

THE EFFECT OF FINITE RESOLUTION ON THE DETERMINATION OF DIFFUSION COEFFICIENTS BY THE FIELD EMISSION FLUCTUATION METHOD

R. GOMER and A. AUERBACH

*Department of Chemistry and James Franck Institute, University of Chicago,
Chicago, Illinois 60637, USA*

Received 29 October 1985; accepted for publication 6 November 1985

Equations for the current correlation functions for round and rectangular probeholes, taking the finite resolution of the field emission microscope into account, are derived and discussed. The effect of finite resolution introduces a fictitious time shift, so that the argument of the previously derived functions $t/\tau_0 \rightarrow t/\tau_0 + 2(\lambda/r_0)^2$ where λ is the resolution parameter for an assumed Gaussian resolution function and r_0 the radius of a round probehole or the full dimension of a rectangular slit, and τ_0 the previously defined relaxation time. This shift causes the current correlation function to decay more slowly than it would for $\lambda = 0$ and thus makes apparent diffusion coefficients, determined by neglecting non-zero λ smaller than they in fact are. Roughly speaking the effect can also be interpreted as causing an increase in the effective probe dimensions by an additive amount 0.75λ . It is also shown that the importance of resolution decreases linearly with increasing emitter radius.

1. Introduction

The field emission current fluctuation method of determining the diffusion coefficients of adsorbates on metal surfaces [1,2] has recently been extended to the determination of diffusion anisotropy by employing a rectangular probe region [3]. For this case the narrow dimension of the region from which emission is obtained can be comparable to the resolution of the microscope itself and this requires re-examination of the equations previously derived for the current correlation function with neglect of resolution effects [1,2].

2. Analogue of $g_1(t)$

We start by deriving an expression for the simplest case which assumes that a fluctuation in field emission current density in an element of area d^2r at r is given by [1,2]

$$\delta j(\mathbf{r}, t) = (c_1 + 2\pi P c_2) \langle j \rangle \delta n(\mathbf{r}, t), \quad (1)$$

where $\langle j \rangle$ is mean current density, $\delta n(\mathbf{r}, t)$ the density fluctuation at \mathbf{r} at time t and c_1 and c_2 constants related to the Fowler–Nordheim equation, which have been defined previously [1]. P is the adsorbate dipole moment. If resolution effects are neglected, the current fluctuation correlation function for probed area A becomes

$$\begin{aligned} f_i(t) &\equiv \langle \Delta i(0) \Delta i(t) \rangle / \langle i \rangle^2 \\ &= \frac{1}{A^2} \left\langle \int_A d^2x \delta j(\mathbf{x}, 0) \int_A d^2x' \delta j(\mathbf{x}', t) \right\rangle \\ &= \frac{(c_1 + 2\pi P c_2)^2}{A^2} \int_A d^2x \int_A d^2x' \langle \delta n(\mathbf{x}, 0) \delta n(\mathbf{x}', t) \rangle \\ &= \frac{S_0 (c_1 + 2\pi P c_2)^2}{A^2} \int_A d^2x \int_A d^2x' \frac{\exp(-|\mathbf{x} - \mathbf{x}'|^2 / 4Dt)}{4\pi Dt}, \end{aligned} \quad (2)$$

where brackets denote ensemble averages,

$$S_0 = \langle (\delta N)^2 \rangle / A \quad (3)$$

and $\langle (\delta N)^2 \rangle$ is the mean adsorbate number (not density) fluctuation in A . The factor $1/A^2$ in the RHS of eq. (2) arises because $\langle \Delta i(0) \Delta i(t) \rangle$ has been divided by $\langle i \rangle^2 = \langle j \rangle^2 A^2$. If resolution is considered we recognize that the current observed in d^2x at \mathbf{x} comes not only from d^2x but from the entire surface suitably weighted by the normalized resolution function $R^\lambda(\mathbf{x}, \mathbf{r})$, which we assume to be

$$R^\lambda(\mathbf{x}, \mathbf{r}) = (1/\pi\lambda^2) \exp[-(\mathbf{x} - \mathbf{r})^2 / \lambda^2], \quad (4)$$

where λ is a resolution length scale, to be discussed later.

