]

These facts indicate the existence of strong *localized* dipoles at the surface, associated with defects, which counteract the normal surface dipole potential. In the case of steps, the microscopic mechanism responsible for the localized dipoles is the Smoluchowski electron smoothing effect.[5] The electron distribution at the surface does not follow the sharp step geometry but rather flows from the upper to the lower terrace, giving rise to a local dipole moment μ_a per step atom which is oriented along the outwards surface normal. Therefore, when a number of defects is present on a surface, their electrostatic potential, at a distance close to the surface, will fluctuate in directions across the surface, depending on the geometric distribution of defects. Variation of this potential is sometimes called the *local work function*,[6] and has been the subject of many studies over the past decade, because it generates local fields on the surface responsible for increased chemical reactivity of surfaces with defects. For example, photoemission of adsorbed xenon[7] (PAX) has been used to show the lowering of the local work function at steps on a metal surface by as much as $\sim 1\,\text{eV}$ compared to the adjacent terrace sites. A similar effect has been recently confirmed by using scanning tunneling microscopy (STM).[8] While techniques such as PAX and STM provide information on the local work function with atomic resolution, they are limited to rather short distances from the surface, of the order of several atomic units. On the other hand, low-energy ion surface scattering[9,10] (ISS) has been shown to be capable of probing distances of around 10 atomic units or more above the surface. This feature has been used recently to study the local work function on surfaces with adsorbed alkali-metal atoms. Moreover, preliminary results[11] show that ISS may also be quite sensitive to the presence of surface steps.

In the present article, we develop a theoretical model for describing statistical properties of the local work function above a surface with steps, for a range of distances from several atomic units to macroscopic distances. The random variable is the position in the plane parallel to the surface, chosen to probe the local work function, while the distance from the surface is considered a deterministic variable. In doing so, we are able to introduce into the theory the information on the statistics of step arrangements across the surface, which may be available from diffraction studies of stepped surfaces,[12] from reflection electron microscopy (REM),[13] or from direct measurements of the terrace lengths by STM.[8] The development of the present theory is somewhat similar to our previous work on statistical properties of the electrostatic potential of the adsorbed atoms in the context of ISS.[10] In modeling stepped surfaces, we actually work with a one-dimensional model of surface defects, where the steps are represented by a system of straight-line dipole rows, parallel to each other, with a certain one-dimensional distribution of their positions on the surface, in the direction perpendicular to steps. In particular, we focus first on the two extreme cases of a perfectly regular and a completely random distribution of steps, but also bring into the theory the temperature effects by using a model for thermal fluctuation of step positions on a surface. We present data on statistical properties of the electrostatic potential of the step dipole rows, probed at a randomly chosen point above the surface (static regime), as well as the correlation function of the potential probed at two different points above the surface (dynamic regime). This latter regime is relevant for studying stepped surfaces by an ISS technique, especially under grazing scattering conditions, which we plan to complete soon. Nevertheless, we believe that the results of the present paper will be useful in many other applications, including (static) PAX and STM techniques, as well as (dynamic) studies of secondary electron and ion emission properties of stepped surfaces, or examination of the role of random surface fields in *time-of-flight* (TOF) measurements.[14]

The paper is organized as follows. In Sec. II, we evaluate the exact and complete probability density for the electrostatic potential at a given distance from the surface for both the regular and the random steps models. Next, the correlation function of the potential is derived in Sec. III for a general step distribution and evaluated for certain special cases, describing thermal fluctuations of step positions. In Sec. IV, we study the effects of the step dipole component parallel to the surface on the probability density and the correlation function of the potential. Our concluding remarks are given in Sec. V. Atomic units are used throughout the paper, unless otherwise explicitly indicated.

II. REGULAR AND RANDOM STEPS

We place the x,y plane in the surface, take all the steps parallel to the y axis, and direct the z axis along the outwards surface normal. The positions of N steps, distributed over the macroscopic length L of the surface along the x axis, are described by an N-body joint-probability density $F_N(x_1,x_2,\dots,x_N)$, which normalizes to unity. For a homogeneous system of steps, the reduced one-body distribution function, which normalizes to N, is given by $f_1(x)=\rho$, where $\rho=N/L=1/\langle l\rangle$ is the linear density (along x axis) of steps. Note that $\langle l\rangle$, the average separation between two adjacent steps, or the average length of terraces between the steps, is usually readily available from experiments and is $\sim 10^2$.

