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# Adhesion in Atomic Scale Metal Contacts

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# Adhesion in Atomic Scale Metal Contacts

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**Abstract:** The adhesion interaction of an Ir tip with Ir and Al surfaces has been investigated using the scanning tunneling microscope. Qualitative differences in the adhesion characteristics have been observed. A cluster model based on effective pair-potentials has been set up to understand adhesion in atomic scale contacts. The model calculation provides a semi-quantitative explanation of the experimental data. In particular it is shown that subtle differences of the atomic interaction potentials have a significant effect on the contact mechanics.

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The study of metallic adhesion has a long history yet our understanding of atomic scale processes is still sketchy [1]. Valuable insight has been provided by recent molecular dynamics simulations [2] but very little is known experimentally about the short-range chemical adhesion interaction which is responsible for the metallic bonding in the contact zone.

In this letter we focus on the interaction between a very sharp metal tip and a flat metal surface. The interaction is investigated experimentally using an ordinary scanning tunneling microscope (STM) with a cantilever spring (CB) as sample stage. The tip of the STM serves simultaneously as a force probe and for tunneling. The latter is exploited to establish a well-defined distance between probe tip and sample. Direct measurement of the tip-sample force is difficult because stiff CBs must be employed to prevent instabilities of the gap. The force gradient, $\nabla F$, on the other hand, is readily detected by means of a dynamic measurement [3]. The basic principle is that the force gradient couples the tip to the CB causing the resonance frequency of the CB to shift in proportion to $\nabla F$.

Experiments were conducted under ultrahigh vacuum conditions ($p \leq 3 \times 10^{-10}$ mbar). Tunneling tips were made of mechanically sharpened Ir wire. Final tip forming was performed *in situ*. Ir samples were prepared by extensively sputter cleaning the surface of CBs made of polycrystalline Ir sheet metal. Typical length, width, and thickness of the beams were 5 mm, 0.5 mm and 50 $\mu$m, respectively, yielding a resonance frequency of $\simeq$1.5 kHz. The spring constant – typically on the order of 100 $\mathrm{Nm}^{-1}$ – was adjusted by positioning the tip between the clamped and the free end of the CB which had a nominal spring constant of $\simeq$50 $\mathrm{Nm}^{-1}$. Al samples were prepared by condensing thin films ($\simeq$1000 Å) onto a substrate Ir-CB at room temperature and a base pressure of $p < 5 \times 10^{-10}$ mbar [4].

The interaction force gradient was measured as a function of tip-sample distance, $z$, defined as the displacement of the tip with respect to a reference position characterized by a specific value of the tunnel resistance, $R_T = 10^7\,\Omega / 10^8\,\Omega$ for the Ir and Al samples, respectively. With the tip at the reference position, the feedback loop which adjusts for a constant tunneling current was interrupted and the tip was ramped towards the surface at a rate of $\simeq 1\,\text{Å}\,s^{-1}$. The tunneling current and the resonance frequency were simultaneously recorded during approach. In order to prevent accidental touching of the surface the tip was rapidly retracted to the reference position as soon as the tunneling resistance dropped below $\simeq 100\,\text{k}\Omega$. After each approach cycle the feedback loop was turned on for 100 ms to compensate for possible drifts.

The results of the experiments are summarized in Fig. 1. Each curve represents an average of 64 approach cycles. Interaction force gradients measured on the Ir sample are negative and rapidly increase in magnitude as $z$ approaches $\simeq -2.6\,\text{Å}$ which is the maximum tip excursion allowed by the tunnel resistance constraint. The observed adhesion characteristics are roughly consistent with the concepts of universal adhesion developed by Rose et al. [5,6]. In a separate experiment the tunnel resistance limit was ignored in order to probe the contact regime. At $z \simeq -2.7\,\text{Å}$ the tunnel resistance abruptly drops by one order of magnitude and subsequently levels off at $\simeq 10\,\text{k}\Omega$. We were not able to measure interaction force gradients reliably in this regime. In addition hysteresis effects were observed which point to irreversible changes of the atomic structure of the tip or the sample surface. The tunnel resistance curve for $z < -2.6\,\text{Å}$ is therefore complemented by one representative example. Adhesion as well as tunnel resistance characteristics for the Al sample are distinctively different. At large tip-sample distance the interaction force gradient is negative, similar to the Ir

sample, but its magnitude does not increase monotonically with decreasing gap width. Instead, a minimum is observed and eventually the force gradient even becomes positive. Exponential tunnel resistance characteristics are observed in the regime of negative interaction force gradients. Simultaneously with the force gradient becoming positive the tunnel resistance curve levels off and approaches a value of $\simeq$100 k$\Omega$. No indication of a discontinuity in the the tunnel resistance at small gap widths can be discerned. However, the tunneling current was significantly less stable for the Al samples than for the Ir samples.

