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# Structure, dynamics and thermodynamics of a metal chiral surface: Cu(532)

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## Abstract

The structure, vibrational dynamics and thermodynamics of a chiral surface, Cu(532), have been calculated using a local approach and the harmonic approximation, with interatomic potentials based on the embedded atom method. Relaxation of the atomic positions to the optimum configuration results in a complex relaxation pattern with strong contractions in the bond length of atoms near the kink and the step sites and an equivalently large expansion near the least under-coordinated surface atoms. The low coordination of the atoms on the surface substantially affects the vibrational dynamics and thermodynamics of this system. The local vibrational density of states shows a deviation from the bulk behaviour that persists down to the tenth layer, resulting in a substantial contribution of the vibrational entropy to the excess free energy amounting to about 90 meV per unit cell at 300 K.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Since the middle of the 19th century, chirality has been seen as an important molecular property. Biological molecules may be chiral, with different enantiomers presenting opposite effects (one may be used to cure and the other may cause harm). The fact that, in nature, most chiral molecules exist only in one of the two possible forms or enantiomers is by itself sufficient to excite scientific curiosity. Since pharmaceutically fabricated chiral molecules exist in both forms, it is of great technological importance to design efficient enantio-selectors that will retain only the desired enantiomer. Since the two enantiomers of a chiral molecule have the same base atomic structure, their electronic structure is the same and they differ only in the

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sequence (clockwise/counter-clockwise) in which the atomic structure is formed. It is hence logical to use templates/substrates that are naturally or by design chiral [1–3].

For several decades, the surface science community has been dealing with detailed analysis of heterogeneous catalysis and regions of low coordination on the surface have often been spotted as being responsible for the onset of catalytic reactivity. Regularly kinked surfaces, which are inherently chiral, have been considered recently for enantio-selectivity [2, 3]. Studies of chiral metal surfaces of Cu and Pt have also been the subject of recent studies [1, 2, 4, 5]. It appears in *ab initio* calculations of Power and Sholl [4] that the difference in the energetics between relaxed and unrelaxed chiral surfaces of Pt may be important in the evaluation of the difference in adsorption energies of the two different enantiomers of a chiral molecule. These differences in energies are in the range of a few tenths of a kcal mol<sup>-1</sup> or about a few tens of meV. For such small differences in the energetics, the question of the importance of thermal effects and of vibrational entropy becomes relevant in the considerations of the free energy.

In this paper, we present results for the structure, dynamics and thermodynamics of a chiral metal surface Cu(532) with the aim of extracting the contribution of vibrational entropy to considerations of surface energetics. In the next section, we present the atomic geometry and theoretical details and in section 3 we discuss our results and conclusions.

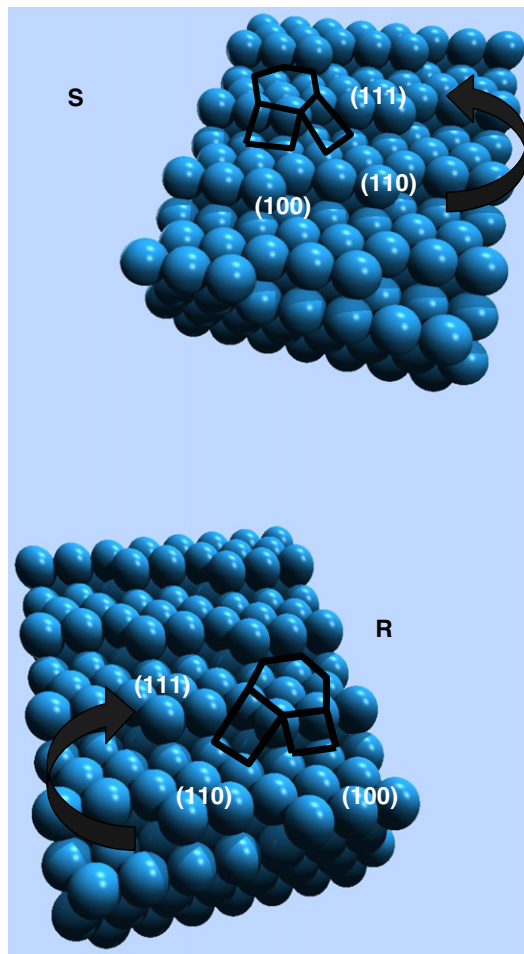
## 2. System geometry and theoretical details

