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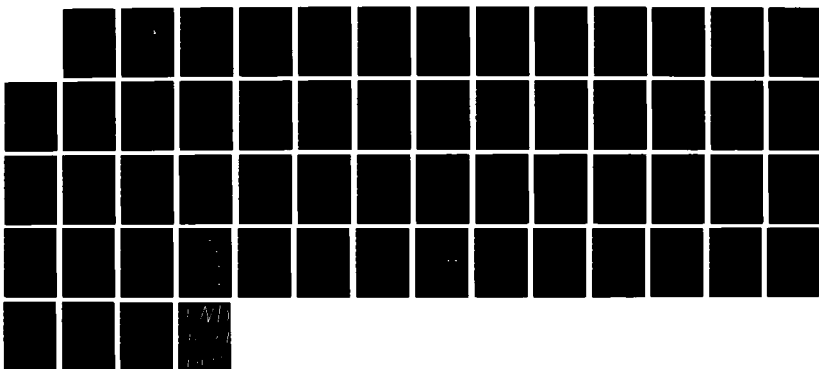
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NEW YORK AT BUFFALO DEPT OF CHEMISTRY S G CHUNG ET AL.
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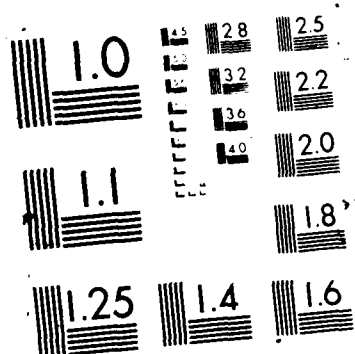
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Contract N00014-86-0043

TECHNICAL REPORT No. 51

Theory of Low-Temperature Adsorption

by

S. G. Chung and Thomas F. George

Prepared for Publication

in

Surface Science

Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

September 1987

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/87/TR-49			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260			7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-0043		
8c. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217			10. SOURCE OF FUNDING NOS.		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE Theory of Low-Temperature Adsorption					
12. PERSONAL AUTHOR(S) S. G. Chung and Thomas F. George					
13a. TYPE OF REPORT		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Yr., Mo., Day) September 1987	
				15. PAGE COUNT 51	
16. SUPPLEMENTARY NOTATION Prepared for publication in Surface Science					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.	LOW-TEMPERATURE ADSORPTION, SMALL WAVE NUMBER LIMIT		
			THEORY, MORSE-TYPE POTENTIALS		
			QUANTUM STICKING COEFFICIENT, INVERSE-SQUARE POTENTIALS		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson			22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

THEORY OF LOW-TEMPERATURE ADSORPTION

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Abstract

A general and qualitatively exact theory is developed for quantum sticking coefficients $\alpha(k)$ in the small wave number limit $k \rightarrow 0$. The theory covers Morse-type to inverse-square potentials, the latter representing long-range potentials. The theory gives unambiguous answers to crucial questions in the problem and helps lead to an overall understanding of low-temperature adsorption.



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I. Introduction

The problem of determining sticking coefficients of an atom on material surfaces is one of the fundamental tasks in surface physics. A general situation is depicted in Fig. 1a. If the kinetic energy of incident atoms or molecules is large compared with the energy scale of the problem, e.g., a potential-well depth of matter-particle interaction, then it is widely believed that the distorted-wave-Born-approximation (DWBA) is quantitatively correct for describing various surface phenomena.^{1,2} On the other hand, when the incident kinetic energy is much smaller than the typical energy scale of the given problem, as realized in low temperatures, there has been a long-standing controversy concerning the validity of the DWBA.³⁻⁷ This is partly due to the lack of accurate experiments at small k and at low temperatures. The only exception is the experiment done by the Edward group.⁸

The present theoretical situation is the following. People believe that a one-dimensional (1-d) simplification, as depicted in Fig. 1b, is good enough to study qualitative properties of the sticking coefficients $\alpha(k)$ at low temperatures. It is noted that a T-shape model as shown in Fig. 1c has a deficiency that there is no momentum sink along the direction of the particle motion. In classical mechanics, a particle would eventually strike the surface no matter how slow it is, releasing some energy to a matter system, and therefore, it would definitely be adsorbed on the surface for vanishingly small incident energy. Quantum mechanically, however, the situation is not quite so obvious. First, it appears natural that in quantum mechanics a low-energy wave function of the atom must have a small wave amplitude at a high potential barrier, i.e., at a surface. This is true for static short-range potentials due to the following reason. Consider a static square-well potential as shown in Fig. 2. The scattering wave function with incident wave number k can be written

$$|k^+\rangle = \begin{cases} A \sin(Kx) & \text{for } 0 \leq x \leq R \\ e^{-ikx} - S(k)e^{ikx} & \text{for } R < x \end{cases} \quad (1.1)$$

where $S(k)$ is an S-matrix element and

$$\frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k^2}{2m} + D \quad , \quad (1.2)$$

where m is the particle mass. Imposing the smoothness condition on $|k^+\rangle$ at $x = R$, one can easily find that

$$A \propto k \quad , \quad S(k) \rightarrow 1 \quad \text{for } k \rightarrow 0 \quad . \quad (1.3)$$

The linear k -dependence of the scattering wave amplitude in the potential-well region immediately leads to a linear k -dependence of the sticking coefficient $\alpha(k)$ at small k . The first quantum-mechanical calculation of $\alpha(k)$ by Lennard-Jones and Devonshire (LJD)³ based on the DWBA is essentially the same as the above argument for the static square-well potential. Based on the LJD calculation for a static Morse potential which decays exponentially at large distance, people next considered various possible mechanisms for realizing finite $\alpha(0)$. These include static long-range potentials, x^{-n} ,⁷ and correlated or many-body motions of the atom-matter system such as polaron⁶ and self-trapping,⁵ but for short-range potentials like square-well and Morse-type. However, all the existing theories share a common deficiency in that they do not answer the following two questions: How important is the long-range character of the matter-particle interaction? How important is the many-body motion of the matter-particle system? It is clear that a satisfactory theory must treat these effects on an equal-footing. Are there any potentials for which $\alpha(0)$ are finite? If there are such potentials, what is a borderline potential which distinguishes between "short-range" potentials for which $\alpha(0) = 0$ and "long-range" potentials for which $\alpha(0) \neq 0$?

In this paper, we shall develop a new theory of quantum sticking coefficients at 0 K. We do not invoke any uncontrolled approximations, and thus give a definitive answer to the problem. Our answer is as follows: (i) Irrespective of the matter-particle interaction potentials, the many-body motion of matter-particle system is not essential for the small- k behavior of $\alpha(k)$. The present theory gives a firm basis to the DWBA. (ii) For potentials decaying faster than x^{-2} at large distance, $\alpha(k) \propto k$ at small k . This is essentially due to the fact that the scattering wave function has a linear k -dependence at small k . The range of the linear k region decreases with increasing long-range character of the matter-particle interactions. The theory encourages experiments at small $k \leq 0.1 \text{ \AA}^{-1}$. For a ^4He atom colliding with a liquid ^4He surface, the present theory predicts a critical wave number $\sim 0.01 \text{ \AA}^{-1}$ below which $\alpha(k)$ depends on k approximately linearly, which provides a deep understanding of the experiment.⁸ (iii) The inverse-square potential is a borderline distinguishing between short-range potentials for which $\alpha(0) = 0$ and long-range potentials for which $\alpha(0) \neq 0$. This conclusion is reached by a DWBA calculation of $\alpha(k)$ for the inverse square potential. Our assertion (i) in this case means that the DWBA result cannot be changed qualitatively by higher-order corrections. This is essentially due to the fact that, unlike the case of short-range potentials, the scattering wave function here has a $\sqrt{k}$ -singularity at small k .

Before getting into detailed descriptions, let us try an intuitive explanation of the present theory and its main results. To do so, consider once more the static square-well potential, Fig. 2. In the above, we have given a standard explanation of $\alpha(0) = 0$. Our method in this simple case would proceed as follows. We first note that the S-matrix element $S(k) = \exp[2i\delta(k)]$, where $\delta(k)$ is a scattering phase shift. But Levinson's theorem⁹ tells us that $\delta(k)$ is related to the number of bound state N of the square-well potential as

$$\delta(+0) = \pi N \quad . \quad (1.4)$$

Now for $k \ll 1$, $S(k) \sim 1$ by (1.4) and $R \sim 0(1)$ for short-range potentials, and therefore

$$|k^+\rangle \approx -2ikx \quad \text{for} \quad R < x \ll 1/k \quad . \quad (1.5)$$

On the other hand, $|k^+\rangle$ in the region $0 \leq x \leq R$ must be a linear combination of two independent solutions of the Schrödinger equation, $e^{\pm iKx}$. Noting that K does not depend on k in the limit $k \rightarrow 0$, and requiring a smooth connection of $|k^+\rangle$ at $x = R$, one can easily see that both two constant factors before $e^{\pm iKx}$ are proportional to k , which leads to the same result as before -- $|k^+\rangle \propto k$ at the potential well, and hence $\alpha(k) \propto k$ for small k . Now the point is, this explanation does not use the boundary condition at $x = 0$, nor does it require details of the wave function in the potential well. Therefore, under the existence of a dynamical version of Levinson's theorem, it can be extended to dynamical cases, which is precisely what we shall do in the next section. The existence of a dynamical version of Levinson's theorem for matter-particle interaction potentials decaying faster than x^{-2} has recently been shown by the present authors.¹⁰

We have organized the present paper as follows. In the next section, short-range potentials are examined based on formal scattering theory and the dynamical Levinson's theorem. In Section III, a numerical calculation of $\alpha(k)$ is carried out based on a self-trapping model, which demonstrates the dynamical Levinson's theorem and determines a standard number β to be introduced in Section II. In Section IV, we examine the inverse square potential which is essentially different from the short-range cases and is outside the scope of the arguments to be presented in Section II. Our DWBA calculation presents, for the first time, an example of finite $\alpha(0)$. Our summary is given in Section V.

(After the completion of the present work, we have noticed the paper by Brivio and Brimley in which the adsorption problem is treated by the Green's function method.²¹⁾

II. Short-Range Potentials

We first examine short-range potentials, that is, those decaying faster than x^{-2} . Let us consider the adatom + 1-d matter Hamiltonian in a collinear configuration (see Fig. 1b),

$$H_{\text{tot}} = H(\tilde{x}, \tilde{p}) + V(\tilde{x}, x) + K(p) \quad , \quad (2.1)$$

where $H(\tilde{x}, \tilde{p})$ is a 1-d matter Hamiltonian with $\tilde{x}$ and $\tilde{p}$, respectively, representing position and momentum vectors for atoms in the 1-d matter, $V(\tilde{x}, x)$ is an interaction potential between the adatom and 1-d matter which we restrict to those decaying faster than x^{-2} at large adatom-matter separation $x \gg 1$, and $K(p)$ is the kinetic energy of adatom. It is noted that the 1-d matter must be of finite size, because otherwise only one phase is possible in one dimension, that is, there is no distinction between gases, liquids and solids.¹¹ This means that the matter does not have a well-defined boundary at finite temperatures, and the question of calculating an adsorption probability becomes meaningless.

A scattering eigenstate of (2.1) with a wave number k can be written as

$$\psi(\tilde{r}, k) = F(\tilde{r}, k) - S(k)F(\tilde{r}, -k) \quad , \quad (2.2)$$

where $\tilde{r} \equiv (\tilde{x}, x)$, $F(\tilde{r}, k)$ is a Jost solution having an asymptotic form $e^{-ikx}\phi_0(\tilde{x})$ at $x \rightarrow \infty$, where $\phi_0(\tilde{x})$ is the ground state of $H(\tilde{x}, \tilde{p})$ ($T = 0$ K), and $S(k) = \exp[2i\delta(k)]$ is an S-matrix element. In a recent paper,¹⁰ we have extended Levinson's theorem in static potential scattering to our dynamical case. We

have shown that for our short-range potential $V(\tilde{x}, x)$, the scattering phase shift $\delta(k)$ is connected to the number of bound states, N , of the total Hamiltonian by

$$\delta(+0) = N\pi \quad . \quad (2.3)$$

On the other hand, an exact expression of an adsorption rate $R(k)$, the number of adsorbed atoms per unit time, is given by time-dependent scattering theory¹² as

$$R(k) = \frac{2\pi}{\hbar} \sum_f \delta(E_k - E_f) |\langle f | V_f | k^+ \rangle|^2 \quad , \quad (2.4)$$

where $E_k = \frac{\hbar^2 k^2}{2m} + E_0$ with E_0 representing the ground state energy of the matter ($T = 0$ K), $\sum_f$ means a summation over final states $|f\rangle$, V_f is a final channel interaction, e.g., creation of phonons, and $|k^+\rangle$ represents a scattering eigenstate of the total Hamiltonian, H_{tot} . The sticking coefficient $\alpha(k)$ is defined as a ratio between $R(k)$ and the flux, the number of incident atoms per unit time, which is given by $\hbar k/m$. Therefore we have

$$\alpha(k) = \frac{2\pi m}{\hbar^2 k} \sum_f \delta(E_k - E_f) |\langle f | V_f | k^+ \rangle|^2 \quad . \quad (2.5)$$

An important observation in (2.5) is that as far as the small- k behavior of $\alpha(k)$ is concerned, it is given essentially by the quantity $|k^+|^2/k$. This is seen as follows. The static potential

$$V(\tilde{x}_0, x) = V(\tilde{x}, x) - V_f \quad , \quad (2.6)$$

where $\tilde{x}_0$ denotes a mean configuration of matter atoms in the ground state $\phi_0(\tilde{x})$, is by assumption a short-range potential, and supports only a finite number of bound states with finite binding energies. Moreover, the final states $|f\rangle$ in

(2.5) are eigenstates of the unperturbed Hamiltonian $H_{\text{tot}} - V_f$. Therefore, in the limit $k \rightarrow 0$, all the quantities other than $|k^+\rangle^2/k$ in (2.5) do not depend on k .