To understand adhesion in atomic scale metal contacts, we have set up a cluster model to calculate the forces between a metal tip and a flat metal surface. The surface is that of a three-layer cluster of hexagonal symmetry with a total of 211 atoms. The tip consists of a base layer of 48 atoms, a second layer of 12 atoms and a single additional atom on top of that. Clusters of this size cannot be treated *ab initio* at present, so the semi-empirical embedded atom method is an attractive alternative [7]. Unfortunately, the relevant parameters for Ir have not been determined as yet. We therefore resort to a model in which the total energy is calculated by summing nearest neighbor two-body interactions. For this we could use the interaction between two isolated atoms, calculated by some first-principles method. Summing such (pure) two-body interactions to obtain the energy of large clusters would, however, ignore all many-body effects in metals. We therefore determine effective nearest neighbor interactions by calculating smaller clusters consisting of seven atoms arranged in two parallel triangles with the seventh atom in between. To get the effective interaction energy between two like atoms, we assume all distances, $d$, in the cluster to be the same and define

$$v_{m-m}(d) = \frac{1}{6}(E_7 - 2E_3 - E_1) \qquad (1)$$

where $E_n$ is the total electronic energy of a cluster consisting of $n$ atoms. To get the effective two-body interaction between two different metals, we take a tetrahedral cluster of the first metal interacting with a triangular cluster of the second metal at a distance $d$ from the tip of the tetrahedron and define

$$V_{m_1-m_2}(d) = \frac{1}{3}(E_7 - E_3^{(m2)} - E_4^{(m1)}) \ . \qquad (2)$$

The bond lengths in the individual clusters are adjusted to minimize the respective energies, thus obtaining their respective equilibrium geometries. For the calculation of (1) and (2) we have used the ASED-MO method, a semi-empirical tight-binding model with matrix elements calculated in an extended Hückel scheme [8]. In Fig. 2 we plot (1) and (2) rescaling the energy, $V$, and the distance, $d$, by the respective values at the potential minimum. The Ir-Ir potential (solid line) falls off exponentially with a decay constant as expected from universality theory [5]. It is important for our present study that the Al-Al potential (dotted line) is different. In particular, it falls off much more slowly with decay constants varying with distance, features that cannot be reconciled within the concept of universality. Similar behavior has been found in an earlier calculation [9]. The rescaled potential for the Ir-Al interaction (dashed line) is qualitatively similar to the Al-Al potential except that it decays more rapidly at large separations. To test the reliability of the ASED-MO method, we have calculated the Al-Al interaction (1) using spin density functional theory with both local and nonlocal approximations to the exchange and correlation energy [10]. As expected, we find a smaller binding energy for the Al-Al system but the rescaled curve is in very good agreement with the ASED-MO results. As a final check on the quality of the effective two-body interaction (1) as determined by the ASED-MO method,

we calculate the energy of a large cluster of up to 211 metal atoms by summing nearest neighbor interactions pairwise and minimizing the lattice constant. For the latter we typically achieve agreement with experimental values of within 0.05 Å.

In the first set of calculations of the interaction energies and the force gradients between an Ir tip and a planar Ir and Al surface, we kept the lattice spacings in both clusters at their equilibrium positions, see dashed curves in Fig. 3. Note that the nominal gap width $Z$ measures the distance between the apex atom and the top atomic layer of the sample. The nominal gap width minus a constant offset corresponds to the experimental tip excursion scale $z$. The experimental data (Fig. 1) is reproduced rather well for the Ir surface. However, the calculated force gradient of the Al surface deviates significantly from the measured data: being in particular, one order of magnitude too large (right-hand scale in Fig. 3b). Good qualitative agreement is achieved by replacing the Ir atom at the apex of the tip by an Al atom (dotted curve). It is conceivable that the tip accidentally touched the Al surface in the course of the experiment and that some Al atoms were picked up by the tip (note that the tunneling current exhibited substantial fluctuations with the Al samples). The measured force gradient is slightly larger than that predicted by the model calculation. The discrepancy can be explained by the fact that the latter assumes a single atom tip whereas such a perfect tip geometry was most likely not achieved in the experiment.