Thus the total current density at \mathbf{x} is

$$j(\mathbf{x}) = \int_{\infty} \frac{d^2\mathbf{r}}{\pi\lambda^2} \exp[-(\mathbf{x} - \mathbf{r})^2 / \lambda^2] j_e(\mathbf{r}), \quad (5)$$

where $j_e(\mathbf{r})$ refers to current density emitted at \mathbf{r} . It also follows from the normalization of R^λ that

$$\langle j(\mathbf{x}) \rangle = \langle j_e(\mathbf{r}) \rangle = \langle j \rangle, \quad (6)$$

so that the average current $\langle i \rangle$ collected from A is

$$\langle i \rangle = A \langle j \rangle, \quad (7)$$

which must be true for spatially invariant $\langle j \rangle$ regardless of resolution. If we now consider the current density fluctuation at \mathbf{x} we find from eqs. (1) and (4)

$$\delta j(\mathbf{x}) = (c_1 + 2\pi P c_2) \langle j \rangle \int_{\infty} \frac{d^2 \mathbf{r}}{\pi \lambda^2} \exp[-(\mathbf{x} - \mathbf{r})^2 / \lambda^2] \delta n(\mathbf{r}). \tag{8}$$

Thus the analogue of (2) becomes

$$f_i(t) = \frac{(c_1 + 2\pi P c_2)^2 S_0}{A^2 \pi^2 \lambda^4} \int_A d^2 \mathbf{x} \int_A d^2 \mathbf{x}' \int_{\infty} d^2 \mathbf{r} \int_{\infty} d^2 \mathbf{r}' \exp[-(\mathbf{x} - \mathbf{r})^2 / \lambda^2] \times \exp[-(\mathbf{x}' - \mathbf{r}') / \lambda^2] \frac{\exp(-|\mathbf{r} - \mathbf{r}'|^2 / 4Dt)}{4\pi Dt}. \tag{9}$$

To proceed we use the identity

$$\int_{-\infty}^{\infty} du \exp[-(x - u)^2 / a^2] \exp[-(y - u)^2 / b^2] = \left(\frac{\pi a^2 b^2}{a^2 + b^2} \right)^{1/2} \exp[-(x - y)^2 / (a^2 + b^2)], \tag{10}$$

written here in one dimension. Since $(\mathbf{r} - \rho)^2 = (r_x - \rho_x)^2 + (r_y - \rho_y)^2$ in two dimensions, eq. (8) for 2D integrals is obtained by removing the square root sign in the pre-exponential term. Integration of eq. (9) over $d^2 \mathbf{r}$ and $d^2 \mathbf{r}'$ then yields

$$f_i(t) = \frac{(c_1 + 2\pi P c_2) S_0}{A^2} \int_A d^2 \mathbf{x} \int_A d^2 \mathbf{x}' \frac{\exp[-|\mathbf{x} - \mathbf{x}'|^2 / (4Dt + 2\lambda^2)]}{\pi(4Dt + 2\lambda^2)}. \tag{11}$$

This is precisely the previous result eq. (2) if $4Dt$ is everywhere replaced by $4Dt + 2\lambda^2$.

The physical significance of this is that finite resolution translates the *current* (not number) correlation function in time as if some diffusion, i.e. smearing out of the original delta functions, which can be thought to represent the fluctuation at $t = 0$ had effectively occurred prior to $t = 0$.

For a round probehole of radius r_0 the normalized time $\tau[1]$

$$\tau = t / \tau_0, \tag{12}$$

with

$$\tau_0 = r_0^2 / 4D, \tag{13}$$

therefore goes over into

$$\tau' = t / \tau_0 + 2 (\lambda / r_0)^2, \tag{14}$$

while for a rectangular probe of dimensions $2a \times 2b$ along the x and y axes

$$\tau'_x = t / \tau_x + \frac{1}{2} (\lambda / a)^2, \quad \tau'_y = t / \tau_y + \frac{1}{2} (\lambda / b)^2 \tag{15}$$

with

$$\tau_x = a^2 / D, \quad \tau_y = b^2 / D. \tag{16}$$

It is trivial to extend the result to anisotropic diffusion for a rectangular probe. One obtains in the approximation of eq. (11)

$$f_i(t) = \frac{(c_1 + 2\pi P c_2)^2 S_0}{A^2} \phi_1(\tau'_y) \phi_1(\tau'_x), \quad (17)$$

with ϕ_1 defined previously [3] and eqs. (16) replaced by

$$\tau_x = a^2/D_{xx}, \quad \tau_y = b^2/D_{yy} \quad (18)$$

for a probe $2a \times 2b$ oriented as before, assuming x and y to be principal axes so that

$$D = \begin{pmatrix} D_{xx} & 0 \\ 0 & D_{yy} \end{pmatrix}. \quad (19)$$

3. General case

Eq. (1) assumes in essence that local work function is determined by local density. More precisely, however, we should write [1,2]

$$\delta_j(\mathbf{r}) = c_1 \delta n(\mathbf{r}) + c_2 \delta \phi(\mathbf{r}), \quad (20)$$

where

$$\delta \phi(\mathbf{r}) = \int_{\infty} d^2y \frac{Pd}{[(\mathbf{r}-\mathbf{y})^2 + d^2]^{3/2}} \delta n(\mathbf{y}). \quad (21)$$