The system studied here is Cu(532), a kinked surface formed from a vicinal surface of Cu(111). By nature, all kinked surfaces are chiral. Since a kink is at the intersection of three planes (here (111), (100) and (110)), the arrangement of these three planes around the corner classifies the surface as being of the R or the S type. (Here we follow the notation that has been discussed in detail by Power and Sholl [4] and Ahmadi *et al* [6].) In figure 1 we show a hard sphere model of Cu(532)<sup>S</sup> and Cu(532)<sup>R</sup>. Note that the S surface corresponds to a counter-clockwise sequence of (111)–(100)–(110) while the R refers to a clockwise one. Note also that on this surface the step separating two kinks is formed by two atoms forming a (100) micro-facet, with a three-atom-wide terrace. The surface unit cell consists of eight atoms with coordination ranging between 6 and 11. The ninth atom is a neighbour of the kink atom with coordination 12, labelled here BNN (bulk nearest neighbour). We shall see here as in our earlier work [8, 12, 13] that the BNN plays an important role in determining the characteristics of this system.

In figure 2, we show a top view of this surface along with the coordination of atoms on layers one (kink) to nine (BNN) (6, 7, 8, 9, 9, 10, 10, 11, and 12).

The interaction between Cu atoms is described by a many-body, embedded atom method (EAM) [7] potential. We have extensively used this potential to study the structure and dynamics of several low and high Miller index surfaces of Cu, Ag, Ni and Pd [8]. For Cu(532), after constructing the system in the bulk truncated positions, we apply standard conjugate gradient procedure to determine the minimum energy configuration. To calculate the vibrational density of states we use a real space Green's function method [9].

The advantage of this method is that one calculates the total density of states with no *a priori* choice of wavevector, as would be the case in calculations based on the wavevector or '*k*-space'. Also, with some effort, one can get the polarization of the vibrational modes from the imaginary part of the columns of the Green's functions associated with the system. This method exploits the fact that, for a system with a finite range of interatomic interactions, the force constant matrix can always be written in a block tridiagonal form [9] in which the sub-matrices along the diagonal represent interactions between atoms within a chosen local region and the sub-matrices along the 'off-diagonal' correspond to interactions between neighbouring localities. Thus an infinite/semi-infinite system is converted quite naturally into



**Figure 1.** Geometry of an fcc(532) showing the two possible orientations.

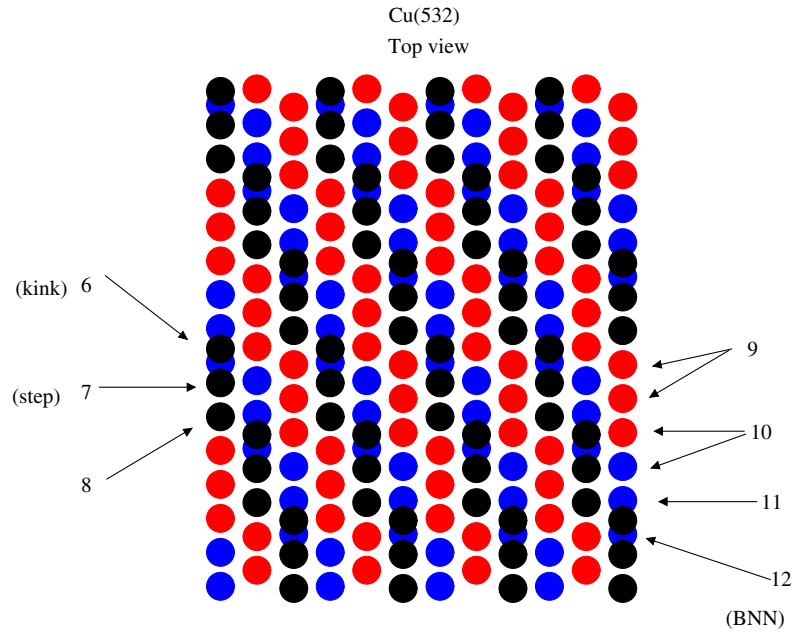
an infinite/semi-infinite set of local regions. There is hence no *a priori* truncation in the system size, as would be the case for matrix diagonalization methods based on  $k$ -space. The real space Green's function method also has an advantage over the familiar 'continued fraction' method [10] as it does not involve truncation schemes to determine the recursion coefficients. Rather a more general and simpler recursive scheme is applied [11]. The vibrational density of states corresponding to locality  $l$  is related to the trace of the Green's function by the well known relation