We now explore the small- k behavior of the exact scattering eigenstate $|k^+\rangle$. From the dynamical Levinson's theorem (2.3), for $k \ll 1$ the S-matrix element $S(k) = \exp[2i\delta(k)] \sim 1$ in (2.2). Let us define a reduced potential

$$V(\tilde{x}_0, x) / (\frac{\hbar^2}{2m}) \equiv U(x) \quad . \quad (2.7)$$

and consider large distances R and R' such that

$$-U(R) = k^2 \ll -U(R') \ll \{-U(x)\}_{\text{max}} \quad . \quad (2.8)$$

This means that the matter system is still in the ground state in the region $R' < x$, and that the Jost solution in (2.2) is $F(\tilde{r}, k) \approx e^{-ikx} \phi_0(\tilde{x})$ in the region $R < x$. Thus we have

$$\begin{aligned} |k^+\rangle &\approx (e^{-ikx} - e^{ikx}) \phi_0(\tilde{x}) \\ &\approx -2ikx \phi_0(\tilde{x}) \quad \text{for} \quad R < x < \frac{1}{k} \quad , \end{aligned} \quad (2.9)$$

where in the second expression, we have assumed the inequality

$$kR < 1. \quad (2.10)$$

Next consider the region $R' < x < R$, where the particle motion is described by Schrödinger equation

$$\left\{ -\frac{d^2}{dx^2} + U(x) \right\} \psi = k^2 \psi \quad . \quad (2.11)$$

Instead of explicitly solving (2.11) for respective potentials $U(x)$, however, we simply point out that the particle motion in this region must be somewhere between the two extreme cases, $U(x) = U(R)$ and $U(x) = U(R')$, as shown by two

horizontal dashed lines in Fig. 3. But one can easily see that in both cases the smoothness requirement of $|k^+ \rangle$ at $x = R$ [cf. (2.9)] leads to $|k^+ \rangle \propto k$ at $R' < x < R$. This fact in turn leads to $|k^+ \rangle \propto k$ at $0 < x < R'$, because in this region, $|k^+ \rangle$ can depend on k only through a constant prefactor which, however, again by smoothness of $|k^+ \rangle$ at $x = R'$, must be proportional to k . In this way we reach

$$|k^+ \rangle \propto k \quad 0 < x < R. \quad (2.12)$$

From (2.12) we have

$$\alpha(k) \propto |k^+ \rangle^2 / k \propto k. \quad (2.13)$$

We remember, however, that (2.13) is derived under the condition (2.10) and $S(k) \sim 1$. Little is known about the small- k dependence of $S(k)$. Our analysis below and numerical calculations in the next section for a Morse potential show that the latter condition imposes a similar restriction on k as (2.10). To analyze (2.10) for typical long-distance behaviors of the reduced potential $U(x)$, let us introduce a standard number $\beta < 1$ in analogy to the "standard value" in the Lindemann formula for melting,¹³ and replace (2.10) by

$$kR \leq \beta. \quad (2.14)$$

With this β we can predict for each given potential a critical wave number k_c such that

$$\alpha(k) \propto k \quad \text{at} \quad k \leq k_c. \quad (2.15)$$

From (2.14) and $U(R) = k^2$, one can easily obtain the following results:

- (i) Exponential decay $U(x) \sim -ye^{-\kappa x}$,

$$-(k_c/\kappa)\ln(k_c^2/\gamma) = \beta \quad (2.16)$$

(ii) Algebraic decay $U(x) \sim -\gamma x^{-n}$ ($n > 2$) ,

$$\gamma^{1/n} k_c^{1-2/n} = \beta \quad (2.17)$$

The results (2.16) and (2.17) make two predictions. First, the critical wave number k_c decreases with increasing long-range character of the potential. Our numerical calculations of $\alpha(k)$ in the next section for a Morse potential (2.16) with $\gamma = 48 \text{ \AA}^{-1}$ and $\kappa = 1.4 \text{ \AA}^{-1}$ (numbers for the W-He system^{14,15}) show that $k_c \sim 0.1 \text{ \AA}^{-1}$. Substituting these numbers into (2.16) gives

$$\beta \sim 0.6 \quad (2.18)$$

The ^4He atom colliding on a liquid ^4He surface is described by a van der Waals potential (2.17) with $n = 3$ and $\gamma = 20 \text{ \AA}$. Using $\beta \sim 0.6$ in (2.17), we have $k_c \sim 0.01 \text{ \AA}^{-1}$ for this case, which is in good agreement with experiment.⁸ Second, from (2.17) k_c approaches zero quite rapidly as the exponent n approaches 2 from above, as depicted in Fig. 4 for $\gamma = 20$ and $\beta = 0.6$. This strongly suggests finite $\alpha(0)$ for an inverse square potential, and that $n = 2$ is a borderline distinguishing between "short-range" potentials $n > 2$ and "long-range" potentials $n \leq 2$. We note that the $n = 2$ specialty is beyond physical intuition, but is clear mathematically as signaled in several ways: the dynamical Levinson's theorem (2.3) breaks down for $n \leq 2$, the inequality (2.10) does not hold for $n \leq 2$, and the zero-energy scattering wave function has a singularity at $n = 2$. This last fact is seen as follows. For $k = 0$ and $U(x) = -\gamma x^{-n}$, (2.11) becomes

$$\psi'' + \gamma x^{-n} \psi = 0 \quad (2.19)$$

A general solution of (2.19) is

$$\psi = \sqrt{x} Z_{\frac{1}{2-n}} \left(\frac{2\sqrt{Y}}{2-n} x^{1-n/2} \right), \quad (2.20)$$

where Z_v is a solution of Bessel's differential equation

$$Z_v'' + \frac{1}{x} Z_v' + \left(1 - \frac{v^2}{x^2}\right) Z_v = 0. \quad (2.21)$$

The singularity of ψ at $n = 2$ is clear in (2.20). In Section IV, we shall present a thorough study of the inverse square potential and show that the quantum sticking coefficient $\alpha(k)$ is finite in the limit $k \rightarrow 0$, thus confirming the above prediction that $n = 2$ is a borderline.

III. Determination of β

In this section, we consider a self-trapping model for the adsorption of He atom on W. A collinear configuration of He and W is shown in Fig. 5. By calculating the sticking coefficient $\alpha(k)$ as a function of the wave number k , we shall demonstrate the dynamical Levinson's theorem (2.3) and determine the standard number β . The model assumes a harmonic lattice, $H_{ph} = \sum_q \hbar \omega_q a_q^\dagger a_q$, a surface W atom plus He atom interacting through a Morse potential, and the surface W atom seeing another Morse potential created by the end W atom of the 1-d lattice in its equilibrium (taken to be $x = 0$)

$$H_{s+a} = p_s^2/2M + U(x_s) + p_a^2/2m + U(x_a - x_s). \quad (3.1)$$

The dynamical interaction between the harmonic lattice and the surface W atom takes the form (one-phonon process)

$$H_{int} = - \sum_q \left(\frac{\hbar}{2N_0 M \omega_q} \right)^{1/2} (a_q^\dagger + a_{-q}) \frac{dU(x_s)}{dx_s} \theta(t), \quad (3.2)$$

where N_0 is the number of lattice atoms, and the unit step function $\theta(t)$ means that $|k^+\rangle$ here is a scattering eigenstate of H_{s+a} , not that of the total Hamiltonian. In analogy to the second-order optical process, this is a luminescence component approximation thereby neglecting Raman components, which is expected to be good for short-range potentials of the Morse type. To calculate $\alpha(k)$ by (2.5), we note that here V_f is H_{int} at $t > 0$, and the final state is $|f\rangle = a_q^\dagger |0\rangle |b\rangle$, where $|0\rangle$ is the phonon vacuum and $|b\rangle$ represents a bound state of H_{s+a} .

To solve the Schrödinger equation

$$H_{s+a}\psi = E\psi, \quad (3.3)$$

which is the main task in this section, we now specify the W-He and W-W Morse potentials as

$$\begin{bmatrix} \bar{U}(x+x_s^0) \\ U(x+x_a^0) \end{bmatrix} = \begin{bmatrix} \bar{D} \\ D \end{bmatrix} (e^{-2\kappa x} - 2e^{-\kappa x}), \quad (3.4)$$

where $x_s^0 = 3 \text{ \AA}$, $x_a^0 = 3.6 \text{ \AA}$, $\bar{D} = 0.99 \text{ eV}$, $D = 10 \text{ meV}$ and $\kappa \approx 1.4 \text{ \AA}^{-1}$.^{14,15} The phonon dispersion ω_q is given in terms of the W-W interaction potential $\bar{U}$ as

$$M\omega_q^2 = 2\bar{U}_{xx}(x=x_s^0)[1 - \cos(qx_s^0)]. \quad (3.5)$$

It is worth noting that the problem (3.3) is essentially a three-body one and an analytic solution is not available even for the simplest interaction potentials, e.g., the square-well. The best we can do is to construct perturbative and variational wave functions and solve (3.3) numerically. In doing so, we note the following. First, the one-body problem for Morse potentials is exactly solvable. Appendix A summarizes some results about Morse potentials. In the case of the W-He Morse potential $U(x)$, the quantity K as defined in (A.3) is

about 7.4, which by (A.6) means that there are four bound states with the lowest binding energy $-1.52 \times 10^{-21} \text{ J} \approx -9 \text{ meV}$. Similarly for the W-W Morse potential $\bar{U}(x)$, there are about 200 bound states. Measuring the energy from that of the lowest bound state, the first four bound states have energies 0 ($n = 0$), 1.35 ($n = 1$), 2.69 ($n = 2$) and 3.94 ($n = 3$) in the unit of 10^{-21} J . The one-particle energy spectra for the W-W and W-He Morse potentials are schematically summarized in Fig. 6. It is now clear from energy considerations that as long as k is small, the first three bound states are good enough to describe the motion of the surface W-atom. As for the motion of He, there are two situations. When the He atom is far away from the surface, the surface W-atom is in the ground state and the wave function is written as

$$\psi = \psi_{\text{asym}}(x_s, x_a) = C\phi_0(x_s)[e^{-ikx_a} - S(k)e^{ikx_a}] \quad (3.6)$$

where $\phi_0(x_s)$ is the ground state of the surface w-atom as given by (A.2), and $C = 0$ for bound states $|b\rangle$ and $C = 1$ for the scattering state $|k^+\rangle$. Near the surface, on the other hand, the wave function can be written as

$$\psi = \psi_{\text{surf}}(x_s, x_a) = \sum_{p=0}^{M-1} g_p(x_a)\phi_p(x_s) \quad (3.7)$$

where the g_p 's describe a fully correlated motion of He near the surface.

According to the energy consideration above, we take $M = 3$ hereafter. One may suggest the use of the variable $x_a - x_s$ in place of x_a in (3.7) and expand the He motion g_p in terms of the eigenstates $\{\phi_n\}$ in (A.2) for the W-He Morse potential U . This scheme is not efficient, however, because of complexities arising from the kinetic energy term $p_s^2/2M$ in (3.1). We find that the Gaussian-weighted Hermite polynomials are the best suited orthonormal complete set over which to expand localized g_p -functions:

$$h_q = \bar{N}_q e^{-T^2 x^2/4} H_q(Tx) \quad q = 0, 1, 2, \dots, \quad (3.8)$$

where $\bar{N}_q = [T/q! \sqrt{2\pi}]^{1/2}$ and the H_q 's are Hermite polynomials. In Appendix B, we have described Hermite polynomials and related integrals which appear in the calculation of the Hamiltonian matrix elements. The scale factor T in (3.8) must be best fitted according to the degree of locality of the g_p 's. To check the efficiency of the h_q expansion, we have expanded the first four bound states of the W-He Morse potential in terms of the h_q 's. We have found that 14 h_q 's reproduce these four wave functions very well, with $\leq 1\%$ relative error in wave amplitudes.

Based on these preliminary arguments, we now consider the following variational wave functions for the eigenstates of H_{s+a} :

$$\psi(x_s, x_a) = \psi_{\text{asym}} \phi(x_a) + \sum_{i=0}^2 \sum_{j=0}^{N-1} C_{ij} \phi_i(x_s) h_j(x_a), \quad (3.9)$$

where $\phi(x_a)$ is an error function preventing the He-atom from penetrating into the matter,

$$\phi(x) = \frac{v}{\sqrt{\pi}} \int_{-\infty}^{x-x_a^0-x_s^0-\sqrt{2}/v} dt e^{-v^2 t^2}, \quad (3.10)$$

where v is a variational parameter. First consider the bound states $|b\rangle$.