The integrand in eq. (21) represents the contribution to the potential at a distance d above the point \mathbf{r} on the surface from a point dipole at \mathbf{y} on the surface. The dipole is so defined that $2\pi P \langle n \rangle$ rather than $4\pi P \langle n \rangle$ represents the average work function increment of a layer of $\langle n \rangle$ dipoles per unit area. The distance $d = 5 \text{ \AA}$ enters because in field emission the potential at this distance is most relevant [1]. This more exact representation of $\delta \phi$ introduces non-local effects and leads to three functions g_1 , g_2 , g_3 and the form (if resolution is neglected)

$$f_i(t) = (S_0/A^2) [c_1^2 g_1(t) + (2\pi P c_2)^2 g_2(t) + 2c_1 c_2 2\pi P g_3(t)], \quad (22)$$

as shown previously [1]. We must now find the analogue of eq. (22), by writing

$$\begin{aligned} f_i(t) = & \frac{1}{A^2} \left\langle \int_A d^2x \int_A \frac{d^2r}{\pi \lambda^2} \exp[-(x-r)^2/\lambda^2] \right. \\ & \times [c_1 \delta n(\mathbf{r}, 0) + c_2 \delta \phi(\mathbf{r}, 0)] \\ & \left. \times \int_A d^2x' \int_A \frac{d^2r'}{\pi \lambda^2} \exp[-(x'-r')^2/\lambda^2] [c_1 \delta n(\mathbf{r}', t) + c_2 \delta \phi(\mathbf{r}', t)] \right\rangle \quad (23) \end{aligned}$$

and then using eq. (21) in eq. (23). The result will also be of the form (22), with the first term giving $(S_0 c_1 / A^2) g_1(\tau')$ with τ' given by eq. (14) for a circular probe. The integrals occurring in the analogues of g_2 and g_3 are not tractable and would have to be handled numerically. From the expression of $\delta\phi(\mathbf{r})$, eq. (21), one can see that the non-local effects have a length scale of order d , which is much smaller than other lengths in this problem, namely the resolution λ and the radius r_0 . Thus it introduces changes in g_1 which would be similar to the effect of finite resolution λ ; we therefore approximate the integrand in eq. (21) by a Gaussian form which permits the "contraction" described by eq. (10). We write

$$(P/d^2) [(\mathbf{r}-\mathbf{y})^2/d^2 + 1]^{-3/2} \approx (P/d^2) \exp[-(\mathbf{r}-\mathbf{y})^2/2d^2]. \tag{24}$$

The factor 2 in the exponent ensures that the integrals over infinity of both sides of eq. (24) considered as functions of $\rho = \mathbf{r}-\mathbf{y}$ give the same value, $2\pi P$.

The integrations can now be carried out as before and we obtain

$$f_i(t) = \left[\langle (\delta N)^2 \rangle / A^2 \right] \left[c_1^2 g_1(\tau') + (2\pi P c_2)^2 g_1(\tau'') + 2c_1 c_2 2\pi P g_1(\tau''') \right. \\ \left. + O(d/\lambda)^3 + O(d/r_0)^3 \right] \tag{25}$$

for a circular probe of radius r_0 with

$$\tau' = t/\tau_0 + 2(\lambda/r_0)^2, \tag{26a}$$

$$\tau'' = t/\tau_0 + 2(\lambda/r_0)^2 + 4(d/r_0)^2, \tag{26b}$$

$$\tau''' = t/\tau_0 + 2(\lambda/r_0)^2 + 2(d/r_0)^2. \tag{26c}$$

$g_1(\tau')$ is given explicitly by

$$g_1(\tau') = \frac{r_0^2}{A} \frac{1}{\pi\tau'} \int_A d^2\rho \int_A d^2\rho' \exp(-|\rho-\rho'|^2/\tau'), \tag{27}$$