In the second calculation the positions of the tip and sample atoms are allowed to relax in response to the interaction forces that keep the base layers of each cluster fixed. Tip and surface relaxations along the tip axis are shown in Fig. 4 as solid and dashed curves, respectively. Relaxation causes the actual gap width, defined as the average separation between the tip atom and the nearest

atoms in the surface, to decrease more rapidly than $Z$. Correspondingly the force gradient curves also change as shown by the solid curves in Fig. 3. Relaxation effects are particularly pronounced for the Ir-Ir system (Fig. 4a). At the onset of making contact, the apex atom on the tip has moved towards the surface by as much as 0.5 Å with a smaller upward motion of the surface atoms under the tip. With the tip atom more or less hovering between the two clusters to form a metallic bridge. This sudden change explains why the tunneling resistance drops abruptly at very small gap widths.

For the Al-coated Ir tip approaching an Al surface, much smaller force gradients are obtained as a consequence of the peculiarity of the Al-Al potential, see Fig. 2. Correspondingly, relaxation of the atomic positions (Fig. 4b) is substantially smaller; it does not exceed a tenth of an angstrom. Note that the outwards motion of the apex and surface atoms is reversed when the force gradient is positive. This feature stabilizes the gap to a certain degree. A steep rise of the atomic displacements is also obtained. The discontinuity is not nearly as dramatic as for the Ir-Ir system and it occurs much closer to the equilibrium position where atomic displacements become zero again. No evidence for a jump to contact was observed in the experiment, however, and this might be explained by the smallness of the atomic displacements.

As a final point we should comment on the fact that the distance scale of the theoretical force gradients is smaller than the experimental data by about a factor of 1.5. We can see two reasons for this discrepancy. (i) Our effective nearest neighbor interactions account well for only the short-ranged interactions, but should be modified at large separations by a more slowly varying dispersion like force. (ii) Our model calculation assumes close-packed surfaces whereas

polycrystalline samples were investigated in the experiment and hence the surfaces of the samples were not perfectly smooth on an atomic scale. Therefore the actual gap width fluctuates slightly depending on the lateral tip position which in turn leads to a broadening of the measured force gradient curves.

In summary qualitative differences in the adhesion interaction of an Ir tip with Ir and Al surfaces have been observed experimentally. They can be understood to arise (i) from small deviations from universality in the effective nearest neighbor interaction and (ii) from the deformation of the lattice as the tip approaches. There is a direct correlation between the interaction force gradient and these distortions which in turn determine the formation of an atomic scale contact. Our model calculations provide a semi-quantitative explanation of the experimental data. We have discussed the reasons for small discrepancies. Improvements can be made by setting up (vastly more complicated and less transparent) *ab initio* cluster calculations that account for many-body and long-range interactions.

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**References**

[1] See e.g.: D.H. Buckley, J. Ferrante, M.D. Pashley and J.R. Smith, Materials Science and Engineering **83**, 177 (1986)

[2] U. Landman, W.D. Luedtke, N.A. Burnham and R.J. Colton, Science **255**, 454 (1990)

[3] U. Dürig, O. Züger and A. Stalder, J. Appl. Phys. September (1992)

[4] Integrity of the Al surface is assured by the fact that negative interaction force gradients are observed whereas the force gradient is positive on the oxydized surface (see Ref. 3).

[5] J.H. Rose, J.R. Smith and J. Ferrante, Phys. Rev B **28**, 1835 (1983)

[6] U. Dürig, O. Züger and D.W. Pohl, Phys. Rev. Lett. **65**, 349 (1990)

[7] M.S. Daw and M.I. Baskes, Phys. Rev. B **29**, 6443 (1984)

[8] A.B. Anderson, J. Chem. Phys. **60**, 2477 (1974)

[9] M.I. Baskes and C.F. Melius, Phys. Rev. B **20**, 3197 (1979)

[10] See e.g. D.R. Salahub et al., in "Theory and Applications of Density Functional Approaches to Chemistry", eds. J. Labanowski and J. Andzeln (Springer Verlag, Berlin, 1991)

**Figure Captions**

**Fig. 1:**

Interaction force gradient $\nabla F$ and tunnel resistance $R_T$ versus tip displacement $z$ measured with the STM using an Ir tip and (a) polycrystalline Ir (b) polycrystalline Al as sample.