Substituting (3.6) with $C = 0$ and (3.9) into (3.3) and operating

$$\iint dx_s dx_a \phi_l(x_s) h_m(x_a),$$

we obtain a set of coupled algebraic equations for the coefficients C_{ij} 's:

$$\sum_{ij} H_{lm,ij} C_{ij}^b = \epsilon C_{lm}^b, \quad (3.11)$$

where

$$H_{lm,ij} = \epsilon_i \delta_{li} \delta_{mj} - \delta_{li} P_{mj} + \epsilon_g U_{lm,ij}, \quad (3.12)$$

and where $\epsilon_i \equiv 2mE_i/\hbar^2$, $\epsilon \equiv 2mE/\hbar^2$, $\epsilon_g \equiv 2\tilde{D}m/\hbar^2$, and P_{mj} and $U_{lm,ij}$, respectively, are given by (B.7) and (B.9). Starting with (3.6) and $C = 1$, one can obtain a similar equation as (3.11) for the scattering state $|k^+\rangle$. It is noted that unlike the case of bound states, the eigenenergy is already known as $E_k = \hbar^2 k^2/2m$. However, there is an additional unknown, $S(k)$, and some additional matrix elements associated with this variable. We have obtained

$$\left[\begin{array}{c|c} H_{lm,ij} - \epsilon_k \delta_{li} \delta_{mj} & -H_{lm}^* \\ \hline H_{ij}^* & H_{ss} \end{array} \right] \begin{bmatrix} C_{ij}^s \\ S(k) \end{bmatrix} = \begin{bmatrix} -H_{lm} \\ H_s \end{bmatrix}, \quad (3.13)$$

where $\epsilon_k = k^2$, and H_{lm} , H_s and H_{ss} are certain integrals involving the error function Φ , (3.10), and are given in Appendix C.

We can now calculate the sticking coefficient $\alpha(k)$ as defined by (2.5). As noted before, our self-trapping model assumes the one-phonon final states $|f\rangle = a_q^\dagger |0\rangle |b\rangle$ and takes as $|k^+\rangle$ the scattering eigenstate of H_{s+a} , and here V_f is H_{int} , (3.2), at $t > 0$. Let

$$- \frac{\hbar^2}{2m} b_\ell^2, \quad \ell = 1, 2, \dots, \ell_0$$

be the binding energy of the ℓ -th bound state. With the phonon spectrum (3.5), the energy conservation in (2.5) becomes

$$\delta(E_k - E_f) = \frac{1}{\hbar k \sqrt{D/M}} \frac{1}{x_s^0 \sqrt{2-B_\ell^2}} \{ \delta(q-q_0) + \delta(q+q_0) \}, \quad (3.14)$$

where

$$B_\ell = \frac{1}{4\kappa} \sqrt{M/m} \sqrt{\hbar^2/m\tilde{D}} (k^2 + b_\ell^2), \quad q_0 = \frac{1}{x_s} \cos^{-1}(1-B_\ell^2) \quad (3.15)$$

As for the matrix element in (2.5), from (3.2), (3.6) and (3.9) we have

$$|\langle f | V_f | k^+ \rangle|^2 = \frac{(2\kappa\tilde{D})^2 \hbar}{2N_0 M \omega_q} |M_\ell|^2 \quad (3.16)$$

with

$$\begin{aligned} M_\ell &= \sum_{ij} C_{ij}^\ell \int dx h_j \phi \{e^{-ikx} - S(k)e^{ikx}\} \int dx \phi_i \phi_0 \tilde{U}'(x)/2\kappa\tilde{D} \\ &\quad + \sum_{ij} C_{ij}^\ell \sum_p C_{pj}^s \int dx \phi_i \phi_p \tilde{U}'(x)/2\kappa\tilde{D} \\ &= \sum_{ij} C_{ij}^\ell \{Y(j,0) - S(k)Y^*(j,0)\} \frac{N_i N_0}{\kappa K^2} \{KJ(K;i,0;1) - J(K;i,0;2)\} \\ &\quad + \sum_{ij} C_{ij}^\ell \sum_p C_{pj}^s \frac{N_i N_p}{\kappa K^2} \{KJ(K;i,p;1) - J(K;i,p;2)\} \quad (3.17) \end{aligned}$$

where (A.11) and (C.6) are used. Substituting (3.14) and (3.16) into (2.5) gives

$$\alpha(k) = \frac{8\kappa(\frac{m}{M})^{\frac{1}{2}}(\frac{m\tilde{D}}{\hbar^2})^{3/2}}{\sum_{\ell=1}^{\ell_0} \sqrt{2-B_\ell^2}} \frac{1}{k^2 + b_\ell^2} |M_\ell|^2 \quad (3.18)$$

We have numerically solved (3.11) and (3.13) and obtained b_ℓ , C_{ij}^ℓ , $S(k)$ and C_{ij}^s . We have then evaluated $\alpha(k)$ based on (3.15), (3.17) and (3.18). The stability and convergence of the numerical calculation has been checked by changing variational parameters T and v , as well as the number of Gaussian-weighted Hermite polynomials, h_q . To test the validity of our numerical calculations, we have first checked if the numerically obtained binding energies

are reasonable. We have found four bound states with energies -20.087, -9.053, -2.939 and -1.837 in the unit of $\text{\AA}^{-2}$. Simple estimates of these energies are the four binding energies of the W-He Morse potential, assuming the surface W-atom to be in the ground state ϕ_0 . From (A.6), in the same unit of $\text{\AA}^{-2}$, these estimates are -20.133, -9.530, -2.846 and -0.082, which are close to the numerical results, thus demonstrating the validity of our numerical calculations. Figure 7 contains our final results for $T = 2$, $v = 1$ and $N = 21$. Part a shows that the S-matrix element takes the limit $S(k) \rightarrow 1$ as $k \rightarrow 0$, demonstrating the dynamical Levinson's theorem, (2.3). Part b shows $\alpha(k)$ as a function of the wave number k . The approximate linear k -dependence of $\alpha(k)$ is seen below $k_c = 0.1 \text{\AA}^{-1}$. Substituting this into (2.16) with $\kappa = 1.4 \text{\AA}^{-1}$ and $\gamma = 48 \text{\AA}^{-2}$ gives $\beta \sim 0.6$.

IV. Inverse-Square Potential

In the preceding two sections, we have investigated short-range cases, i.e., the particle-matter interaction potentials decaying faster than x^{-2} at large distance, $x \gg 1$. Due to the existence of the dynamical Levinson's theorem (2.3), we could develop a general and accurate theory for the small- k behavior of the sticking coefficients $\alpha(k)$. As we have found, $\alpha(k) \propto k$, thus verifying that the DWBA is qualitatively correct in this case. One important result is that $\alpha(k) \propto k$ only at $k \leq k_c$, and the critical wave number k_c decreases with increasing long-range character of the potentials. In particular, as Fig. 4 shows, the theory predicts that $k_c = 0$ and hence $\alpha(0)$ is finite for an inverse-square potential. In other words, it predicts that the inverse-square potential is a borderline distinguishing between short-range potentials for which $\alpha(0) = 0$ and long-range potentials for which $\alpha(0)$ is finite. In this section, we shall carry out a one-phonon mediated DWBA

calculation of the sticking coefficient for an inverse square potential, and show that this is indeed the case.

Before getting into details, it is useful to look at the problem of sticking coefficients from the viewpoint of formal perturbation theory. The exact scattering eigenstate $|k^+\rangle$ in (2.5) can be written as

$$|k^+\rangle = \sum_{n=0}^{\infty} (G_0 V_f)^n |k\rangle, \quad (4.1)$$

where V_f is a dynamical interaction between the adatom and matter, $|k\rangle$ is an exact scattering eigenstate for a static adatom-matter potential, and $G_0 \equiv (\epsilon_k - H + i0^+)^{-1}$ is an adatom propagator with the Hamiltonian H describing the adatom moving in the static adatom-matter potential. Substituting (4.1) into (2.5) provides a power series expansion of $\alpha(k)$ with respect to V_f , whose lowest order, $O(V_f^2)$, is the DWBA. In the case of short-range potentials, the DWBA gives a vanishing $\alpha(0)$, and it has been a challenging question if the inclusion of higher-order terms can bring about a qualitatively different answer, namely a finite $\alpha(0)$. In the case of the inverse-square potential, on the other hand, as we shall see below, the DWBA already gives a finite $\alpha(0)$. Now an important point is that the DWBA is the only term to $O(V_f^2)$. This means that an exact $\alpha(0)$ is also finite in general. In other words, as far as the qualitative small- k -behavior of $\alpha(k)$ is concerned, there is no significant many-body effects in the case of the inverse-square potential.

Another important remark is on the dimensionality of the problem. As we have noted in Section I, a 1-d model of infinite size is physically meaningless for the study of adsorption. Therefore, when one uses the 1-d model, the system size must be finite, so that the phonon spectrum has a gap. In the case of short-range potentials, the number of bound states is finite, and therefore a

cutoff is effectively introduced in the phonon spectrum. This is why the commonly used infinite 1-d model does not show any difficulty. For the inverse-square potential, on the other hand, as we shall see below, there are infinitely many shallow bound states which strongly couple to very "soft" phonons, leading to an infrared catastrophe to be explained. We thus encounter a finite-size problem in a 1-d model for the inverse-square potential. To avoid this problem, we shall extend the commonly used 1-d model to higher dimensions -- two and three -- thereby expecting that the phonon density of states at higher dimensions would suppress the contribution of very soft phonons and remove the infrared catastrophe.

Let us consider a particle of mass m striking the material surface in the normal direction. The Hamiltonian is written in general as

$$H = p^2/2m + H_{ph} + \sum_{i=1}^{N_0} V(\vec{r} - \vec{R}_i) . \quad (4.2)$$

Writing $\vec{R}_i = \vec{R}_{i0} + \delta\vec{R}_i$ and following the standard procedures, we divide the third term into a static potential

$$v(z) = \sum_i V(\vec{r} - \vec{R}_{i0}) \quad (4.3)$$

and a dynamical interaction

$$\begin{aligned} V_f &= - \sum_i \vec{\nabla} V(\vec{r} - \vec{R}_{i0}) \cdot \delta\vec{R}_i \\ &= - \sum_{\vec{q}\lambda} \sum_{\vec{G}} i N_0 (\vec{q} + \vec{G}) \cdot \vec{\epsilon}_{\vec{q}\lambda} e^{i(\vec{q} + \vec{G}) \cdot \vec{r}} \\ &\quad \times V_{\vec{q} + \vec{G}} \sqrt{\frac{\hbar}{2N_0 M \omega_{\vec{q}\lambda}}} (a_{\vec{q}\lambda}^\dagger + a_{-\vec{q}\lambda}) . \end{aligned} \quad (4.4)$$

In (4.3), we have assumed a translational symmetry parallel to the surface. In (4.4), $\vec{\epsilon}_{\vec{q}\lambda}$ is a phonon polarization, $V_{\vec{Q}}$ is a Fourier $\vec{Q}$ -component, and $\vec{G}$ is a reciprocal lattice vector. Now the one-phonon mediated DWBA for a sticking coefficient $\alpha(k)$ means that in (2.5), the final state is $|f\rangle = a_{\vec{q}\lambda}^\dagger |0\rangle |b\rangle e^{i\vec{k}_{\parallel} \cdot \vec{r}_{\parallel}}$, and $|k^+\rangle$ and $|b\rangle$ are, respectively, scattering and bound eigenstates of the static potential $v(z)$. Here the subscript $\parallel$ denotes a component parallel to the surface. From (2.5) and (4.4) we have

$$\alpha(k) = \frac{2\pi m}{\hbar^2 k} \sum_{b, \vec{q}\lambda} \delta\left\{\frac{\hbar^2}{2m}(k^2 - q_{\parallel}^2 + b^2) - \hbar\omega_{\vec{q}\lambda}\right\} |M|^2 \quad (4.5)$$

with

$$M = \sqrt{\frac{\hbar}{2N_0 M \omega_{\vec{q}\lambda}}} iN_0 \sum_{\vec{G} = (0,0,G_z)} \langle b | e^{i(q_z + G_z)z} | k^+ \rangle \times (\vec{q} + \vec{G}) \cdot \vec{\epsilon}_{\vec{q}\lambda} V_{\vec{q}+\vec{G}} \quad (4.6)$$

In deriving (4.5) and (4.6), we have put $G_{\parallel} = 0$ because at low energy a nonzero $G_{\parallel}$ does not satisfy energy conservation. Moreover, in a standard situation, such as a He-atom colliding on W-matter, we see from energy conservation that $q \ll 1$, which enables us to neglect the $q_{\parallel}^2$ -term compared with $\omega_{\vec{q}\lambda}$ in (4.5), and approximate (4.6) as

$$M = \sqrt{\frac{\hbar}{2N_0 M \omega_{\vec{q}\lambda}}} N_0 \langle b | \int_{G_z} e^{iG_z z} iG_z \epsilon_{\vec{q}\lambda}^z V_{G_z} | k^+ \rangle \quad (4.7)$$

We note that the $G_z = 0$ term in (4.6) is negligibly small. On the other hand, one can easily show that

$$v(z) = N_0 \int_{G_z} e^{iG_z z} V_{G_z} . \quad (4.8)$$

With (4.8), (4.7) can be written as

$$M = \langle b | \epsilon_{\vec{q}\lambda}^z \sqrt{\frac{\hbar}{2N_0 M \omega_{\vec{q}\lambda}}} \frac{dv(z)}{dz} | k^+ \rangle . \quad (4.9)$$

Here it is noteworthy that the result (4.9) justifies replacing the dynamical interaction (4.4) by an effective one,

$$V_f = \int_{\vec{q}\lambda} \sqrt{\frac{\hbar}{2N_0 M \omega_{\vec{q}\lambda}}} (a_{\vec{q}\lambda}^\dagger + a_{-\vec{q}\lambda}) \frac{dv(z)}{dz} , \quad (4.10)$$

which is a natural extension of the commonly used 1-d model of low-temperature adsorption to higher dimensions.