$$g_l(\omega^2) = -\frac{1}{3n_l\pi} \lim_{\varepsilon \rightarrow 0} \text{Im Tr} [G_{ll}(\omega^2 + i\varepsilon)]$$

with

$$N_l(\omega) = 2\omega g_l(\omega^2),$$

where  $G_{ll}$  is the Green's function sub-matrix associated with locality  $l$  and  $n_l$  is the number of atoms in this locality. The Cu(532) unit cell contains eight atoms (with coordination between 6 and 11) and the cut-off radius of the EAM for Cu is about 5 Å. We choose the first locality to contain atoms in layers 1–40. This ensures a block-tridiagonal form of the



**Figure 2.** Top view of an fcc(532) showing the coordination of the top nine atoms.

force constant matrix. Once the local vibrational density of states is calculated, we can easily determine the local thermodynamic properties of the system in the harmonic approximation. The contributions of the local vibrational free energy  $F_{\text{loc}}^{\text{vib}}$ , the local vibrational entropy  $S_{\text{loc}}^{\text{vib}}$ , and the local mean square vibrational amplitude are thus given by

$$F_{\text{loc}}^{\text{vib}} = k_{\text{B}} T \int_0^{\infty} \ln(2 \sinh(x)) N_l(\omega) d\omega,$$

$$S_{\text{loc}}^{\text{vib}} = k_{\text{B}} \int_0^{\infty} (x \coth(x) - \ln(2 \sinh(x))) N_l(\omega) d\omega,$$

and

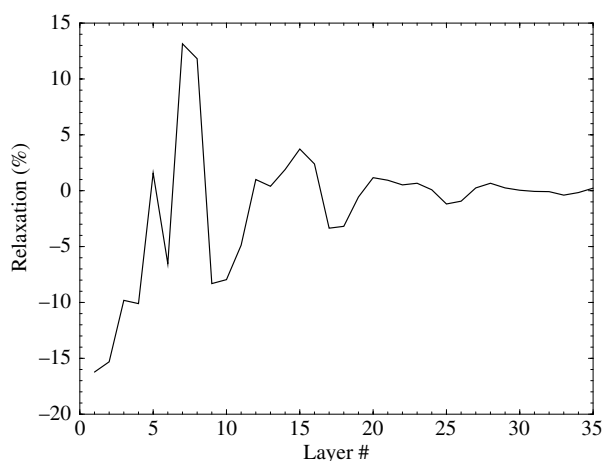
$$\langle u_l^2 \rangle = (h/2M) \int_0^{\infty} \frac{1}{\omega} \coth(x) N_l(\omega) d\omega,$$

with  $x = (h\omega/2k_{\text{B}}T)$ ,  $k_{\text{B}}$  the Boltzman constant,  $T$  the temperature and  $M$  the atomic mass.