Assuming that all the steps are monatomic, with a step height d, we denote by μ the linear density (along y axis) of the dipole moment of the dipole row, associated with each step. If the lattice spacing along the step is a, then $\mu=\mu_a/a$, where the dipole moment per step atom μ_a may be estimated as qd, based on microscopic measurements or calculations[15] of the charge redistribution q per step atom due to the Smoluchowski smoothing effect. We assume in this and the following section that the dipole moment is predominantly perpendicular to the surface, $\mu=\mu_\perp>0$, so that the potential due to a single step[8] is $V(x,z)=2\mu_\perp z/(x^2+z^2)$ for distances $z\gg d$. The total potential, probed at the point (x,z), is the sum $U(x,z)=\Sigma_n V(x-x_n,z)$. Therefore, the average potential, for any distribution of steps, reduces to

$$\langle U\rangle=\int dx\, f_1(x)V(x,z)=2\pi\rho\mu_\perp, \tag{1}$$

which is independent of z and equals precisely the magnitude of the macroscopic work function lowering $|\Delta\phi|$ (typical values are $|\Delta\phi|\sim 10^{-2}$).

For the case of regularly spaced steps, such as a vicinal surface at low temperatures, the total potential is a periodic function of x with the period $\langle l\rangle$, for which the Fourier cosine series can be summed, as follows:

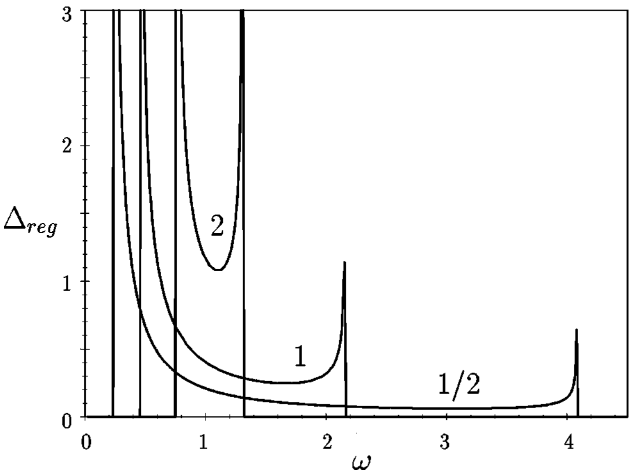

FIG. 1. Probability density of the potential for the regular steps model, versus reduced potential ω, shown for several values of the reduced distance, $\zeta=1/2,1$, and 2.

$$U_{period}(x,z)=\langle U\rangle\frac{\sinh\left(\frac{2\pi}{\langle l\rangle}z\right)}{\cosh\left(\frac{2\pi}{\langle l\rangle}z\right)-\cos\left(\frac{2\pi}{\langle l\rangle}x\right)}. \tag{2}$$

Since this periodic potential is probed at a randomly chosen coordinate x, its probability density may be expressed as

$$D_{reg}(U;z)=\frac{1}{\langle l\rangle}\int_{-\langle l\rangle/2}^{\langle l\rangle/2}dx\,\delta[U-U_{period}(x;z)]. \tag{3}$$

On introducing reduced quantities $\zeta=2\pi\rho z$, $\omega=U/\langle U\rangle$ and $\Delta(\omega;\zeta)=\langle U\rangle D(U;z)$, one obtains

$$\Delta_{reg}(\omega;\zeta)=\frac{1}{\pi\omega}(2\omega\coth\zeta-\omega^2-1)^{-1/2}\times H(2\omega\coth\zeta-\omega^2-1), \tag{4}$$

where H stands for the Heaviside step function. $\Delta_{reg}(\omega;\zeta)$ is shown in Fig. 1 for several values of the reduced distance ζ. The vertical lines represent the lowest, $\tanh(\zeta/2)$, and the highest, $\coth(\zeta/2)$, value of the reduced potential ω for a given distance ζ, where $\Delta_{reg}(\omega;\zeta)$ exhibits integrable discontinuities.

In general, the probability density of the total potential is the ensemble average $D(U;z)=\langle\delta[U-\Sigma_n V(x-x_n,z)]\rangle$, taken with respect to the N-body probability density F_N. When the probability of a step occurring anywhere on the surface of the length L is unaffected by the presence of other steps, the N-body probability density is simply $F_N=L^{-N}$. We call this model of noninteracting steps the *random model*, and obtain the probability density of the total potential, probed at the distance z, in the form

$$D_{rand}(U;z)=\int_{-\infty}^{\infty}\frac{dt}{2\pi}\exp\left\{itU-\rho\int_{-\infty}^{\infty}dx\times\{1-\exp[-itV(x,z)]\}\right\}, \tag{5}$$

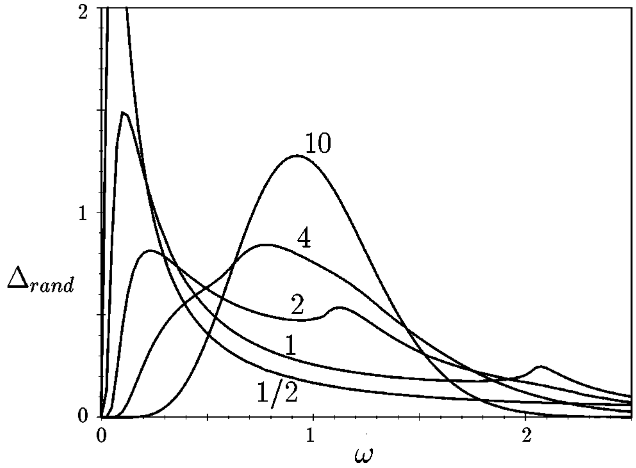

FIG. 2. Probability density of the potential for the random steps model, versus reduced potential ω, shown for several values of the reduced distance, $\zeta=1/2$, 1, 2, 4, and 10.