To explicitly evaluate (4.5) and (4.9) for $\alpha(k)$, we must specify the static potential $v(z)$ and the phonon dispersion $\omega_{\vec{q}\lambda}$. For the static potential we take the form

$$v(z) = \begin{cases} -\frac{\hbar^2}{2m} \gamma z^{-2} & z \geq z_0 \\ \infty & z < z_0 \end{cases} , \quad (4.11)$$

where $z = z_0$ denotes the surface. It is noted that our phonon argument above is not consistent with the long-range potential, (4.11). Conduction electrons will be more relevant than phonons for the long-range interaction.¹⁷ However, as will become clear below, the specific form of the interaction term V_f is not essential for finiteness of $\alpha(0)$, and (4.10) is good enough to study qualitative aspects of quantum adsorption for the long-range potential. For a similar reason, we consider W and He as an example of matter and atom. Clearly the W-He interaction is not of the type (4.11), and the choice of W and He here is simply

for the purpose of specifying the atom and the phonon dispersion. We replace $\omega_{\vec{q}\lambda}$ by $\omega_{\vec{q}}$ of (3.5), which upon substitution of (3.4) becomes

$$\omega_{\vec{q}} = 2\kappa \left[\frac{\tilde{D}}{M} (1 - \cos(qx_s^0)) \right]^{1/2} . \quad (4.12)$$

This is based on the observation that (4.12) gives a sound velocity $\sim 4 \times 10^3$ m/s, which is close to the geometrical mean of the longitudinal and transverse sound velocities in three dimensions, $\sim 3.4 \times 10^3$ m/s. With this simplification and

$$\sum_{\lambda} (\epsilon_{\vec{q}\lambda}^z)^2 = 1 , \quad (4.13)$$

the dimensionality, D , appears only in the phonon density of states

$$\Sigma_{\vec{q}} = \frac{L^D}{2\pi(x_s^0)^{D-1}} \int_0^\infty dq \rho_D(q) \quad (4.14a)$$

with

$$\rho_D(q) = 2 \quad (D = 1), \quad x_s^0 q \quad (D = 2) \text{ and } (x_s^0 q)^2 / \pi \quad (D = 3) . \quad (4.14b)$$

Our final task towards the calculation of $\alpha(k)$ is to solve the Schrödinger equation²²

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + v(z) \right\} \psi = \frac{\hbar^2}{2m} \epsilon^2 \psi , \quad (4.15)$$

which is carried out in Appendix D. Figure 8 contains the long-range potential (4.11) in the unit of $\text{\AA}^{-2}$ with $z_0 = 0.5 \text{ \AA}$ and $\mu = \sqrt{\gamma - \frac{1}{4}} = 5.0$, and its bound states calculated from (D.9). From (3.14), (4.5), (4.9) and (4.11)-(4.14), we have

$$\alpha(k) = \frac{(2\gamma)^2 \hbar}{4k\kappa\sqrt{DM}} \sum_{\ell=1}^{\infty} \rho_D(q_0) \frac{1}{\sqrt{2 - B_{\ell}^2}} \frac{1}{k^2 + b_{\ell}^2} |\langle \ell | z^{-3} | k^+ \rangle|^2, \quad (4.16)$$

where b_{ℓ} is the ℓ -th b as given by (D.9), and $|\ell\rangle$ is the ℓ -th bound state (D.14), with the first bound state being the lowest bound state. Substituting (D.4), (D.6), (D.14) and (D.18) into (4.16) gives

$$\begin{aligned} \alpha(k) = & \frac{4\pi\hbar}{\kappa\sqrt{DM}} \frac{\gamma^2}{z_0^2} e^{-\pi\mu} |J_{\nu}(kz_0)|^{-2} \sum_{\ell=1}^{\infty} \rho_D(q_0) \\ & \times \frac{1}{\sqrt{2 - B_{\ell}^2}} \frac{1}{k^2 + b_{\ell}^2} |I_{-\nu+1}(b_{\ell}z_0) - I_{\nu-1}(b_{\ell}z_0)|^{-2} |M_{\ell}|^2 \end{aligned} \quad (4.17)$$

where $\nu = \sqrt{1 - \gamma^2}$ and

$$\begin{aligned} M_{\ell} \equiv & \int_{z_0}^{\infty} dz z^{-3} \{J_{\nu}(kz)J_{-\nu}(kz_0) - J_{-\nu}(kz)J_{\nu}(kz_0)\} \\ & \times \{I_{\nu}(b_{\ell}z) - I_{-\nu}(b_{\ell}z)\}. \end{aligned} \quad (4.18)$$

For given values of parameters z_0 , μ and k , one can calculate the prefactor in (4.17) and bound-state spectrum b_{ℓ} by (D.9), (D.11) and (D.12), which in turn determines B_{ℓ} and $\rho_D(q_0)$ by (3.15) and (4.14b), and $|I_{-\nu+1}(b_{\ell}z_0) - I_{\nu-1}(b_{\ell}z_0)|^{-2}$ by (D.11). Finally, the matrix element (4.18) can be evaluated numerically, with some remarks given in Appendix E.

We can now discuss some properties of $\alpha(k)$. First of all, the finiteness of $\alpha(0)$ can be seen as follows. Consider the lowest bound-state contribution in (4.16). It is clear in this expression that in the limit $k \rightarrow 0$, the k -dependence of $\alpha(k)$ is determined by that of the quantity $|k^+|^2/k$, which, however, approaches a constant due to the $\sqrt{k}$ -dependence of $|k^+ \rangle$ in the limit $k \rightarrow 0$, (D.7). Therefore, the lowest-bound-state contribution to $\alpha(0)$ and hence the

value of $\alpha(0)$ itself is constant. An important point here is that this conclusion of finite $\alpha(0)$ does not use details of the interaction H_{int} . Thus, we have seen that the finiteness of $\alpha(0)$ is a general consequence of the inverse-square potential. Secondly, we have observed a logarithmic divergence of $\alpha(k)$ in the 1-d case,

$$\alpha(k)_{D=1} \propto -\ln k \quad \text{for } k \rightarrow 0. \quad (4.19)$$

To see the origin of this catastrophe, consider the matrix element M_ℓ in the limit $k, b \rightarrow 0$. In this limit, substituting (D.2) and (D.11) into (4.18) gives

$$\begin{aligned} M_\ell &\propto \int_1^\infty dz \, z^{-2} (z^\nu - z^{-\nu}) \left\{ \frac{\Gamma(1-\nu)}{\Gamma(1+\nu)} (\delta_\ell z)^\nu - (\delta_\ell z)^{-\nu} \right\} \\ &\propto \frac{\Gamma(1-\nu)}{\Gamma(1+\nu)} \delta_\ell^\nu \frac{1}{1-2\nu} - \delta_\ell^{-\nu} \frac{1}{1+2\nu}, \end{aligned} \quad (4.20)$$

where $\delta_\ell \equiv b_\ell z_0/2$. From (4.20) and (D.12) we have

$$|M_\ell|^2 \propto -\nu^2/|1+2\nu|^4 = \text{constant}. \quad (4.21)$$

On the other hand, in the same limit $k, b \rightarrow 0$, (D.2), (3.15), (D.18) and (D.19) give

$$\begin{aligned} |J_\nu(kz_0)|^2 &\rightarrow \text{constant}, \quad B_\ell \rightarrow 0 \\ |I_{-\nu+1}(\delta_\ell) - I_{\nu-1}(\delta_\ell)| &\propto \delta_\ell^{-1}. \end{aligned} \quad (4.22)$$

Substituting (4.21) and (4.22) into (4.17) and using the density of bound states (D.13), we find the contribution of the bound states $0 \leq b \leq b_0 \ll 1$ to $\alpha(k)$ as

$$\propto \int_0^{b_0} db \, \rho_D(k^2 + b^2) \frac{b}{k^2 + b^2} \quad (4.23)$$

which, for $D = 1$, diverges logarithmically in the limit $k \rightarrow 0$. That is, in the limit $k \rightarrow 0$, each of the contributions from very shallow bound states remains finite, and $\alpha(k)$ diverges logarithmically due to the linearly diverging density of bound states. However, as we have pointed out in Section I, the obtained infrared catastrophe does not imply a new surface many-body problem, but reveals a pathological aspect of the infinite 1-d model.

Finally, we have numerically evaluated (4.17) and (4.18) for the $D = 1, 2$ and 3 cases. Figure 9 contains sticking coefficients $\alpha(k)$ as functions of the wave number k . The parameters used are $z_0 = 0.5 \text{ \AA}$ and $\mu = 5.0$. Note that a logarithmic divergence of $\alpha(k)$ in the $D = 1$ case is spurious. Although the infinite 2-d model has in general the same pathological aspect as the 1-d model in that there can be no lattice formations in one and two dimensions just as there can be no spontaneous magnetizations in the isotropic Heisenberg model in these dimensions,²⁰ the spurious contribution of very soft phonons is suppressed by the decreasing phonon density of states at $q \rightarrow 0$ [cf. (4.14b)], as a tiny difference between $\alpha(0)$ and $\alpha(2)$ in the $D = 2$ curve demonstrates. The results for the cases $D = 2$ and 3 demonstrate finite $\alpha(0)$ for the inverse-square potential.

V. Summary

In this paper we have developed a new theory of quantum sticking coefficients at 0 K. Based on the dynamical Levinson's theorem, we have first considered the cases where the adatom-matter interaction potentials decay faster than x^{-2} . We have demonstrated that the many-body motion of adatom-matter system is not essential in determining the low-energy behavior of the sticking coefficients. The essence is instead in the long-distant part of the interaction. The theory predicts that $\alpha(k) \propto k$ at $k \leq k_c$, and that the critical

wave number k_c decrease with increasing long-range character of the adatom-matter interaction. To give a quantitative measure of k_c , we have introduced the standard number β in analogy to the "standard value" in the Lindeman melting formula. To determine β , we have considered a self-trapping model for the W-He system. By carrying out precise numerical evaluations of $\alpha(k)$, we have determined that $\beta \approx 0.6$. As a test of the present theory, we have then applied our results to the case of ^4He -atom colliding with a liquid ^4He surface, for which accurate experimental data are available. The theory predicts that $\alpha(k) \propto k$ at $k \leq 0.01 \text{ \AA}^{-1}$, in good agreement with experiments. Next, we have considered the inverse-square potential. Our study based on the dynamical Levinson's theorem has already verified that $k_c \rightarrow 0$ as the potential approaches the inverse-square one, which strongly indicates a finite $\alpha(0)$ for the inverse-square potential. We have carried out the one-phonon-mediated DWBA for the quantum sticking coefficient at 0 K and have shown that the inverse-square potential is a borderline distinguishing between "short-range" potentials for which $\alpha(0) = 0$ and long-range potentials for which $\alpha(0) \neq 0$. We note that the finite $\alpha(0)$ result of DWBA would hardly be changed qualitatively by including higher-order corrections. It is also noted that this result depends on the fact that the scattering wave function has a $\sqrt{k}$ -singularity in the small- k limit, in sharp contrast to the linear k -dependence in the case of short-range potentials, and therefore it is a general consequence of the inverse-square potential. In brief, the essence of quantum sticking coefficients at 0 K is in the k -dependence of the scattering wave function $|k^+\rangle$ in the low-energy limit $k \rightarrow 0$. For short-range potentials, $|k^+\rangle$ has a linear k -dependence which leads to a linearly vanishing $\alpha(k)$. On the other hand, for long-range potentials, $|k^+\rangle$ has a $\sqrt{k}$ -singularity leading to a finite $\alpha(0)$.

Acknowledgments

This research was supported by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009, the Office of Naval Research and the National Science Foundation under Grant CHE-8620274. The United States Government is authorized to reproduce and distribute reprints notwithstanding any copyright notation hereon.