and so on. Here $\rho = \mathbf{x}/r_0$, $\rho' = \mathbf{x}'/r_0$. By analogous procedures one obtains for anisotropic D

$$f_i = \left[\langle (\delta N)^2 \rangle / A^2 \right] \phi_1(t/\tau'_y) \left[c_1^2 \phi_1(\tau'_x) + (2\pi P c_2)^2 \phi_1(\tau''_x) \right. \\ \left. + 2c_1 c_2 2\pi P \phi_1(\tau'''_x) \right] \tag{28}$$

with

$$\tau'_y \approx t/\tau_y + \frac{1}{2}(\lambda/b)^2, \tag{29a}$$

$$\tau'_x = t/\tau_x + \frac{1}{2}(\lambda/a)^2, \tag{29b}$$

$$\tau''_x = t/\tau_x + \frac{1}{2}(\lambda/a)^2 + (d/a)^2, \tag{29c}$$

$$\tau'''_x = t/\tau_x + \frac{1}{2}(\lambda/a)^2 + \frac{1}{2}(d/a)^2, \tag{29d}$$

with $\phi_1(\tau'_y)$ and $\phi_1(\tau'_x)$ given by

$$\phi_1(\tau'_x) = \frac{1}{2} \int_{-1}^1 dx \int_{-1}^1 dx' \frac{\exp\left[-(x-x')^2/4\tau'_x\right]}{(4\pi\tau'_x)^{1/2}}, \quad (30a)$$

$$\phi_1(\tau'_y) = \frac{1}{2} \int_{-1}^1 dy \int_{-1}^1 dy' \frac{\exp\left[-(y-y')^2/4\tau'_y\right]}{(4\pi\tau'_y)^{1/2}}, \quad (30b)$$

and so on. The integral in eq. (25) has been previously computed numerically [1] and the integral in eqs. (30) can be obtained analytically [1].

It is interesting to look at the structure of eqs. (25) and (28). The effect of having to sum once over dipoles in order to obtain the analogue of g_3 or ϕ_3 introduces an additional (non-dimensional) "time" $2(d/r_0)^2$ or $\frac{1}{2}(d/a)^2$ and the double sum over dipoles introduces twice these shifts into the analogues of g_2 or ϕ_2 . This result can again be understood by the previous argument: Some fuzzing out is introduced into the current fluctuation correlation function and manifests itself as apparent diffusion even when real time $t = 0$. It is also obvious from the form of eqs. (26) and (29) that all the shifts become decreasingly important as real time increases. Qualitatively these features can be seen in the plots of g_2 and g_3 versus τ in ref. [1] (where τ as used in the present paper is labelled t) for various values of $z = d/r_0$. As τ increases the curves approach fairly closely to that for $z = 0$, i.e. g_1 . Thus the approximation of the integrals over the dipole potential, eq. (21) by a Gaussian is justified. In the presence of the main shift, $2(\lambda/r_0)^2$ or its analogue for the rectangular case the effect on g of the shifts resulting from the dipole integrations is small and will not depend strongly on the exact form of the approximation for eq. (22). Approximately then when $(\lambda/r_0)^2 < (d/r_0)^2$ (or $(\lambda/a)^2 < (d/a)^2$) it is appropriate to use the old forms of the correlation function which neglect resolution, while when the inequality is reversed the new forms can be used virtually with neglect of the $(d/r_0)^2$ or $(d/a)^2$ contributions so that a single function, $g_1(t/\tau_0 + 2(\lambda/r_0)^2)$ or $\phi_1(t/\tau_x + \frac{1}{2}(\lambda/a)^2)$ can be used.

4. Resolution

The resolution of a field emission microscope is determined mainly by the fact that emitted electrons have a finite component of transverse momentum which is conserved in tunneling [4]. The most probable displacement of an electron originating at some point on the emitter from the position it would have on the screen if it had zero transverse velocity, divided by the magnification M is roughly the quantity λ . Thus we can take to first approximation [4]

$$\lambda = 1.3 \times 10^{-4} \beta (r_t/k\alpha\phi^{1/2})^{1/2} \text{ cm}, \quad (31)$$

where $\beta \approx 1.5$ is a compression factor, r_t the emitter radius, $\alpha \approx 0.8-0.9$ an image correction, ϕ the emitter work function and $k \approx 3.5$ [5], a quantity occurring in the field voltage proportionality

$$F = V/k. \tag{32}$$

The radius (or other relevant dimension) of the probed region is given by

$$r_0 = r_p/M = r_p\beta r_t/x, \tag{33}$$

where x is tip to screen, i.e. tip to probehole distance, and r_p probehole dimension.