which, in terms of reduced quantities, is

$$\Delta_{rand}(\omega;\zeta)=\frac{\zeta}{\pi}\int_0^\infty d\tau\cos\{\zeta\tau[\omega-J_0(\tau)\cos\tau -J_1(\tau)\sin\tau]\}\exp\{-\zeta\tau[J_0(\tau)\sin\tau -J_1(\tau)\cos\tau]\}, \tag{6}$$

where $J_{0,1}$ stand for the ordinary Bessel functions. $\Delta_{rand}(\omega;\zeta)$ has been evaluated for several values of the reduced distance ζ, and the results are shown in Fig. 2. Note that, for sufficiently large distances ζ, this function becomes a Gaussian, peaked at $\omega=1$. For intermediate values of ζ, $\Delta_{rand}(\omega;\zeta)$ broadens and becomes very skewed and, interestingly, develops peaks reminiscent of the edge discontinuities of $\Delta_{reg}(\omega;\zeta)$. For lower values of ζ, the bulk of the function $\Delta_{rand}(\omega;\zeta)$ looks very much like its regular counterpart in Fig. 1.

It should be noted that the first moment of $\Delta(\omega;\zeta)$, for both types of step distributions, is $\langle\omega\rangle=1$. In order to give the idea of the degree of fluctuation of the potential at the distance z, we evaluate the variance $\langle\langle U^2(z)\rangle\rangle=\langle U^2(z)\rangle-\langle U\rangle^2$. Introducing the reduced width $W(\zeta)=\langle\omega^2\rangle-1=\langle\langle U^2(z)\rangle\rangle/\langle U\rangle^2$, we find

$$W_{reg}(\zeta)=\coth\zeta-1,\quad W_{rand}=1/\zeta. \tag{7}$$

The fluctuation of the potential above the stepped surface is exponentially suppressed with increasing ζ for regular steps, but has a very long range of order $\sqrt{W}\sim\zeta^{-1/2}$, far above the surface with random steps. At short distances, $\zeta\ll 1$, the potential fluctuation, for both types of step distributions, has the magnitude $\sqrt{\langle\langle U^2(z)\rangle\rangle}=\langle U\rangle/\sqrt{\zeta}$, which may be of the order of 0.1 or 1 eV.

III. CORRELATION FUNCTION OF POTENTIAL

While the results of the preceding section refer to static properties of the local work function, we wish to explore here the dynamic regime of probing the total potential of the stepped surfaces at two points (x_1,z_1) and (x_2,z_2), where $z_1>0$ and $z_2>0$. To this end, we derive the correlation function of the total potential in terms of the reduced two-body distribution function $f_2(x_1,x_2)$ [which normalizes to $N(N-1)$], as follows

$$C(x_2-x_1;z_1,z_2)\equiv\langle U(x_1;z_1)U(x_2;z_2)\rangle-\langle U\rangle^2 =\int dx_1'\int dx_2'\,V(x_1-x_1',z_1)V(x_2-x_2',z_2)\times[\rho\delta(x_2'-x_1')+f_2(x_2'-x_1')-\rho^2]. \tag{8}$$

We have used here the fact that $f_1(x)=\rho$ and $f_2(x_1,x_2)=f_2(x_1-x_2)=f_2(x_2-x_1)$ for a translationally invariant system of steps.

It is instructive, at this point, to make contact with the probability density $P(l)$ of the terrace lengths l between two consecutive steps. This function is, in principle, directly available from STM or REM measurements,[8,13] or may be related to the diffraction data from stepped surfaces.[12] Moreover, significant theoretical advances have been achieved in modeling $P(l)$ to reflect the thermodynamics of stepped surfaces.[12,16] Note that $P(l)$ is normalized to unity, with the mean $\langle l\rangle$ and the variance $\sigma^2=\langle l^2\rangle-\langle l\rangle^2$. Taking the limit $L\to\infty$, together with $N\to\infty$, and noting that $f_2(x)\,dx$ represents the probability of having a step in dx at x, given a step at the origin, we may write

$$f_2(x)=\rho\sum_{n=1}^{\infty}\int_0^\infty dl_1\,P(l_1)\cdots\int_0^\infty dl_n\,P(l_n)\times\left[\delta\left(x-\sum_{j=1}^{n}l_j\right)+\delta\left(x+\sum_{j=1}^{n}l_j\right)\right]. \tag{9}$$