Appendix A. Some Results about Morse Potentials

The one-body problem for a Morse potential,

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + D(e^{-\kappa x} - 2e^{-\kappa x}) \right\} \phi(x) = E\phi(x) , \quad (\text{A.1})$$

is exactly solvable.¹⁴ The bound states are

$$\phi_n = N_n e^{-z/2} z^{(K-2n-1)/2} F_n(z) , \quad (\text{A.2})$$

where

$$K \equiv 2\sqrt{2mD}/\hbar\kappa , \quad z \equiv Ke^{-\kappa x} , \quad (\text{A.3})$$

and the F_n 's are Laguerre polynomials,

$$F_n(z) = L_n^{K-2n-1}(z) \equiv \sum_{m=0}^n (-1)^m \binom{K-n-1}{n-m} \frac{z^m}{m!} \quad (\text{A.4})$$

satisfying the differential equation

$$z \frac{d^2 F}{dz^2} + (K-2n-z) \frac{dF}{dz} + nF = 0 . \quad (\text{A.5})$$

The corresponding binding energies are

$$E_n = -\frac{\kappa^2 \hbar^2}{8m} (K-2n-1)^2 \quad 0 \leq n \leq [(K-1)/2] . \quad (\text{A.6})$$

The normalization constant N_n is determined by the orthonormal condition

$$\begin{aligned} \delta_{ij} &= \int_{-\infty}^{\infty} dx \phi_i(x) \phi_j(x) \\ &= \frac{N_i N_j}{\kappa} \int_0^{\infty} dz e^{-z} z^{K-i-j-2} L_i^{K-2i-1}(z) L_j^{K-2j-1}(z) . \end{aligned} \quad (\text{A.7})$$

The integral in (A.7) is a special case ($\xi = 0$) of the Nieto and Simmons

integral¹⁶

$$J(K; i, j; \xi) \equiv \int_0^\infty dz e^{-z} z^{K-i-j-2+\xi} L_i^{K-2i-1}(z) L_j^{K-2j-1}(z) \\ = \sum_{m=0}^j (-1)^m \binom{K-j-1}{j-m} \frac{1}{m!} \frac{\Gamma(K-i-j-1+\xi+m) \Gamma(j+1-\xi-m)}{i! \Gamma(j-i+1-\xi-m)}, \quad (A.8)$$

where Γ is a gamma function. In particular,

$$J(K; i, i; 0) = \binom{K-i-1}{i} \Gamma(K-2i-1), \quad (A.9)$$

from which the normalization constant N_i is determined as

$$N_i = \sqrt{K! (K-2i-1)! / (i-1)!}. \quad (A.10)$$

Similarly,

$$\int_{-\infty}^{\infty} dx \phi_i \phi_j e^{ikx} = \frac{K! N_i N_j}{\kappa} J(K; i, j; -\ell). \quad (A.11)$$

Appendix B. Hermite Polynomials and Related Integrals

The Hermite polynomials

$$H_n(x) = \sum_{r=0}^{[n/2]} (-1)^r (2r-1)!! \binom{n}{2r} x^{n-2r} \quad (B.1)$$

have the properties

$$H_n'' - x H_n' + n H_n = 0 \quad (B.2)$$

$$H_{n+1} - x H_n + n H_{n-1} = 0 \quad (B.3)$$

$$H_n' = n H_{n-1} \quad (B.4)$$

$$\int_{-\infty}^{\infty} dx e^{-x^2/2} H_m H_n = \sqrt{2\pi} n! \delta_{mn} . \quad (B.5)$$

Using (B.2)-(B.4), we obtain

$$h_n'' = N_n e^{-T^2 x^2/4} T^2 (T^2 x^2/4 - 1/2 - n) H_n(Tx) . \quad (B.6)$$

With (B.3), (B.5) and (B.6) we have

$$\begin{aligned} P_{mn} &\equiv \int_{-\infty}^{\infty} dx h_m h_n'' \\ &= N_m N_n T \int_{-\infty}^{\infty} dx e^{-x^2/2} (x^2/4 - 1/2 - n) H_m H_n \\ &= \frac{T^2}{4} [-(2n+1) \delta_{mn} + \sqrt{(n+1)(n+2)} \delta_{m-1, n+1} \\ &\quad + \sqrt{n(n-1)} \delta_{m+1, n-1}] . \end{aligned} \quad (B.7)$$

Next, using the expansion (B.1) we have

$$\begin{aligned} Q_{mn}(A) &\equiv \int_{-\infty}^{\infty} dx h_m e^{-Ax} h_n \\ &= \frac{N_m N_n}{T} \sum_{r=0}^{[m/2]} \sum_{r'=0}^{[n/2]} (-1)^{r+r'} (2r-1)!! (2r'-1)!! \\ &\quad \times \binom{m}{2r} \binom{n}{2r'} \int_{-\infty}^{\infty} dx e^{-x^2/2 - Ax/T} x^{m-2r+n-2r'} \\ &= \frac{(-A/T)^{m+n}}{\sqrt{m!n!}} e^{A^2/2T^2} \sum_{r=0}^{[m/2]} \sum_{r'=0}^{[n/2]} \sum_{k=0}^{[(m+n)/2]-r-r'} (-1)^{r+r'} \\ &\quad \times (2r-1)!! (2r'-1)!! (2k-1)!! (A/T)^{-2r-2r'-2k} \\ &\quad \times \binom{m}{2r} \binom{n}{2r'} \binom{m+n-2r-2r'}{2k} . \end{aligned} \quad (B.8)$$

Using (A.11) and (B.8) we evaluate the integral

$$\begin{aligned}
 U_{lm,ij} &\equiv \frac{1}{D} \iint dx_s dx_a \phi_l(x_s) \phi_i(x_s) U(x_a - x_s) h_m(x_a) h_j(x_s) \\
 &= \int dx \phi_l \phi_i e^{2\kappa x} \int dx h_m h_j e^{-2\kappa x} - 2\{2\kappa \rightarrow \kappa \text{ in the first term}\} \\
 &= \frac{K^2 N_l N_i}{\kappa} J(K; l, i; -2) Q_{mj}(2\kappa) \\
 &\quad - 2 \frac{KN_l N_i}{\kappa} J(K; l, i; -1) Q_{mj}(\kappa) .
 \end{aligned} \tag{B.9}$$

Appendix C. Some Integrals Involving ϕ

First consider the integral

$$\begin{aligned}
 H_{lm} &\equiv \frac{2m}{\hbar^2} \iint dx_s dx_a \phi_l \phi_0 h_m e^{-ikx_a} \\
 &\quad \times \left\{ -\frac{\hbar^2}{2m} (-2ik\phi' + \phi'') + U(x_a - x_s) \phi \right\} \\
 &\equiv -\delta_{l0} A + \epsilon_g B .
 \end{aligned} \tag{C.1}$$

With (3.8), (3.10) and (B.3), A becomes

$$\begin{aligned}
 A &= (-2ikv/\sqrt{\pi} + 2\sqrt{2}v^2/\sqrt{\pi}) R(m, ik) \\
 &\quad - \frac{2v^3}{\sqrt{\pi}T} \{ \sqrt{m+1} R(m+1, ik) + \sqrt{m} R(m-1, ik) \} ,
 \end{aligned} \tag{C.2}$$

where we have defined

$$R(m, c) \equiv \int dx h_m e^{-cx} e^{-v^2(x - \sqrt{2}/v)^2} . \tag{C.3}$$

Using (3.8) and (B.1) and carrying out a standard Gaussian integral, we obtain

$$R(m, c) = \sqrt{2\pi/m!T} e^{-2} e^{(2\sqrt{2}u-c)^2/(T^2+4v^2)}$$

$$\begin{aligned}
& \times \sum_{r=0}^{[m/2]} \sum_{\ell=0}^{[m/2]-r} (-1)^r (2r-1)!! (2\ell-1)!! \binom{m}{2r} \binom{m-2r}{2\ell} \\
& \times \left(\frac{2T^2}{T^2+4v^2} \right)^{m-2r-\ell+1/2} \left(\frac{2\sqrt{2}v-c}{T} \right)^{m-2r-2\ell} .
\end{aligned} \quad (C.4)$$

As for the term B, from (3.4) and (A.11) it becomes

$$B = \frac{K^2 N_\ell N_0}{\kappa} J(K; \ell, 0; -2) Y(m, 2\kappa) - 2 \frac{KN_\ell N_0}{\kappa} J(K; \ell, 0; -1) Y(m, \kappa) , \quad (C.5)$$

where we have defined

$$Y(m, c) \equiv \int dx h_m \Phi e^{-(c+ik)x} . \quad (C.6)$$

Integrating by parts and using (3.8), (3.10), (B.3), and (B.4), we have

$$\begin{aligned}
Y(m, c) &= \frac{1}{c+ik} \frac{v}{\sqrt{\pi}} \int dx h_m e^{-(c+ik)x} e^{-v^2(x-\sqrt{2}/v)^2} \\
&+ \frac{1}{c+ik} \frac{T}{2} \{ \sqrt{m} Y(m-1, c) - \sqrt{m+1} Y(m+1, c) \} .
\end{aligned} \quad (C.7)$$

From (C.3) and (C.7) we have the recursion relation

$$\begin{aligned}
Y(m+1, c) &= - \frac{2(c+ik)}{T\sqrt{m+1}} Y(m, c) + \frac{\sqrt{m}}{\sqrt{m+1}} Y(m-1, c) \\
&+ \frac{2v}{T\sqrt{\pi}\sqrt{m+1}} R(m, c+ik) .
\end{aligned} \quad (C.8)$$

The first term $Y(0, c)$ cannot be evaluated analytically, but the dimension of integrations can be reduced from 2 to 1. In the expression

$$\begin{aligned}
W(c, T, k, v) \equiv Y(0, c) &= \int dx h_0 \Phi e^{-(c+ik)x} \\
&= \frac{N_0 v}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx e^{\frac{-T^2}{4}(x+\sqrt{2}/v)^2 - (c+ik)(x+\sqrt{2}/v)} \int_{-\infty}^x dt e^{-v^2 t^2} ,
\end{aligned} \quad (C.9)$$

we make the variable change $t \rightarrow x+t$, and the order of integrations as

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^x dt \rightarrow \int_{-\infty}^{\infty} dx \int_{-\infty}^0 dt \rightarrow \int_{-\infty}^0 dt \int_{-\infty}^{\infty} dx .$$

Carrying out a Gaussian integral over x , we reach the results

$$Y(0,c) = \frac{2N_0 v}{\sqrt{4v^2 + T^2}} e^{-2} e^{(c+ik-2\sqrt{2}v)^2/(4v^2+T^2)} \\ \times \int_{-\infty}^0 dt \exp\left[-\frac{v^2 T^2}{4v^2+T^2} \left\{t^2 - \frac{4}{T^2}(T^2/\sqrt{2}v + c + ik)t\right\}\right] . \quad (C.10)$$

Next consider integrals which involve the error function ϕ twice. First consider

$$H_{ss}^1(k) \equiv -\frac{2m}{\hbar^2} \iint dx_s dx_a \phi_0^2 \phi^2 e^{2ikx_a} U(x_a - x_s) \\ = -\frac{\epsilon_K K^2 N_0^2}{\kappa} J(K;0,0;-2) G(k,2\kappa) + \frac{2\epsilon_K K N_0^2}{\kappa} J(K;0,0;-1) G(k,\kappa) , \quad (C.11)$$

where

$$G(k,c) \equiv \int dx \phi^2 e^{(2ik-c)x} . \quad (C.12)$$

With the use of (3.10), an integration by parts and (C.9), we have

$$G(k,c) = \frac{e^{-2}}{c-2ik} \sqrt{\frac{4u}{\sqrt{2\pi}}} W(c-2\sqrt{2}v, 2v, -2k, v) . \quad (C.13)$$

We must also carry out the following integrations:

$$H_s^2 \equiv \int dx \phi(\phi''-2ik\phi') = -(ik+v/\sqrt{2\pi}) . \quad (C.14)$$

$$H_{ss}^2 \equiv \int dx \phi(\phi''+2ik\phi') e^{2ikx} = -\frac{v}{\sqrt{2\pi}} e^{-k^2/2v^2 + 2\sqrt{2}ik/v} . \quad (C.15)$$

H_s and H_{ss} in (3.13) are then given by

$$H_s = H_{ss}^1(0) + H_s^2 . \quad (C.16)$$

$$H_{ss} = H_{ss}^1(k) + H_{ss}^2 \quad . \quad (C.17)$$

Appendix D. Solution of (4.15)

The solution of (4.15) can be written as

$$\psi = \sqrt{z} [AJ_{\nu}(\epsilon z) + BJ_{-\nu}(\epsilon z)] \quad , \quad (D.1)$$

where $\gamma \equiv 1/4 - \nu^2 \equiv 1/4 + \mu^2$, and A and B are constants of integration. J_{ν} is the Bessel function of the first kind,¹⁸

$$J_{\nu}(z) = (z/2)^{\nu} \sum_{n=0}^{\infty} \frac{(-1)^n (z/2)^{2n}}{n! \Gamma(\nu + n + 1)} \quad . \quad (D.2)$$

Since (4.15) is real, we can take ψ as real. First consider a scattering state, where $\epsilon = k$ is positive. Noting that $J_{\nu}^*(z) = J_{-\nu}(z)$, we can satisfy the reality condition and the boundary condition $\psi(z_0) = 0$ by taking

$$B^* = A = iJ_{-\nu}(kz_0) \quad . \quad (D.3)$$

With (D.1) and (D.3) we now write the scattering state as

$$|k^+\rangle = iN_k \sqrt{z} [J_{\nu}(kz)J_{-\nu}(kz_0) - J_{-\nu}(kz)J_{\nu}(kz_0)] \quad . \quad (D.4)$$

To find the normalization factor N_k , note the asymptotic property at $|z| \rightarrow \infty$,¹⁸

$$J_{\nu}(z) \sim \sqrt{\frac{2}{\pi z}} \cos(z - \frac{2\nu + 1}{4} \pi) \quad . \quad (D.5)$$

By setting the prefactor of the e^{-ikz} component in $|k^+\rangle$ at $z \rightarrow \infty$ equal to 1, N_k is given by

$$\begin{aligned} N_k &= \sqrt{2\pi k} |J_{-\nu}(kz_0) e^{-\pi\mu/2} - J_{\nu}(kz_0) e^{\pi\mu/2}|^{-1} \\ &= \sqrt{2\pi k} e^{-\pi\mu/2} / |J_{\nu}(kz_0)| \quad , \end{aligned} \quad (D.6)$$

where in the second expression we have assumed $\mu \gg 1$. The case $\mu \leq 1$ corresponds to an unrealistically narrow and deep potential. A particular interest is in the limit $k \rightarrow 0$, where from (D.2), (D.4) and (D.6) we have for $z \ll k^{-1}$

$$|k^+\rangle_{k \rightarrow 0} = i\sqrt{kz/\mu} [(z/z_0)^\nu - (z/z_0)^{-\nu}] \propto \sqrt{k} . \quad (D.7)$$

This $\sqrt{k}$ -singularity of the scattering state $|k^+\rangle$ is in sharp contrast to the linear k -dependence of $|k^+\rangle$ for the short-range potentials, (2.12). As we see in the text, this is the key point of finite $\alpha(0)$ for the inverse-square potential.