Consequently,

$$(\lambda/r_0)^2 = 2.54 \times 10^{-9} x^2/r_p^2 r_t, \tag{34}$$

assuming $\phi = 5.0$ eV. Thus the importance of including resolution decreases linearly with increasing tip radius. For typical values of $r_p = 0.075$ cm, $x = 3.5$ cm, $(\lambda/r_0)^2 = 5.6 \times 10^{-6}/r_t$. For $r_t = 3 \times 10^{-5}$ cm for instance $(\lambda/r_0)^2 = 0.19$.

5. Effect of resolution on measured values of D

The experimentally accessible quantity is $f_i(t)/f_i(0)$ versus $\log t$ where t is real time. Thus the correct value of τ_0 and hence D will be obtained if this curve is compared with

$$g_1(t/\tau_0 + 2(\lambda/r_0)^2)/g_1(2(\lambda/r_0)^2),$$

plotted versus $\log(t/\tau_0)$, i.e. $\log \tau$. The value of D_{true} so obtained is always larger than that of D_{app} , found by comparing $f_i(t)/f_i(0)$ versus $\log t$ with $g_1(\tau')$ versus $\log \tau'$. This latter comparison will not give a perfect fit over the entire range of τ' values but gives reasonable agreement for $\tau' \leq 5-10$, as illustrated in fig. 1 for the one-dimensional case for $\frac{1}{2}(\lambda/a)^2 = 2.47$. For this example $t/\tau_x = 0.7$ corresponds to $\tau' = 0.1$ or since

$$D_{\text{true}} = a^2/\tau_x = a^2/(t/0.7) \tag{35}$$

and

$$D_{\text{apparent}} = a^2/\tau'_x = a^2/(t/0.1), \tag{36}$$

$$D_{\text{true}}/D_{\text{apparent}} \approx 0.7/0.1 \approx 7. \tag{37}$$

This result can also be interpreted by saying that the effect of resolution is to increase the effective probe dimension so that using eq. (36), which corresponds to comparing the experimental curves with the theoretical curve based on $\lambda = 0$, requires increasing the effective value of r_0 or a . In the particular

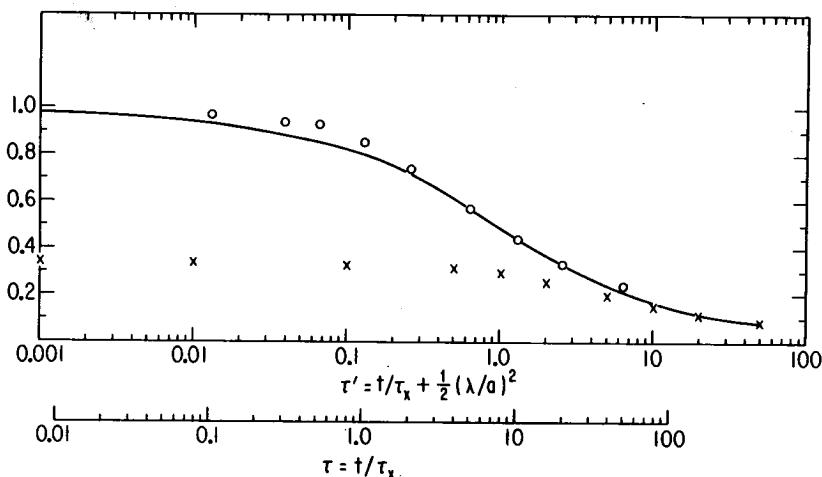


Fig. 1. Comparison of $\phi_1(t/\tau_x + \frac{1}{2}(\lambda/a)^2)$ versus $\log(t/\tau_x + \frac{1}{2}(\lambda/a)^2)$ (solid line) (i.e. $\phi_1(\tau')$ versus $\log \tau'$) with $\phi_1(t/\tau_x + \frac{1}{2}(\lambda/a)^2)/\phi_1(\frac{1}{2}(\lambda/a)^2)$ versus $\log(t/\tau_x)$, (O), for $\frac{1}{2}(\lambda/a)^2 = 2.47$. The curves have been displaced horizontally for best fit, which occurs when $\tau = t/\tau_x \approx 7(t/\tau_x + \frac{1}{2}(\lambda/a)^2)$. Also shown is a comparison of the solid line with the unnormalized $\phi_1(t/\tau_x + \frac{1}{2}(\lambda/a)^2)$ versus t/τ_x curve, (X), matched at very large values of t/τ_x ; this is accomplished here by letting the τ and τ' scales coincide. At small values of t/τ_x , $\phi_1(t/\tau_x + \frac{1}{2}(\lambda/a)^2)$ corresponds to $\phi_1(2.47) = 0.34$.