Going to the Fourier transform with respect to the x coordinate, the correlation function becomes

$$C(x_2-x_2;z_1,z_2)=\frac{\langle U\rangle^2}{2\pi\rho}\int_{-\infty}^{\infty}dk\,S(k)\exp[ik(x_2-x_1)-|k|(z_1+z_2)], \tag{10}$$

where the *structure factor* of the stepped surface is given by

$$S(k)=1+\frac{Q(k-i\eta)}{1-Q(k-i\eta)}+\frac{Q(-k-i\eta)}{1-Q(-k-i\eta)}-2\pi\rho\delta(k), \tag{11}$$

with

$$Q(k)=\int_0^\infty dl\,P(l)\exp(-ikl), \tag{12}$$

and $\eta\to 0^+$ to ensure the convergence of the k integration. Note that, $Q(0)=1$, $Q'(0)=-i\langle l\rangle$, and $Q''(0)=-\langle l^2\rangle$.

Let us define the reduced correlation function $\Gamma(\chi,\zeta)=C(x_2-x_1;z_1,z_2)/\langle U\rangle^2$, where $\chi=\pi\rho(x_2-x_1)$ and $\zeta=\pi\rho(z_1+z_2)$. Static fluctuation of the potential, probed at the point $(x_1,z_1)=(x_2,z_2)$, is then obtained from the width function $W(\zeta)=\Gamma(\chi=0,\zeta)$. For example, random steps are described by the exponential $P(l)=\langle l\rangle^{-1}\exp(-l/\langle l\rangle)$ with $S(k)=1$, so that

$$\Gamma_{rand}(\chi,\zeta)=\frac{\zeta}{\chi^2+\zeta^2}. \tag{13}$$

Regular steps are described by $P(l)=\delta(l-\langle l\rangle)$, so that

$$\Gamma_{reg}(\chi,\zeta)=\frac{\sinh\zeta\cosh\zeta}{\sin^2\chi+\sinh^2\zeta}-1. \tag{14}$$

In order to go beyond these two extreme cases of the step distribution, one has to consider the influence of step interactions on the function $P(l)$. To this end, we may initially neglect all energetic interactions between the steps, except the hard-core repulsion, which prevents steps from crossing each other (no overhangs). It has been shown that, in this case, the universal (temperature-independent) two-body distribution function is[16]

$$f_2(x)=\rho^2\left\{1-\left[\frac{\sin(\pi\rho x)}{\pi\rho x}\right]^2\right\}. \tag{15}$$

Then, the core-repulsion form of the correlation function reads

$$\Gamma_{core}(\chi,\zeta)=\frac{\zeta^2-\chi^2}{2(\zeta^2+\chi^2)^2}\left\{1-e^{-2\zeta}\left[\cos(2\chi)-\frac{2\zeta\chi}{\zeta^2-\chi^2}\sin(2\chi)\right]\right\}, \tag{16}$$

with the corresponding static-regime ($\chi=0$) width

$$W_{core}(\zeta)=(1-e^{-2\zeta})/(2\zeta^2). \tag{17}$$

It should be noted that these results should hold for temperatures up to moderately high values.[16] Thus, the fluctuation of the potential, in the core-repulsion model goes as $\sqrt{\langle\langle U^2(z)\rangle\rangle}=\langle U\rangle/\sqrt{\zeta}$ for $\zeta\ll 1$, as it did for regular and random steps, but has the form $\sqrt{\langle\langle U^2(z)\rangle\rangle}=\mu_\perp/(\sqrt{2}z)$ for large distances z, which is independent of the step density ρ.

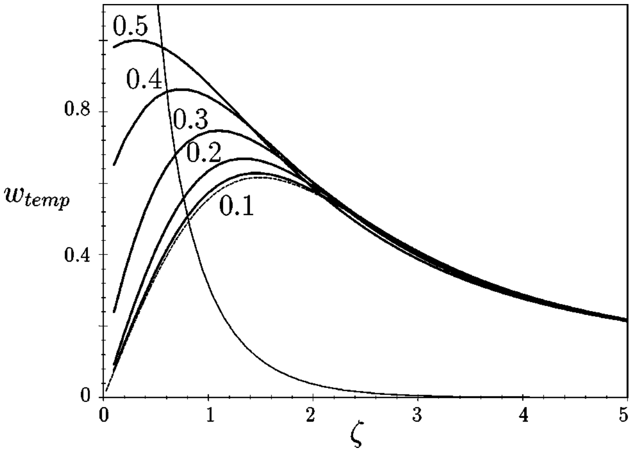

FIG. 3. Temperature-dependent width function of the potential for the Gaussian model vs reduced distance ζ. Thick solid curves are evaluated with $\sigma/\langle l\rangle=0.1$, 0.2, 0.3, 0.4, and 0.5. Dashed line represents analytical limit when $\sigma\rightarrow 0$, while the thin solid line shows the width function of regular steps.