Next we consider bound states. In this case, $\epsilon = ib$ ($b = \text{positive}$). The reality condition is met by taking

$$B = A^* e^{-\pi\mu} . \quad (D.8)$$

On the other hand, the finiteness requirement for the wave function at $z \rightarrow \infty$ leads to a pure imaginary A . With (D.8) and the fact that A is pure imaginary, the boundary condition $\psi(z_0) = 0$ provides the quantization of bound states,

$$I_\nu(bz_0) - I_{-\nu}(bz_0) = 0 , \quad (D.9)$$

where $I_\nu(z)$ is the modified Bessel function of the first kind.¹⁸

Alternatively, one can look at the Jost function $f(-k)$, the prefactor of the e^{-ikz} component in the scattering state $|k^+\rangle$ at $z \rightarrow \infty$,

$$f(-k) = J_\nu(kz_0) e^{\pi\mu/2} - J_{-\nu}(kz_0) e^{-\pi\mu/2} , \quad (D.10)$$

whose zeroes at $k = ib$ in the complex k -plane describe the bound states. The condition $f(-ib) = 0$ is nothing but (D.9). Unlike the short-range potentials studied in Section II, the inverse-square potential has an infinite number of

bound states. To see this, consider the limit $bz_0 \rightarrow 0$. In this limit, only the $n = 0$ term in the power series expansion of $I_\nu(z)$,¹⁸

$$I_\nu(z) = (z/2)^\nu \sum_{n=0}^{\infty} \frac{(z/2)^{2n}}{n! \Gamma(\nu + n + 1)} \quad , \quad (D.11)$$

is kept and the quantization condition (D.9) becomes

$$b = \frac{2}{z_0} e^{\frac{1}{2\nu}} \frac{\Gamma(1+\nu)}{\Gamma(1-\nu)} e^{-\frac{\pi n}{\mu}} \quad , \quad (D.12)$$

where n is any integer such that $bz_0 \ll 1$. That is, there are infinitely-many shallow bound-states, whose density of states diverges at $b \rightarrow 0$ as

$$\rho(b) = \mu/\pi b \quad . \quad (D.13)$$

Finally, to normalize the bound states, we use (D.8) and $\text{Re}A = 0$ to write

$$|b\rangle = iN_b \sqrt{z} [I_\nu(bz) - I_{-\nu}(bz)] \equiv iN_b \sqrt{z} \left[-\frac{2\sin(\pi\nu)}{\pi} K_\nu(bz) \right] \quad . \quad (D.14)$$

With the property¹⁹

$$\left\{ \frac{z^2}{2} [K_\nu^2(\zeta z) - K_{\nu-1}(\zeta z) K_{\nu+1}(\zeta z)] \right\}' = z K_\nu^2(\zeta z) \quad , \quad (D.15)$$

the normalization integral is carried out to give

$$N_b = \frac{\sqrt{2}}{z_0} \frac{\pi}{2\sinh\mu} [K_{\nu-1}(bz_0) K_{\nu+1}(bz_0)]^{-\frac{1}{2}} \quad . \quad (D.16)$$

It is noted that $K_\nu(bz_0) = 0$ due to (D.9) and (D.14). With the use of (D.14) and the recursion formula¹⁸

$$I_{\nu-1}(z) - I_{\nu+1}(z) = (2\nu/z) I_\nu(z) \quad , \quad (D.17)$$

(D.16) can be written as

$$N_b = \frac{\sqrt{2}}{z_0} |I_{-\nu+1}(bz_0) - I_{\nu-1}(bz_0)|^{-1}, \quad (D.18)$$

which is more suitable for numerical calculations based on (D.11). In particular, in the limit $b \rightarrow 0$, from (D.11), (D.12) and (D.18), we have

$$N_b \propto b |1 - (bz_0/2)^{2/\nu(1-\nu)}|^{-1} \propto b. \quad (D.19)$$

Appendix E. Evaluation of (4.18)

Here we give some technical remarks on the numerical evaluation of (4.18). Using $\bar{k} \equiv kz_0$ and $\bar{b} \equiv bz_0$, one can write (4.18) as

$$M_l = \frac{1}{z_0} [J_{-\nu}(\bar{k}) O(\bar{b}, \bar{k}) + \text{c.c.}] \quad (E.1)$$

where

$$O(\bar{b}, \bar{k}) \equiv \int_1^\infty dz z^{-2} [I_\nu(\bar{b}z) - I_{-\nu}(\bar{b}z)] J_\nu(\bar{k}z). \quad (E.2)$$

The first thing to do is to replace ∞ by a finite z_m in (E.2). For a given $\bar{b}$, z_m is roughly a classical turning point of the potential (4.11),

$$z_m \approx \sqrt{\gamma}/\bar{b}. \quad (E.3)$$

Next we evaluate the Bessel functions $I_\nu = I_\nu^*$ and J_ν for the variable ranges $\bar{b} \leq \bar{b}z \leq \sqrt{\gamma}$ and $\bar{k} \leq \bar{k}z \leq \bar{k}z_m$. For a realistic situation $\sqrt{\gamma} \leq 10$, the Bessel function $\tilde{I}_\nu$ can be evaluated accurately by the power series expansion (D.11). On the other hand, even for an interesting situation, $\bar{k} \sim 1$, $\bar{k}z_m \approx \bar{k}\sqrt{\gamma}/\bar{b}$ can be large for small $\bar{b}$. We have found that the power series expansion (D.2) is good for $z \leq 30$. For $z > 30$, one can use Hankel's asymptotic expansion,¹⁸

$$J_\nu(z) = \sqrt{\frac{2}{\pi z}} [P(\nu, z) \cos(z - \frac{2\nu+1}{4}\pi) - Q(\nu, z) \sin(z - \frac{2\nu+1}{4}\pi)] \quad (E.4)$$

where with $\xi \equiv 4\nu^2$,

$$P(\nu, z) = 1 - \frac{(\xi-1)(\xi-9)}{2! (8z)^2} + \frac{(\xi-1)(\xi-9)(\xi-25)(\xi-49)}{4! (8z)^4} \dots \quad (\text{E.5})$$

$$Q(\nu, z) = \frac{\xi-1}{8z} - \frac{(\xi-1)(\xi-9)(\xi-25)}{3! (8z)^3} + \dots \quad (\text{E.6})$$

Though it is a bit time-consuming, the integral representation¹⁸

$$I_\nu(z) = \frac{(z/2)^\nu}{\sqrt{\pi} \Gamma(\nu + \frac{1}{2})} \int_0^\pi d\theta \cos(z \cos \theta) \sin^{2\nu} \theta \quad (\text{E.7})$$

is good for an arbitrary argument z . A caution for the integration in (E.7) is that at small $\theta \ll 1$, the integrand oscillates with a period $\sim \theta$.

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Figure Captions

1. (a) Three-dimensional geometry for the scattering eigenstate characterized by the parallel and perpendicular wave numbers, k_x and k_z .
 (b) One-dimensional simplification when the parallel and perpendicular motions are approximately separable.
 (c) Two-dimensional T-shape model for low-temperature adsorption.
2. Static square-well potential.
3. Schematic figure of the reduced potential $U(x)$ and its modifications (dashed lines) in the region $R' < x < R$.
4. k_c as a function of the exponent n for $\gamma = 20$ and $\beta = 0.6$.
5. Self-trapping model for He adsorption on W.
6. One-particle energy spectra for the surface W-atom and He-atom.
7. (a) $|S|$ and $\text{Re}S$ vs. k . It is seen that $S \rightarrow 1$ as $k \rightarrow 0$.
 (b) $\alpha(k)$ vs. k . Below $k_c \sim 0.1 \text{ \AA}^{-1}$, α has an approximate linear dependence on k .
8. The solid curve is the long-range potential (4.11) in the unit of $\text{\AA}^{-2}$ with $z_0 = 0.5 \text{ \AA}$ and $\mu = 5.0$. The horizontal solid lines denote its bound states calculated from (D.9). Bound states with very small energies are described by (D.12).
9. $\alpha(k)$ vs. k for $D = 1, 2$ and 3 . The parameters are $z_0 = 0.5 \text{ \AA}$ and $\mu = 5.0$. For the $D = 1$ case, a spurious logarithmic singularity is seen for small k , as described in the text. The other cases $D = 2$ and 3 demonstrate finite quantum sticking coefficients at $k \rightarrow 0$.