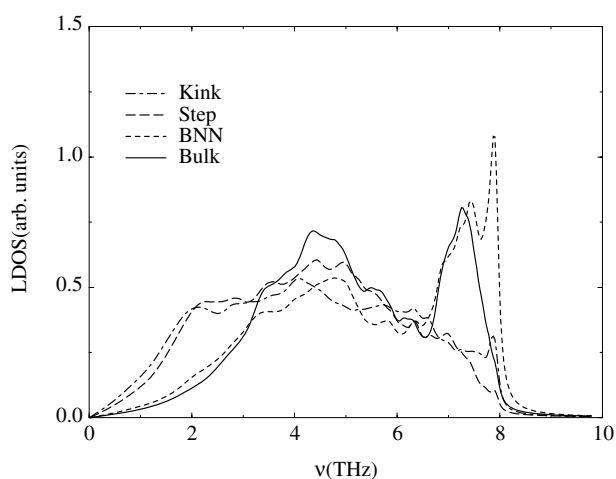
### 3. Results and discussion

We start this section by presenting our results for the atomic relaxation of Cu(532). The general trend observed in the relaxation of vicinal (stepped) surfaces is applicable for this system as well. In particular, the lowest coordinated atoms (those at the kink and step sites) experience a large contraction while atoms that are the least under-coordinated experience a large expansion [8]. In figure 3, we plot the percentile change in the interlayer spacing as compared to the bulk one. The ‘relaxation’ for layer  $l$  in the ordinate axis in figure 3 is given by

$$\Delta d_{l,l+1} = 100(z(l+1) - z(l) - dz_{\text{bulk}})/dz_{\text{bulk}},$$



**Figure 3.** Percentage of the change in the interlayer spacing relative to the bulk.

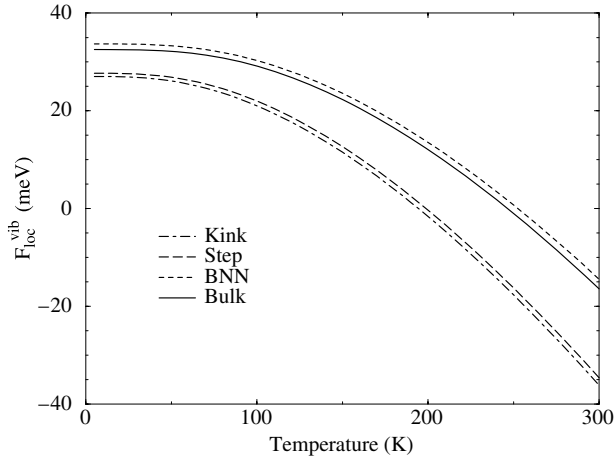


**Figure 4.** Local vibrational density of states for the step, kink, BNN and bulk atoms.

where  $z(l)$  and  $z(l + 1)$  are the  $z$ -coordinates of layers  $l$  and  $(l + 1)$ , respectively and  $dz_{\text{bulk}}$  is the interlayer spacing in the bulk.

From figure 3, we note that the first four interlayer separations experience a contraction (as compared to the bulk one) of 10% or more while  $\Delta d_{78}$  and  $\Delta d_{89}$  show an expansion of about 13% followed by contractions of  $\Delta d_{9,10}$  and  $\Delta d_{10,11}$  of 9%. The relaxation pattern shows oscillations beyond  $\Delta d_{10,11}$ ; however, these are relatively small and can be ignored.

As the loss of neighbours at the surface dictates a complex rearrangement of atomic positions, it also induces dramatic changes in the vibrational density of states of atoms at and near the surface and hence in their thermodynamical properties, as we shall see. The calculated local density of states (LDOS) for the kink, step, BNN and bulk atoms of Cu(532) is shown in figure 4. We note that both the kink and the step atoms (with coordination 6 and 7, respectively) experience substantial enhancement of modes in the low-frequency region accompanied by a significant reduction at the high-frequency end. The large peak above the bulk band shown in