In order to describe the step wandering due to energetic interactions at finite temperatures, one has to focus on the dependence of the potential correlation function on the (temperature-dependent) variance σ^2 of the function $P(l)$. It has been found recently, by using REM measurements,[13] that σ may be a significant fraction of the average terrace length $\langle l\rangle$. We first note that, in general, one has $S(k)\rightarrow\sigma^2/\langle l\rangle^2$ when $k\rightarrow 0$ for any model for $P(l)$, which enables one to express the leading term in the large ζ asymptotics of the potential correlation function as

$$\Gamma_{asymp}(\chi,\zeta)=\frac{\sigma^2}{\langle l\rangle^2}\Gamma_{rand}(\chi,\zeta),\quad \zeta\gg 1. \tag{18}$$

Therefore, the potential fluctuation in the static regime may be of order of $\sqrt{\langle\langle U^2(z)\rangle\rangle}=\langle U\rangle\sigma/\sqrt{2\pi z\langle l\rangle}$ at finite temperatures and large distances, $z\gg\langle l\rangle/(2\pi)$. Note that $\sigma=0$ for regular steps, and $\sigma=\langle l\rangle$ for random steps.

A useful model for $P(l)$, which was successfully used to fit experimental data,[13,16] is the Gaussian $P(l)=(\sqrt{2\pi}\sigma)^{-1}\exp[-(l-\langle l\rangle)^2/(2\sigma^2)]$. Assuming that the deviation of the step distribution from the regular one, with increasing temperature T, is dominated by energetic step interactions, it is instructive to estimate the change of the potential correlation function $\Gamma_{Gauss}(\chi,\zeta)$ in the Gaussian model with increasing σ as a qualitative measure of the temperature effects. It has been shown[13] that σ may be considered proportional to $\langle l\rangle\sqrt{T}$. Noting that the structure factor in Gaussian model reads as

$$S(k)=\frac{\sinh(k^2\sigma^2/2)}{\cosh(k^2\sigma^2/2)-\cos(k\langle l\rangle)}-2\pi\rho\delta(k), \tag{19}$$

we have evaluated the width function $W_{Gauss}(\zeta)=\Gamma_{Gauss}(\chi=0,\zeta)$, and plotted in Fig. 3 the quantity

$$w_{temp}(\zeta)=\frac{\langle l\rangle^2}{\sigma^2}[W_{Gauss}(\zeta)-W_{reg}(\zeta)], \tag{20}$$

in order to stress the role of increasing temperature in deviation from the regular step model, which becomes important for the potential fluctuation at large distances ζ, beyond the exponential termination of the regular step model. The results for $w_{temp}(\zeta)$ are shown in Fig. 3 by thick solid lines for several values of the ratio $\sigma/\langle l\rangle$, while the thin solid line represents $W_{reg}(\zeta)$. Note that, in the limit of very low tem-

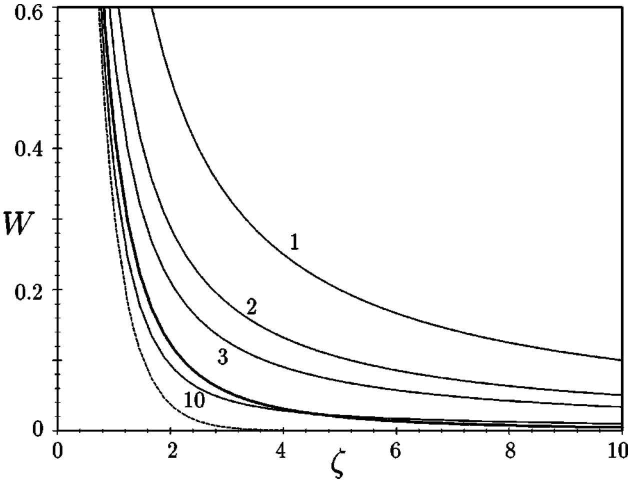

FIG. 4. The width function of the potential versus reduced distance ζ. Thin solid curves represent the gamma model, with the values of the parameter $m=1$ (random steps), 2, 3, and 10. Thick solid curve represents the core-repulsion model, while the dashed line represents the regular steps model.

peratures ($\sigma \ll \langle l \rangle$), one may obtain an analytical estimate for $w_{temp}(\zeta)$ in terms of the digamma function ψ, as follows

$$w_{low\ \ temp}(\zeta)=\frac{2}{\pi}\,\mathrm{Im}\left[\psi'\left(-\frac{i\zeta}{\pi}\right)-\frac{i\zeta}{2\pi}\psi''\left(-\frac{i\zeta}{\pi}\right)\right], \quad (21)$$

which is shown in Fig. 3 by the dashed line. It should be noted that all curves for $w_{temp}(\zeta)$ in Fig. 3 decay as ζ^{-1} for large ζ, in accordance with the general result for the asymptotic limit of the potential fluctuation.