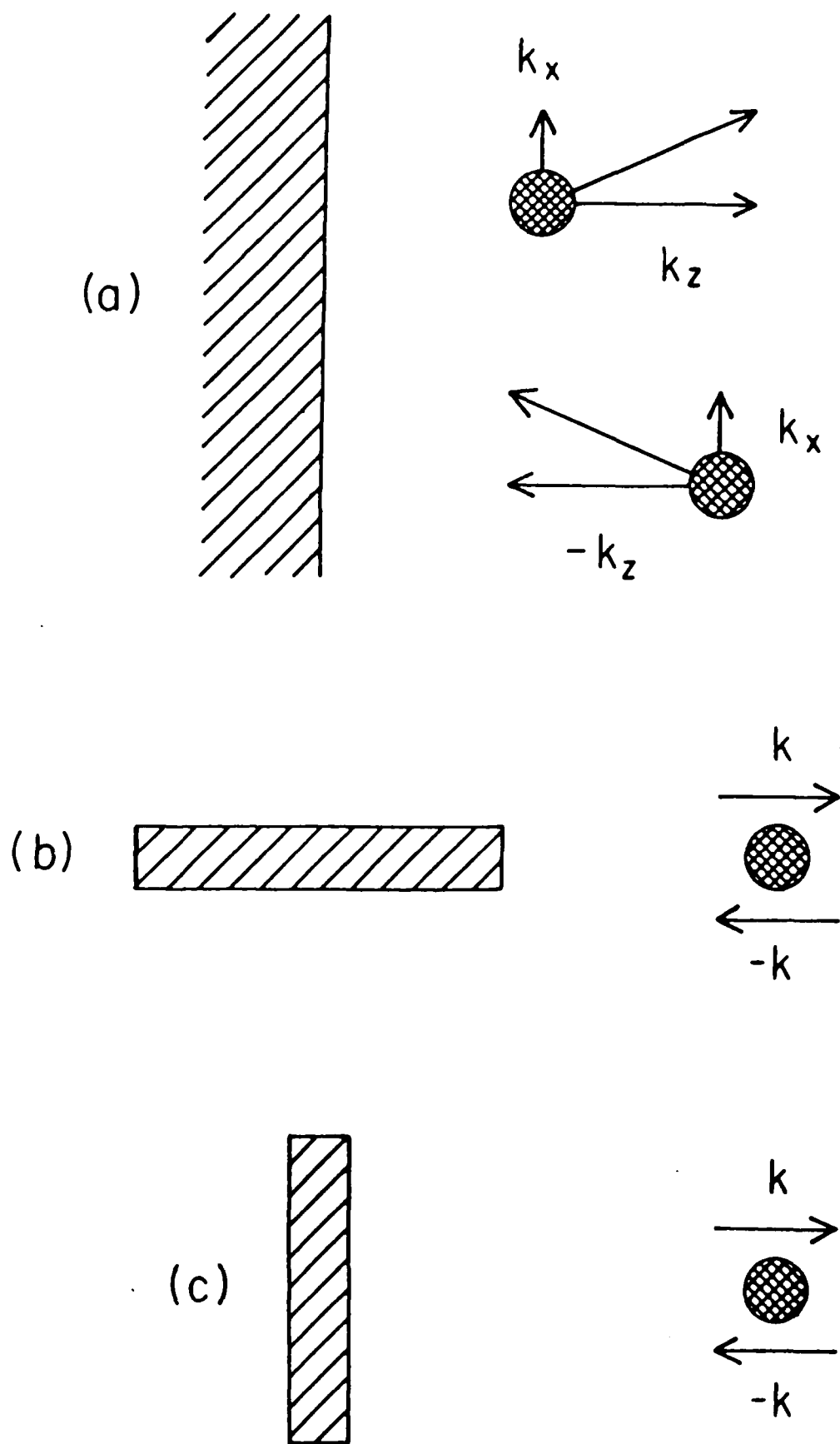


Fig. 1

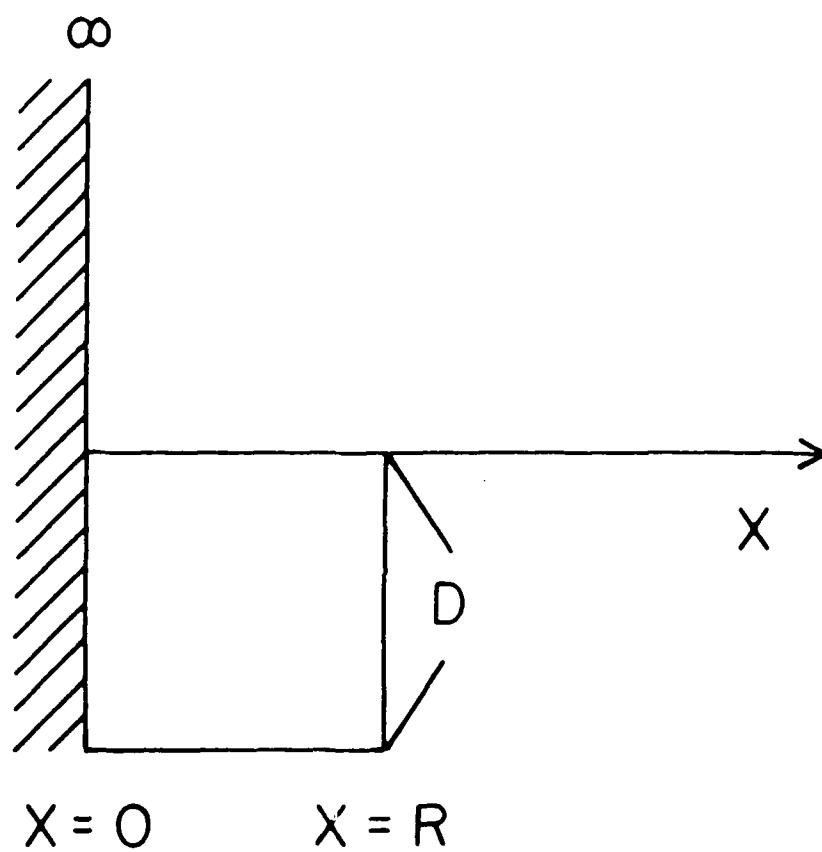


Fig. 2

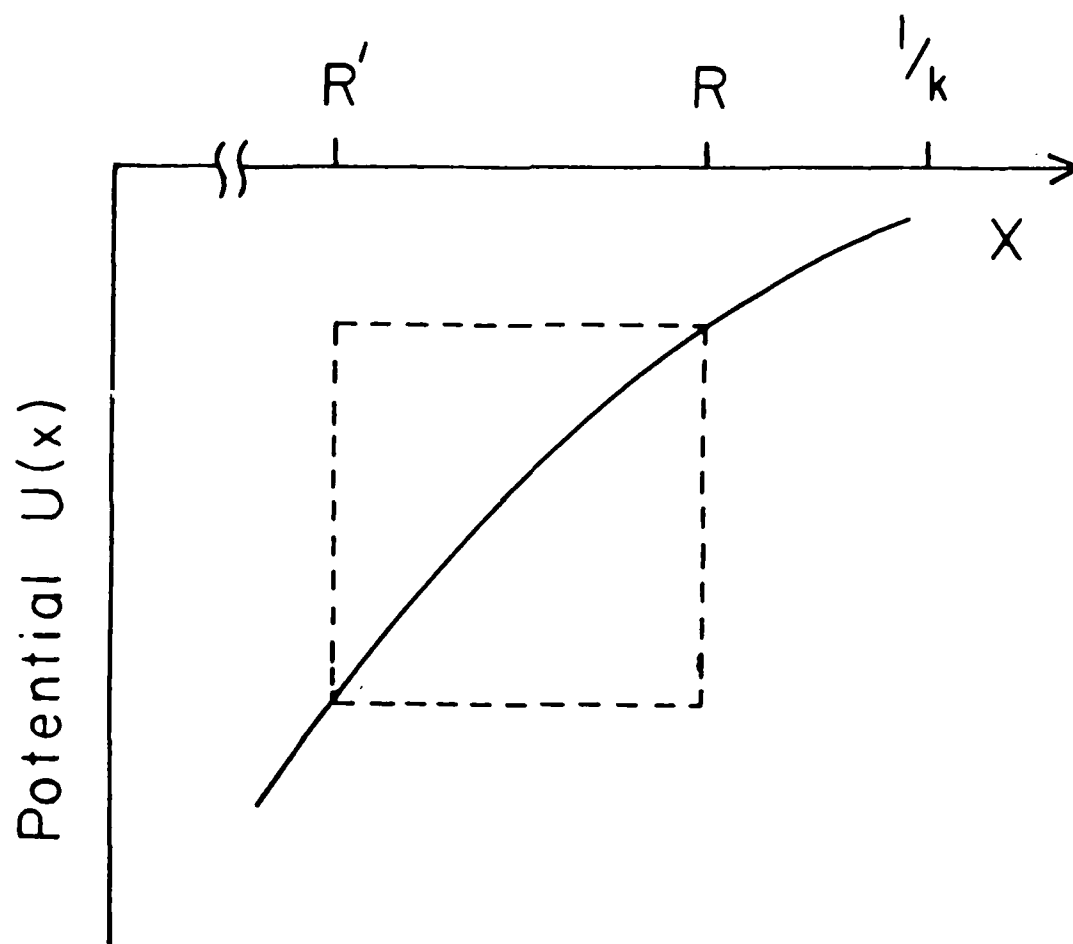


Fig. 3

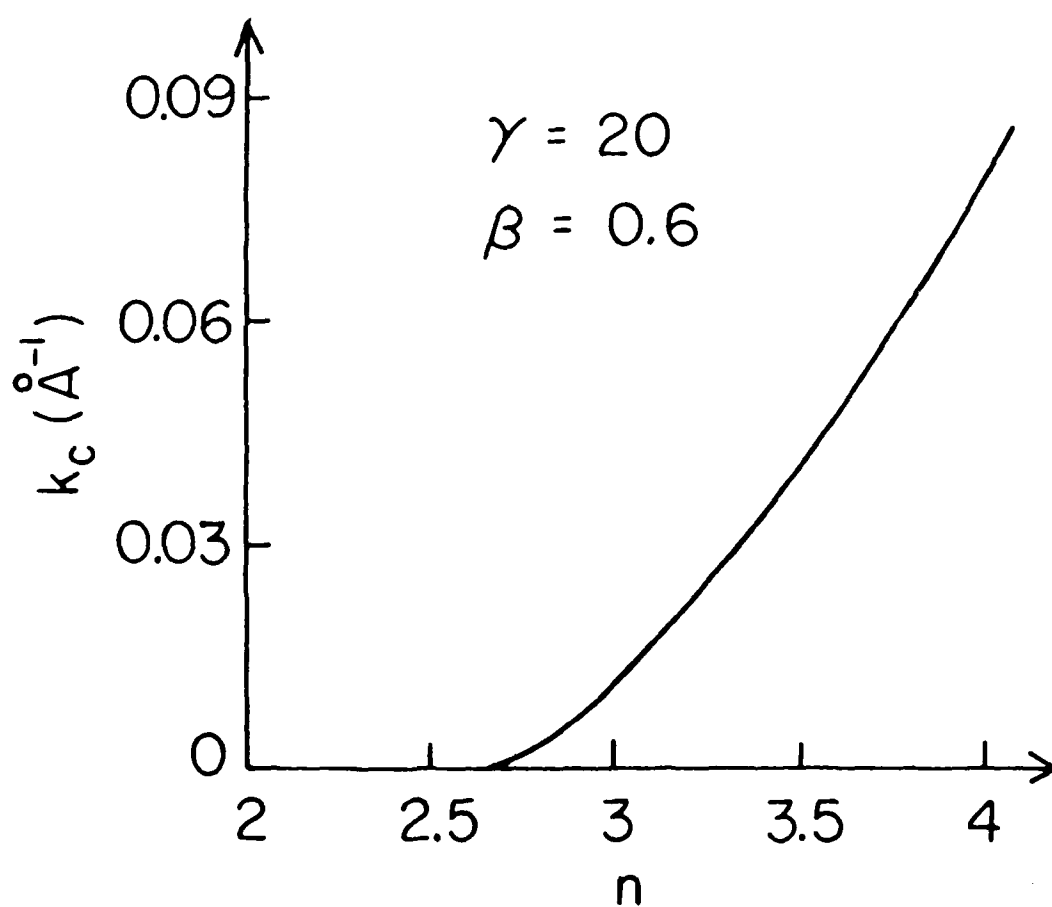


Fig. 4

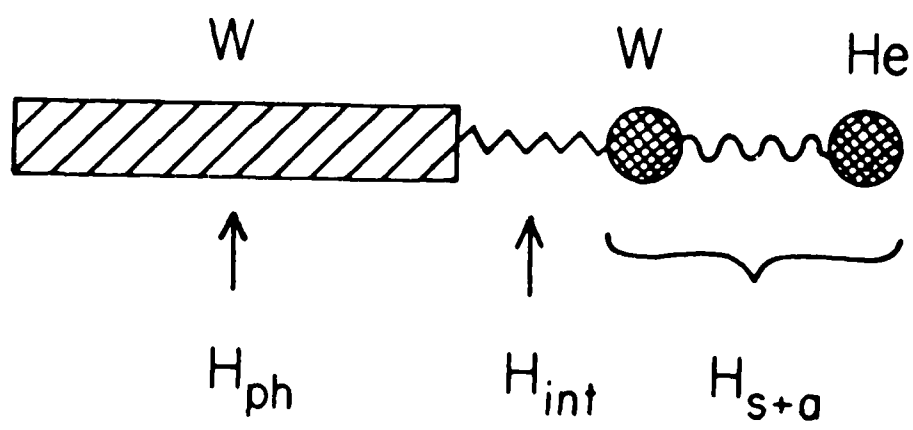


Fig. 5

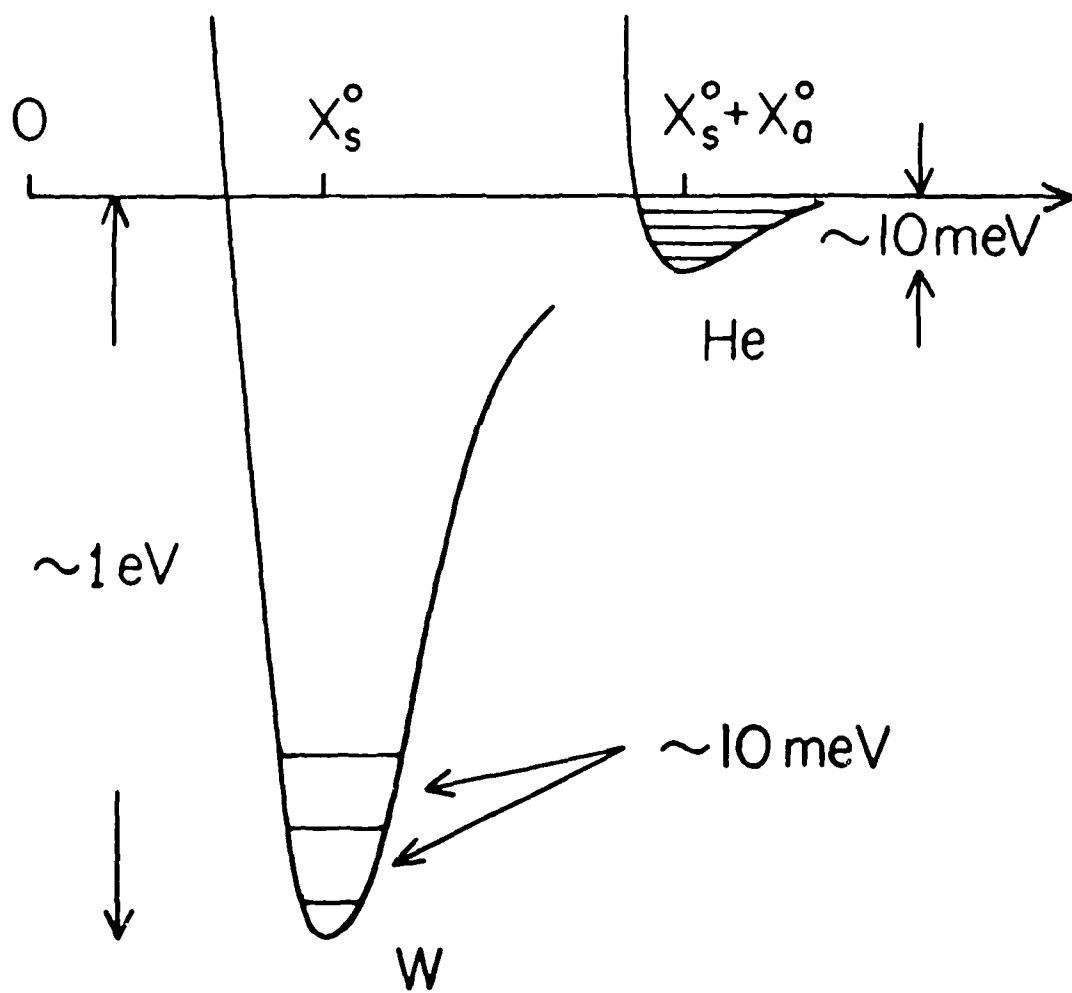