**Fig. 2:**

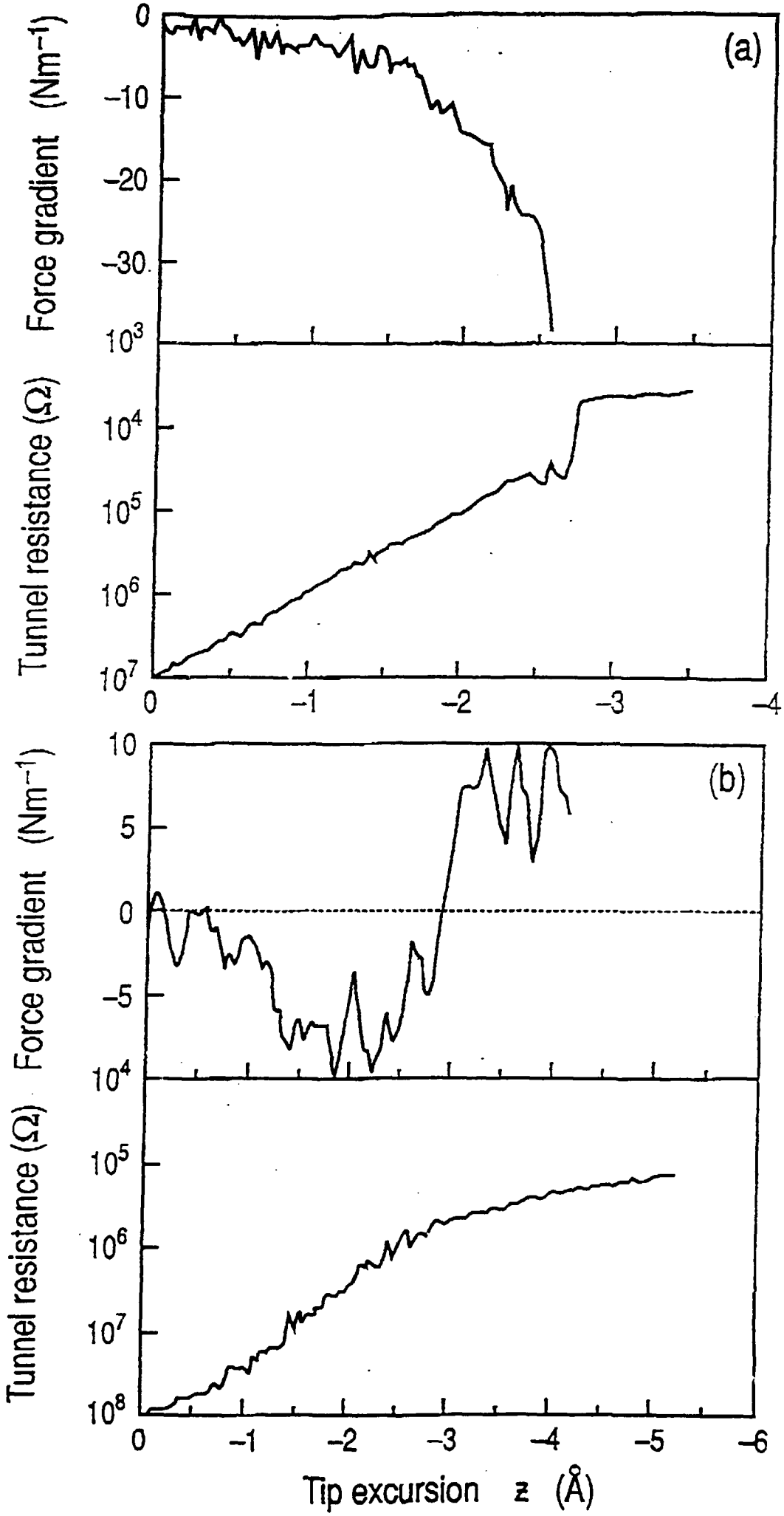
Rescaled nearest neighbor interactions. Solid line: Ir-Ir potential with $V_{eq} = -0.594$ eV, $D_{eq} = 2.68$ Å. Dashed line: Ir-Al potential with $V_{eq} = -0.377$ eV, $D_{eq} = 2.50$ Å. Dotted line: Al-Al potential with $V_{eq} = -0.258$ eV, $D_{eq} = 2.91$ Å.