Another view at the step wandering due to energetic interactions is provided by means of the gamma distribution[12] for the terrace lengths, viz.,

$$P_m(l)=\frac{m^m}{\Gamma(m)}\,\frac{l^{m-1}}{\langle l\rangle^m}\exp\left(-m\frac{l}{\langle l\rangle}\right). \quad (22)$$

Note that $m=1$ corresponds to random steps and increasing values of m describe narrowing of the function $P_m(l)$ due to step-step interactions, such that, $\sigma^2=\langle l\rangle^2/m$. When $m\to\infty$, $P_m(l)$ approaches the regular steps model. In a sense, $P_m(l)$ describes, with increasing m, deviation from the random steps model due to energetic interactions at high temperatures. Noting that the two-body distribution, for the gamma model, reads

$$f_2(x)=\rho^2\,\mathrm{Re}\sum_{j=0}^{m-1}\exp\{i2\pi j/m-m\rho|x|$$
$$\times[1-\exp(i2\pi j/m)]\}, \quad (23)$$

the potential correlation function and the corresponding width function $W_m(\zeta)$ may be evaluated in an analytical (though cumbersome) form. The results for $W_m(\zeta)$ are presented by thin solid lines in Fig. 4 for several values of the parameter m of the gamma model for $P_m(l)$. For the sake of comparison, the core-repulsion result $W_{core}(\zeta)$ is shown in Fig. 4 by a thick solid line, together with the regular steps result $W_{reg}(\zeta)$, which is displayed by the dashed line. One may note that the gamma model gives the longest range for the potential fluctuation, which goes as $\sim(m\zeta)^{-1/2}$ for large ζ, even for large values of the parameter m.

IV. DIPOLE COMPONENT PARALLEL TO SURFACE

In this section we generalize the results of the previous two sections to the case when the dipole moment μ of the steps has components $\mu_\perp$ and $\mu_\parallel$, which are, respectively, perpendicular and parallel to the surface. Then, the potential due to a single step[15] is $V(x,z;s)=2(\mu_\perp z+s\mu_\parallel x)/(x^2+z^2)$, where $s=1$ $(s=-1)$ for a step up (down) along the x axis. Note that, in principle, s is a new random variable for each step. In order to study statistical properties of the total potential $U(x,z)=\Sigma_n V(x-x_n,z;s_n)$, we need generalized N-body joint probability density of steps $G_N(x_1,\ldots,x_N;s_1,\ldots,s_N)$. We assume a factorization of G_N, such that the probability of a step n going up or down is independent of its position x_n and the probabilities of the other $N-1$ steps going up or down, viz.,

$$G_N(x_1,\ldots,x_N;s_1,\ldots,s_N)=F_N(x_1,\ldots,x_N)\prod_{n=1}^{N}h(s_n). \quad (24)$$

Here, F_N is the joint probability density of step positions from Sec. II, while the probability density $h(s)$, which we define by

$$h(s)=u\,\delta(s-1)+(1-u)\,\delta(s+1), \quad (25)$$

assumes that each step has a probability u $(0\leqslant u\leqslant 1)$ of going up. For example, ascending (descending) staircase is obtained with $u=1$ $(u=0)$. Note that $h(s)$ is normalized to unity, with the mean $\langle s\rangle=2u-1$ and the variance $\langle\langle s^2\rangle\rangle\equiv\langle s^2\rangle-\langle s\rangle^2=4u(1-u)$. Of course, the average potential depends only on the perpendicular dipole component,

$$\langle U\rangle=\int dx\int ds\, f_1(x)h(s)V(x,z;s)=2\pi\rho\mu_\perp. \quad (26)$$

The case of regularly spaced steps generalizes to a regular staircase ($u=0$ or $u=1$), for which the periodic potential reads as

$$U_{period}(x,z)=2\pi\rho\,\frac{\mu_\perp\sinh\zeta+\mu_\parallel\sin\chi}{\cosh\zeta-\cos\chi}, \quad (27)$$

where $\zeta=2\pi\rho z$ and $\chi=2\pi\rho x$, with $\mu_\parallel>0$ (<0) for ascending (descending) staircase. It is convenient to introduce

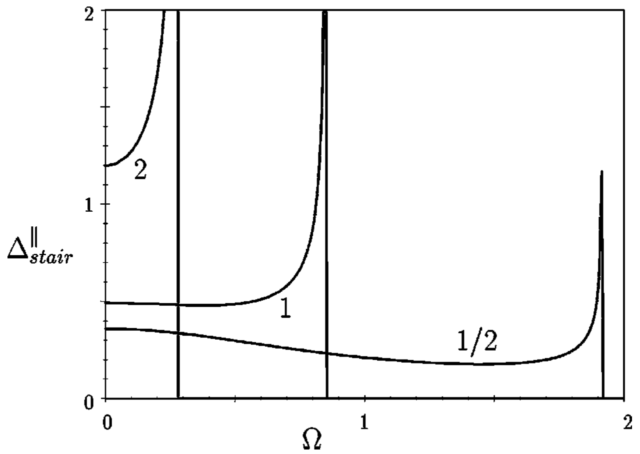

FIG. 5. Probability density of the potential for the regular staircase model, with the dipole moment parallel to the surface, vs reduced potential Ω, shown for several values of the reduced distance, $\zeta = 1/2$, 1, and 2.