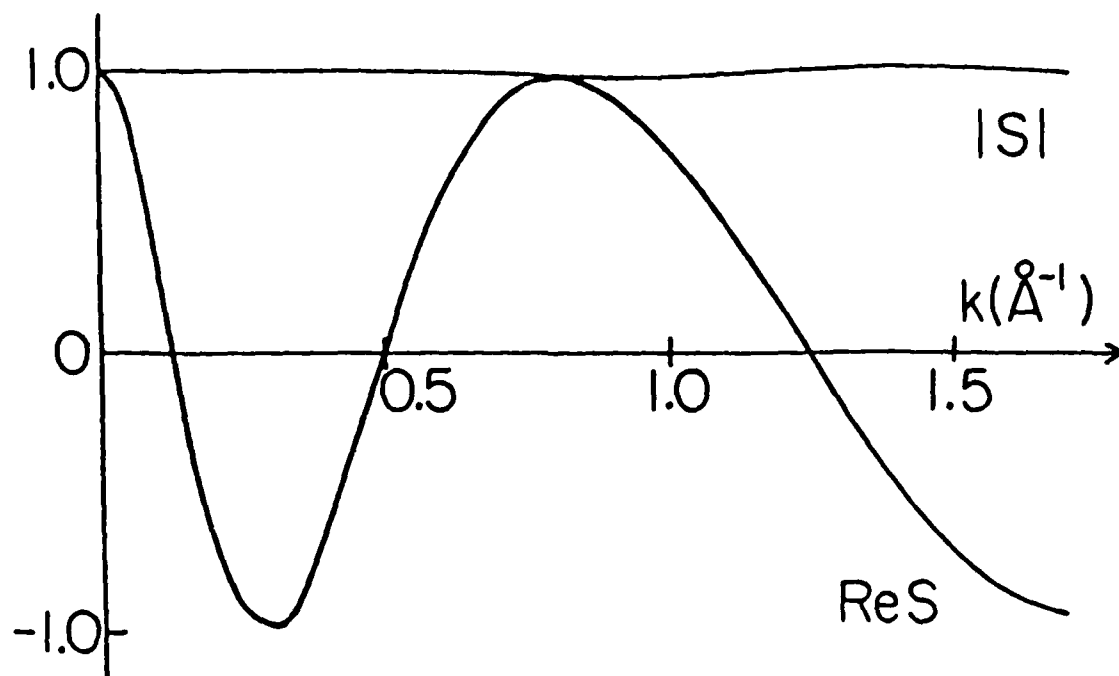
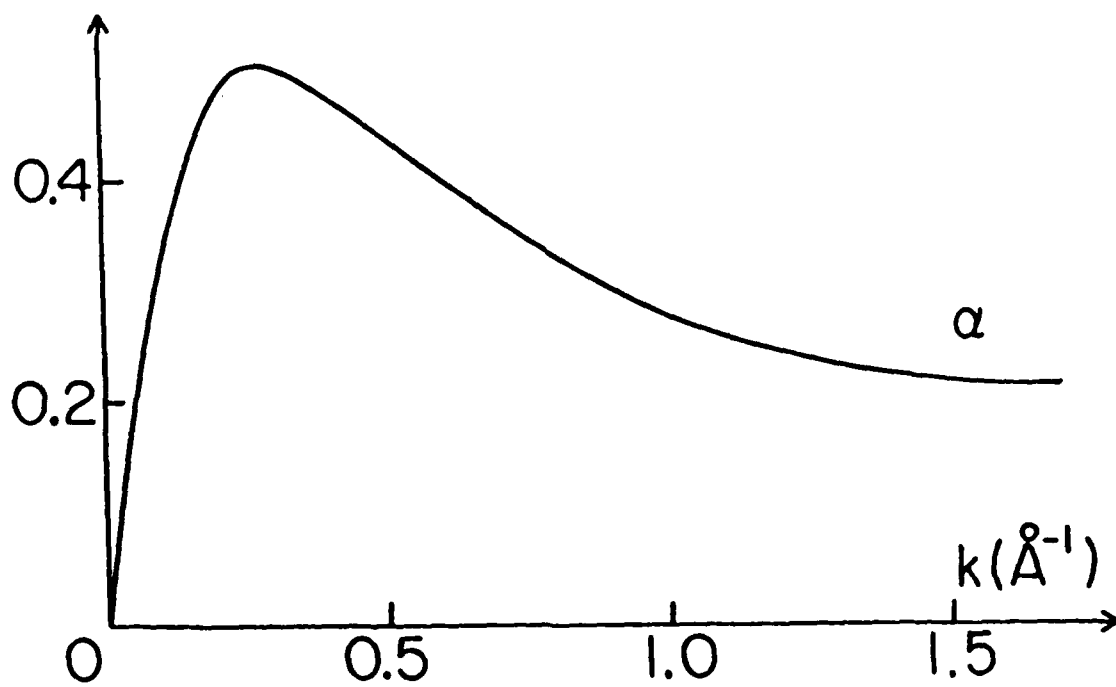


Fig. 6



(a)



(b)

Fig. 7

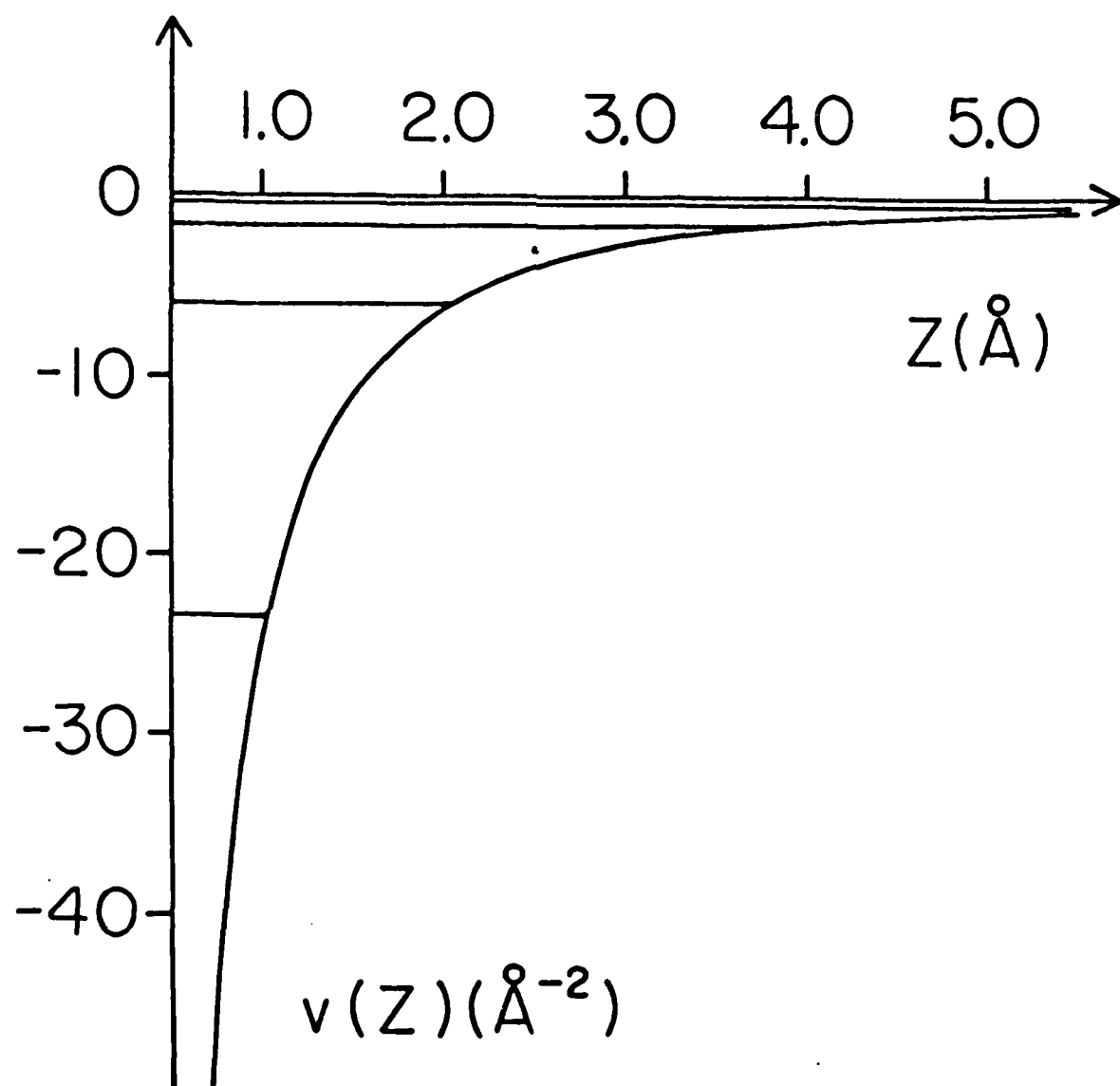


Fig. 8

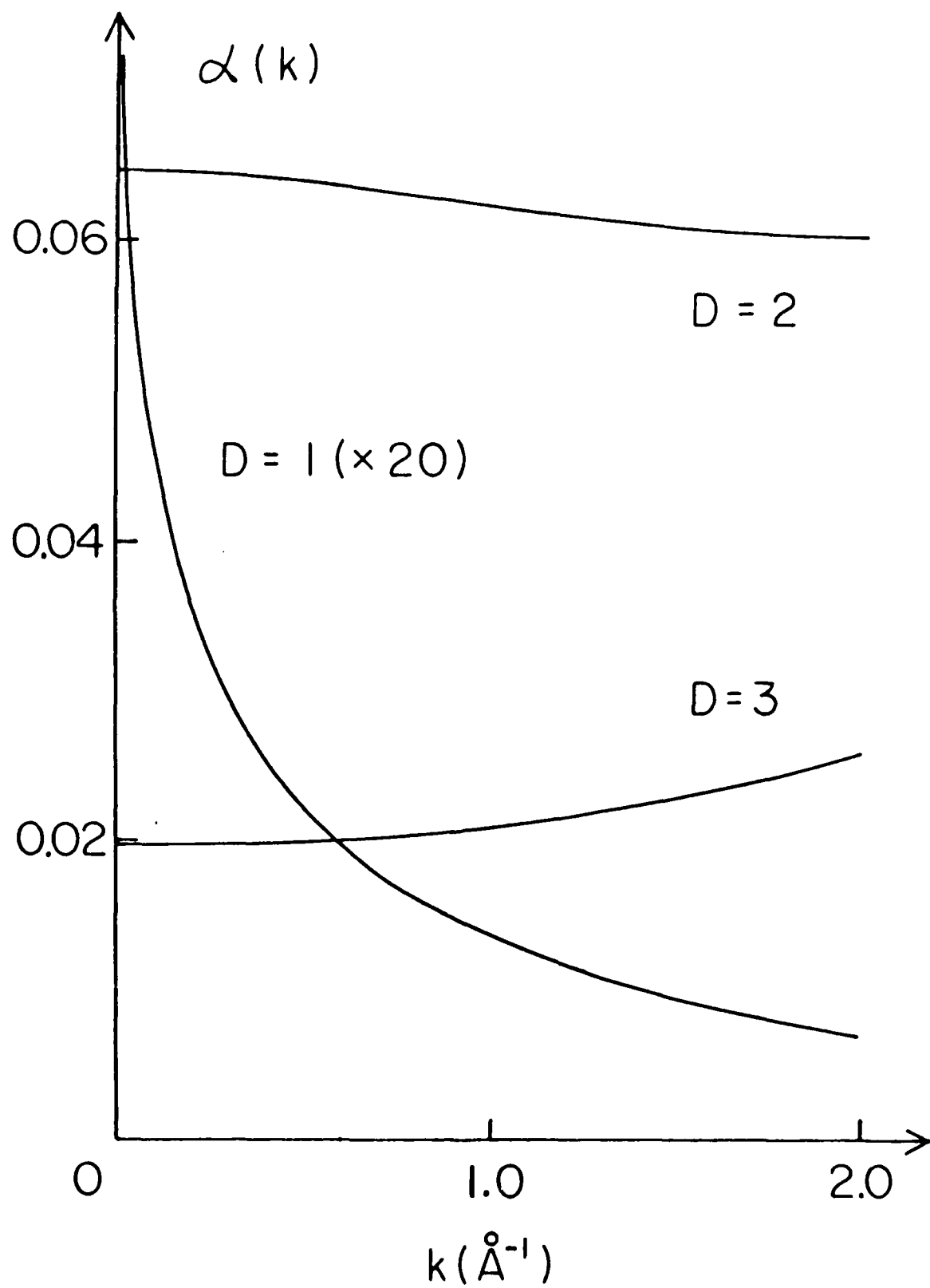


Fig. 9

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