example chosen, which was based on $a = 13.5 \text{ \AA}$ and $\lambda = 30 \text{ \AA}$, $a_{\text{eff}} = a + 0.75\lambda$. Virtually the same correction applies to circular probes.

The above can also be understood in a slightly different way, by noting that it is equivalent to comparing $g_1(t/\tau_0 + 2(\lambda/r_0)^2)/g_1(2(\lambda/r_0)^2)$ versus t/τ_0 with $g_1(t/\tau_0)$ versus t/τ_0 . The latter is the same as $g_1(\tau')$ versus τ' since the name of the argument is immaterial. At $t = 0$, $g_1(t/\tau_0) = 1$ but $g_1(2(\lambda/r_0)^2) < 1$. Since $g_1(t/\tau_0 + 2(\lambda/r_0)^2) \rightarrow g_1(t/\tau_0)$ as t/τ_0 increases, the decay of $g_1(t/\tau_0 + 2(\lambda/r_0)^2)/g_1(2(\lambda/r_0)^2)$ for $0 \leq t/\tau_0$ must be less than that of $g_1(t/\tau_0)$ versus t/τ_0 in the same interval. But $g_1(t/\tau_0 + 2(\lambda/r_0)^2)/g_1(2(\lambda/r_0)^2) = f_i(t)/f_i(0)$ and consequently an attempt to find D_{app} by comparing $f_i(t)/f_i(0)$ versus $\log t$ with $g_1(t/\tau_0)$ versus $\log(t/\tau_0)$, i.e. ignoring the effect of λ , gives a value which is too small. The same argument applies to the one-dimensional case.

Roughly speaking then the effect of finite resolution can be taken into account by correcting the effective probe dimensions by adding $\approx 0.75\lambda$. This correction is also approximately valid for finding $\langle(\delta N)^2\rangle$ as can be seen from eq. (23) or (26).

If λ is calculated from eq. (29) the correction to both D and $\langle(\delta N)^2\rangle$ can be made accurately as outlined above. In principle it is also possible to estimate λ/r_0 experimentally if meaningful measurements can be carried out to times so long that $t/\tau_0 \approx t/\tau_0 + 2(\lambda/r_0)^2$. The $f_i(t)/f_i(0)$ versus $\log t$ curve can

then be matched at very long t to $g_1(\tau')$ versus $\log \tau'$, and this gives τ_0 . If the curves are then compared without additional shifting at small values of t where the $g(\tau')$ curve lies appreciably below $f_i(t)/f_i(0)$ we have

$$f_i(t)/f_i(0) = g_1(\tau')/g_1(2(\lambda/r_0)^2), \quad (38)$$

so that

$$g_1(2(\lambda/r_0)^2) = g_1(\tau')/(f_i(t)/f_i(0)) \quad (39)$$

and $(\lambda/r_0)^2$ can be found from $g_1(x)$ versus x .

For a rectangular probe $f_i(t)/f_i(0)$ becomes a function of τ_x and τ_y at long times and this procedure does not work, but more involved fitting procedures could be used.

Acknowledgements

This work was supported in part by NSF Grant CHE83-16647. We have also benefited from the Materials Research Laboratory of the National Science Foundation at the University of Chicago.

Note added in proof

R. Morin (private communication) has evaluated eq. (23) for arbitrary d in the circular case by Fourier transformation. In the limit of $d/\lambda \ll 1$ his general result reduces to ours, eq. (25).

References

- [1] R. Gomer, *Surface Sci.* 38 (1973) 373.
- [2] G. Mazenko, J.R. Banavar and R. Gomer, *Surface Sci.* 107 (1981) 459.
- [3] M. Tringides and R. Gomer, *Surface Sci.* 155 (1985) 254.
- [4] R. Gomer, *Field Emission and Field Ionization* (Harvard University Press, Cambridge, Mass., 1960) p. 41.
- [5] J.-R. Chen and R. Gomer, *Surface Sci.* 79 (1979) 413.