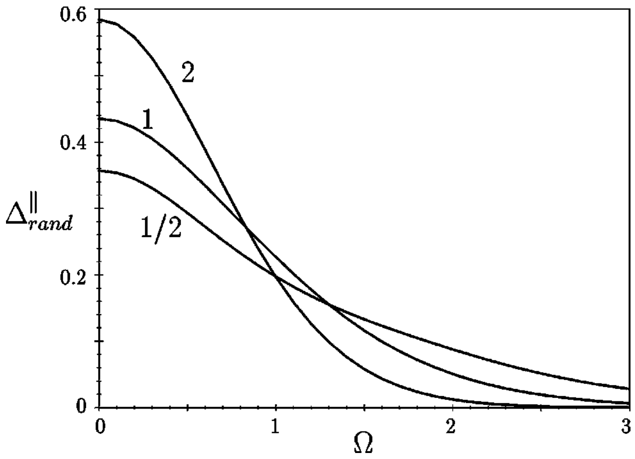

FIG. 6. Probability density of the potential for the random steps model, with the dipole moment parallel to the surface, vs reduced potential Ω, shown for several values of the reduced distance, $\zeta = 1/2$, 1, and 2.

the angle α $(-\pi/2 \leqslant \alpha \leqslant \pi/2)$, such that $\mu_\perp = \mu \cos\alpha$ and $\mu_\parallel = \mu \sin\alpha$, with $\mu = \sqrt{\mu_\perp^2 + \mu_\parallel^2}$ being the total dipole moment. Probability density $D_{stair}(U;z)$ of the potential is obtained in analogy to (3), and the reduced density $\Delta_{stair}(\Omega;\zeta) = 2\pi\rho\mu D_{stair}(U;z)$ reads as

$$\Delta_{stair}(\Omega;\zeta) = \frac{1}{\pi}\,\frac{\Omega\cos\alpha + \coth\zeta\sin^2\alpha}{\Omega^2 + \sin^2\alpha}(2\Omega\coth\zeta\cos\alpha - \Omega^2 - 1 + \coth^2\zeta\sin^2\alpha)^{-1/2}, \tag{28}$$

for $\coth\zeta\cos\alpha - \operatorname{cosech}\zeta < \Omega < \coth\zeta\cos\alpha + \operatorname{cosech}\zeta$, where the reduced potential is defined by $\Omega = U/(2\pi\rho\mu)$. Note that, with the present normalization, $\langle\Omega\rangle = \cos\alpha$. It may be interesting to consider a special case of $\alpha = \pm\pi/2$, such that $\mu_\perp = 0$ and $\mu = |\mu_\parallel|$, which is perhaps not physically feasible, but demonstrates how far above the surface the probability density of the potential extends when the dipole rows have only the component parallel to the surface. Of course, in such a case, $\Delta_{stair}(\Omega;\zeta) \equiv \Delta^{\parallel}_{stair}(\Omega;\zeta)$ is an even function of the reduced potential $\Omega = U/(2\pi\rho|\mu_\parallel|)$, which is shown in Fig. 5 for several values of the reduced distance ζ and for a range of positive values of Ω, where discontinuities are apparent.

Probability density of the potential for the case of random distribution of step positions (in the sense of Sec. II) is given by

$$D_{rand}(U;z) = \int_{-\infty}^{\infty}\frac{dt}{2\pi}\exp\left\{itU - \rho\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}ds\,h(s)\times\{1 - \exp[-itV(x,z;s)]\}\right\}, \tag{29}$$

which turns out to be independent of the probability u for a step going up. For the special case of $\alpha = \pm\pi/2$, we obtain the reduced density $\Delta^{\parallel}_{rand}(\Omega;\zeta) = 2\pi\rho|\mu_\parallel|D_{rand}(U;z)$ as follows:

$$\Delta^{\parallel}_{\mathrm{rand}}(\omega;\zeta) = \frac{\zeta}{\pi}\int_0^{\infty}d\tau\cos(\zeta\tau\Omega)\times\exp\left\{-\tfrac{1}{2}\zeta\tau^2\left[2J_0(\tau) + \pi J_1(\tau)H_0(\tau) - \pi J_0(\tau)H_1(\tau) - \frac{2}{\tau}J_1(\tau)\right]\right\}, \tag{30}$$

where $H_{0,1}$ are Struve functions and $\Omega = U/(2\pi\rho|\mu_\parallel|)$. $\Delta^{\parallel}_{rand}(\Omega;\zeta)$ is again an even function of Ω, which is shown in Fig. 6 for several values of the reduced distance ζ and for a range of positive values of Ω. Contrary to the case of step dipole moments perpendicular to the surface in Sec. II, no apparent signatures of the discontinuities of $\Delta^{\parallel}_{stair}(\Omega;\zeta)$ are present in $\Delta^{\parallel}_{rand}(\Omega;\zeta)$.