**Fig. 3:**

Force gradients, dashed and dotted lines without relaxation and solid lines with relaxation. (a) Ir tip above an Ir surface. (b) Ir tip with an Al atom at its apex above an Al surface; dotted line for a clean Ir tip (note change in scale).

**Fig. 4:**

Tip (solid lines) and surface (dashed lines) relaxations for (a) the Ir-Ir and (b) the Ir(Al)-Al systems.


(a)
Force gradient (Nm⁻¹)
0
−10
−20
−30
Tunnel resistance (Ω)
10³
10⁴
10⁵
10⁶
10⁷
0
−1
−2
−3
−4
(b)
Force gradient (Nm⁻¹)
10
5
0
−5
Tunnel resistance (Ω)
10⁴
10⁵
10⁶
10⁷
10⁸
0
−1
−2
−3
−4
−5
−6
Tip excursion z (Å)

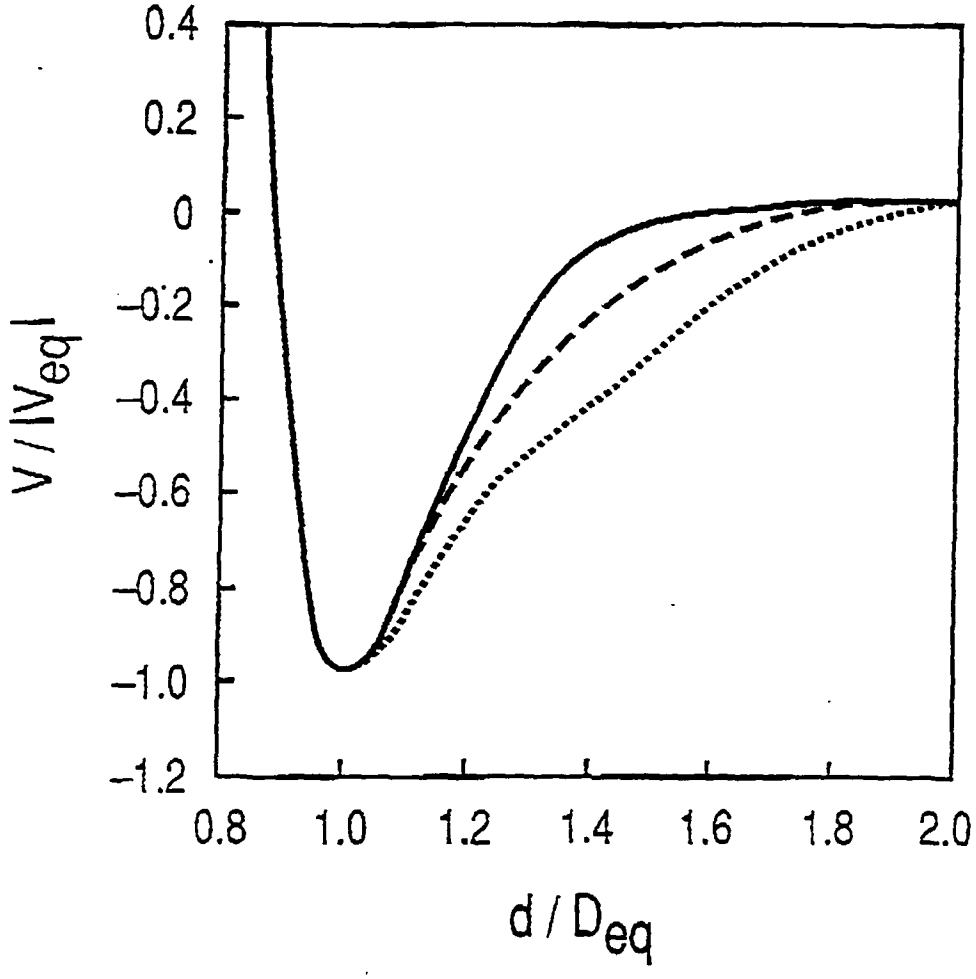



Fig. 2

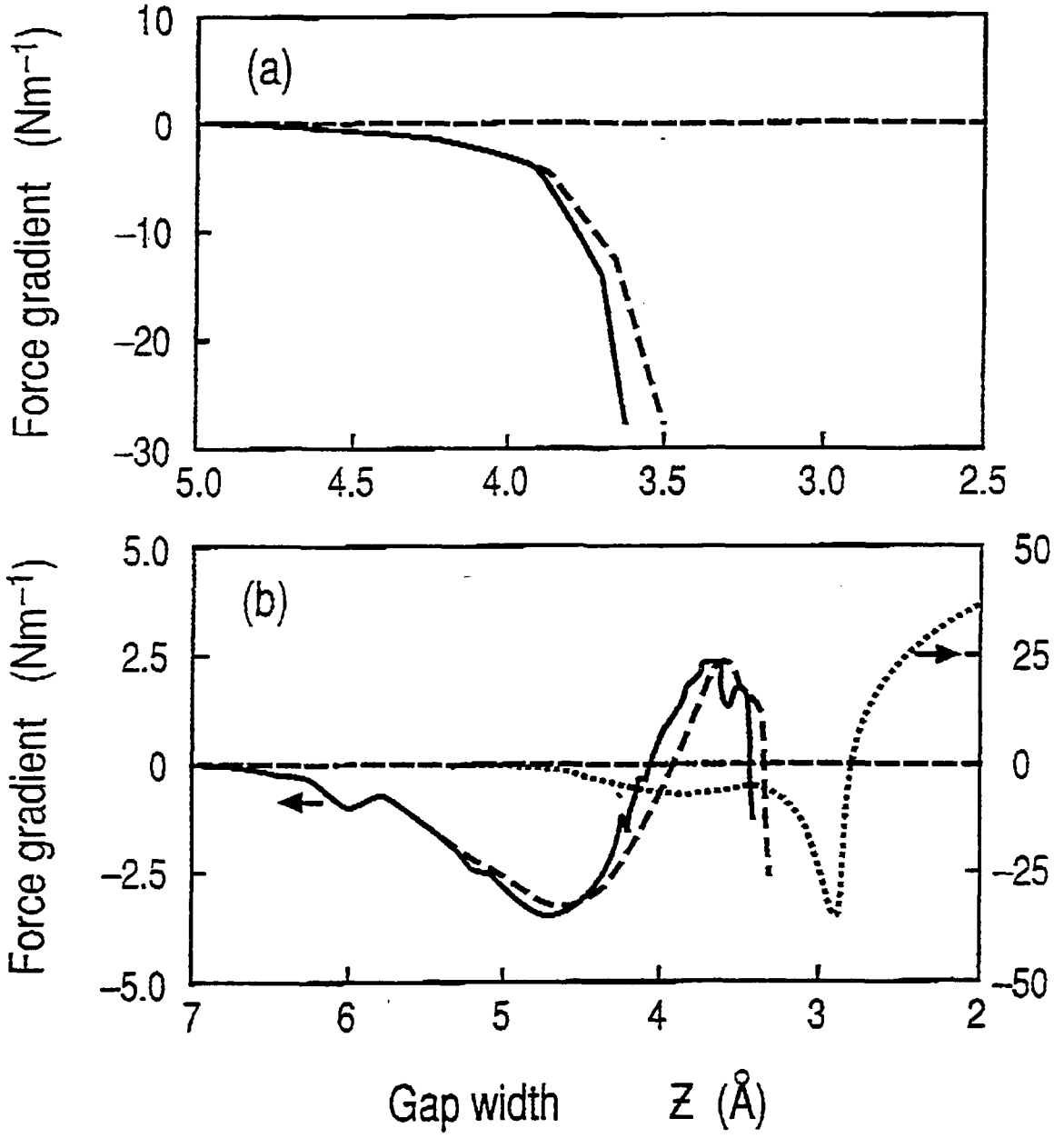

(a)
10
0
−10
−20
−30
Force gradient (Nm⁻¹)
5.0
4.5
4.0
3.5
3.0
2.5
(b)
5.0
2.5
0
−2.5
−5.0
50
25
0
−25
−50
Force gradient (Nm⁻¹)
7
6
5
4
3
2
Gap width z (Å)