Finally, the generalization of the potential correlation function to the case when the dipole moment μ has both components $\mu_\perp$ and $\mu_\parallel$ reads as

$$C(x_2 - x_1; z_1, z_2) = \int dx_1'\int dx_2'\int ds_1\int ds_2\,V(x_1 - x_1', z_1; s_1)V(x_2 - x_2', z_2; s_2)\times\{\rho\delta(x_2' - x_1')h(s_1)\delta(s_2 - s_1) + [f_2(x_2' - x_1') - \rho^2]h(s_1)h(s_2)\}. \tag{31}$$

With the normalization $\Gamma(\chi,\zeta)=(2\pi\rho\mu)^{-2}C(x_2-x_1;z_1,z_2)$, we find

$$\Gamma(\chi,\zeta)=(\cos^2\alpha+\langle s\rangle^2\sin^2\alpha)\Gamma_0(\chi,\zeta)+\langle\langle s^2\rangle\rangle\sin^2\alpha\frac{\zeta}{\zeta^2+\chi^2}, \tag{32}$$

where $\chi=\pi\rho(x_2-x_1)$, $\zeta=\pi\rho(z_1+z_2)$, and $\Gamma_0(\chi,\zeta)$ stands for any of the reduced correlation functions from Sec. III. It is seen that any randomness in the steps going up or down $(0<u<1)$ will yield a long-ranged $(\sim\zeta^{-1/2})$ contribution to the fluctuation of the potential due to the parallel dipole component.

V. CONCLUDING REMARKS

We have analyzed statistical properties of the local electrostatic potential of dipole rows along the steps on a solid surface, which are generated by the Smoluchowski electron smoothing effect. The potential is probed at a randomly chosen point in directions parallel to the surface, with the distances z from the surface ranging from several atomic units to infinity. The complete probability density for observing the potential U at a distance z has been obtained for the model of regularly spaced steps and the model of random steps, when the step dipole moment is predominantly perpendicular to the surface. In the latter case, the probability density shows dramatic and intriguing changes, when the distance z ranges between the values smaller than the average step separation $\langle l\rangle$ and the values bigger than $\langle l\rangle$. In either case, significant dispersion of the potential is observed, as a function of the distance z.

For the regime when the potential is probed at two different points, we have derived a general expression for the correlation function of the potential in terms of the two-body distribution function of the step positions. The latter quantity is expressed in terms of the probability density $P(l)$ for the terrace lengths l between two consecutive steps. In doing so, we were able to test several models for $P(l)$, describing the step wandering due to step-step interactions at finite temperatures. In particular, we have found that the fluctuation of the potential decays exponentially above the surface with regularly spaced steps, but has a long range of the order of $\sigma z^{-1/2}$, whenever the variance σ^2 of $P(l)$ is finite. In a specific case of steps with the core repulsion only, the fluctuation of the potential goes as z^{-1} at large distances, and is independent of the step density $\langle l\rangle^{-1}$. When the distances are short, $z\ll\langle l\rangle$, the potential fluctuation seems to go as $z^{-1/2}$ for all considered models of the step positions.

Finally, we have studied the effects of the step dipole component parallel to the surface by introducing the probability density for the discrete random variable s $(=1$ or $-1)$, describing the steps up or down. The probability density of the total potential for a regular staircase has been obtained in a general form. Results were presented for a special case when the step dipole moment has only the parallel component for the staircase model and the random model. In both models, the probability density is an even function of the potential, which possesses integrable discontinuities in the staircase model, but is a smooth bell-shaped curve in the random model, for a range of distances above the surface. Lastly, the potential correlation function has been derived in a general form, involving the mean $\langle s\rangle$ and the variance $\langle\langle s^2\rangle\rangle$ of the variable s.

A further development of the present theory should deal with a more realistic model for step shapes than the simple straight-line model. In fact, a model Hamiltonian approach has been used[16] to deduce statistical properties of a random function $x=x(y)$, describing the shapes of meandering steps, in the context of step-step interactions. Qualitatively, step meandering effect may be translated into a straight-line step wandering about its mean position along the x axis, which, in turn, can be described by the Gaussian model of Sec. III. However, implementation of the random function $x(y)$ for the step shapes in calculations of the electrostatic potential due to electron smoothing effect requires further refinements at the microscopic level. Namely, one may expect that the electron redistribution along the ''rough'' terrace edges should depend on the local curvature of the steps separating two terraces. If the curvature can be neglected compared to the electron screening length in jellium model, one may assume that the linear density of induced dipoles is constant. Then, the qualitative effect of the meandering step shape amounts to increased dipole density of an effective straight-line step. In any case, quantitative understanding of the role of general step shapes requires further refinements of both the statistical and the microscopic aspects of present theory. In conclusion, we mention that the study of the statistical properties of the electrostatic potential on stepped surfaces cannot be completed before addressing modifications of the image interaction on stepped surfaces.[17]

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