Fig. 3

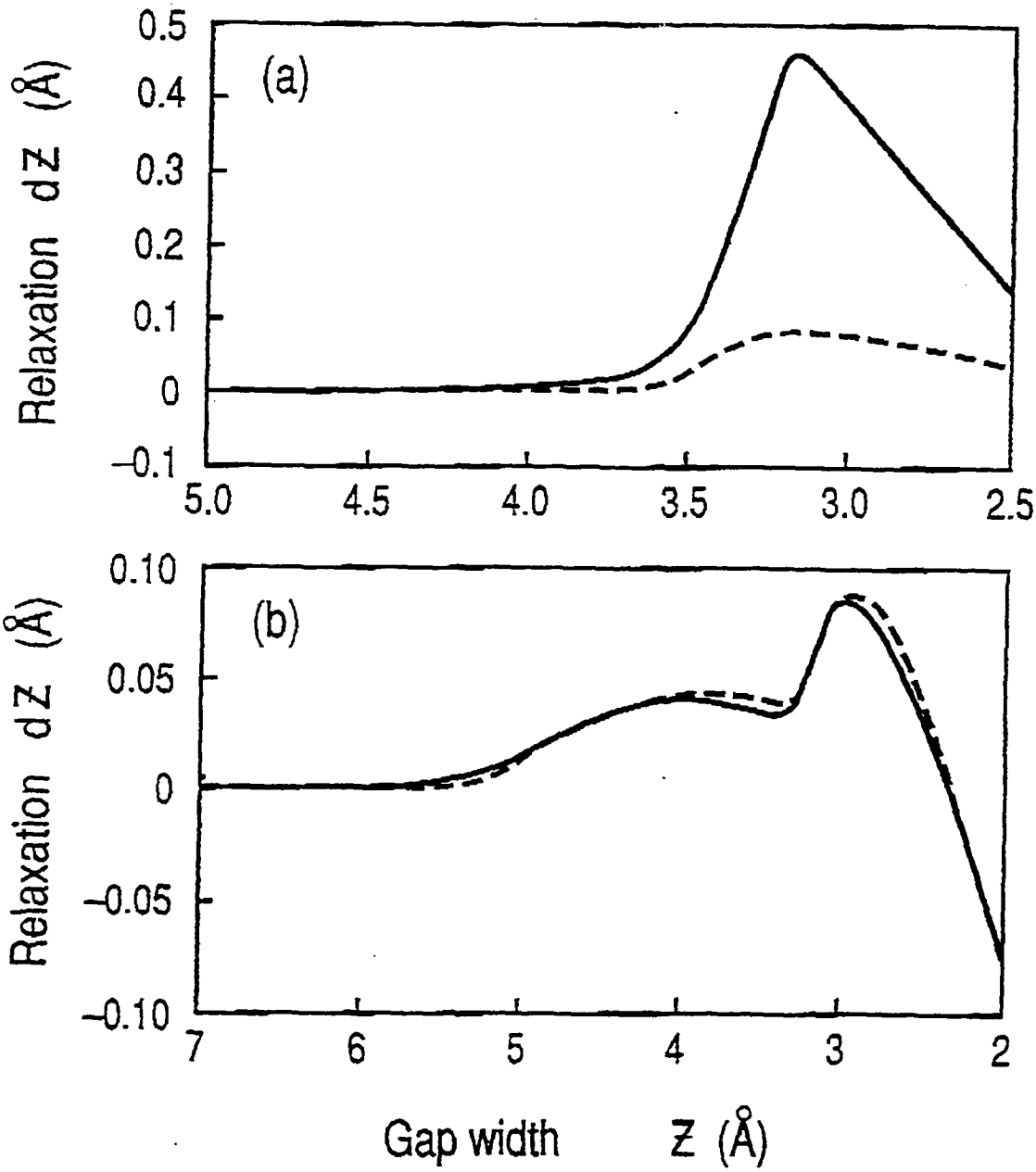

(a)
Relaxation dZ (Å)
0.5
0.4
0.3
0.2
0.1
0
−0.1
5.0
4.5
4.0
3.5
3.0
2.5
(b)
Relaxation dZ (Å)
0.10
0.05
0
−0.05
−0.10
7
6
5
4
3
2
Gap width Z (Å)

Fig. 4