**Figure 5.** Local contributions of the vibrational dynamics to the free energy for the kink, step, BNN and bulk atoms.

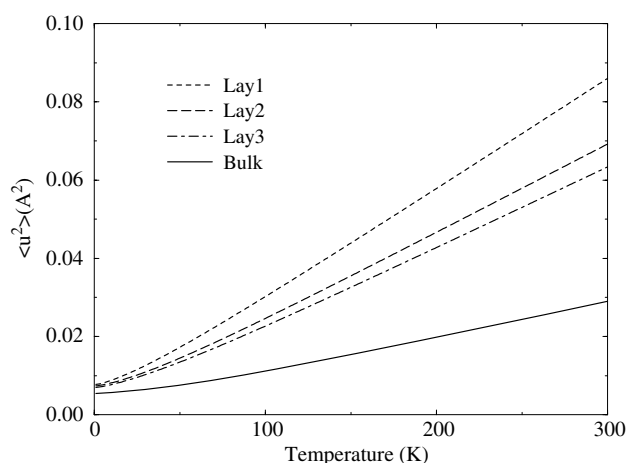
**Table 1.** Local (layer) contributions of the vibrational free energy  $F_{loc}^{vib}$  in meV.

Layer no. (coordination)	0 K	100 K	300 K
1 (6)	27.04	21.04	-36.13
2 (7)	26.69	21.01	-35.60
3 (8)	27.63	22.44	-32.04
4 (9)	28.70	23.90	-29.66
5 (9)	28.66	22.67	-30.33
6 (10)	30.23	25.76	-26.57
7 (10)	29.78	24.61	-26.92
8 (11)	31.00	28.56	-19.45
9 (12)	33.68	31.29	-14.43
Bulk (12)	32.16	29.65	-17.40

the density of states of the BNN is related to the shortening of its bond length with the kink atom, as has already been found on several vicinal surfaces [12].

With the calculated vibrational density of states in hand, one can determine all contributions of vibrational entropy to the thermodynamics of the system. We focus the discussion here on the contribution of the under-coordinated atoms in the system to the vibrational free energy, entropy and mean square vibrational amplitudes. As stated above, these quantities are calculated in the harmonic approximation, which is expected to hold up to room temperature for Cu [14]. The plot in figure 5 of the local vibrational contribution of the kink, step, BNN and bulk atoms shows a much larger tendency of the step and kink atoms to lower the free energy for all temperatures. In table 1, we report the local vibrational contribution to the free energy ( $F_{loc}^{vib}$ ) for atoms in layers one (kink) to nine (BNN). At room temperature, the contributions of the kink and step atoms are 18.73 and 18.20 meV, respectively, lower than that of the bulk atoms, which is a substantial difference. These values are very close to that of a step atom on Cu(211) (19.42 meV) reported earlier [13]. Vibrational contributions from all the atoms in the unit cell to the free energy of Cu(532) sum to an excess of 94.53 meV.

The other thermodynamical quantity of interest that reflects the impact of the environment (coordination and relaxation) is the local vibrational entropy ( $S_{loc}^{vib}$ ). In table 2, we gather this value for atoms in layers 1–9, as well as that for a bulk atom. As one would expect, the lower the coordination, the higher is the local vibrational entropy. As we have seen, low coordination



**Figure 6.** Local mean square vibrational amplitude for the atoms in the first three layers and the bulk.

**Table 2.** Local (layer) vibrational entropy  $S_{\text{loc}}^{\text{vib}}$  in  $k_B/\text{atom}$ .

Layer no.	0 K	100 K	300 K
1	0.023	1.721	4.543
2	0.017	1.677	4.514
3	0.015	1.571	4.384
4	0.012	1.482	4.264
5	0.012	1.542	4.356
6	0.014	1.385	4.121
7	0.011	1.431	4.248
8	0.010	1.258	3.942
9	0.006	1.131	3.760
Bulk	0.005	1.169	3.859

results in a higher population of vibrational states at low frequencies yielding higher entropy. On the other hand, a slight ‘over-coordination’ of the BNN atom, resulting from the inward relaxation around the kink atom, pushes its vibrational entropy lower than that of the bulk. We note also a slight non-monotonic decrease of the local vibrational entropy of atoms in layers 5 and 7, which reflects the local expansion of the interlayer separations. Finally, a quantity of direct relevance to the analysis of experimental structural data, the mean square vibrational amplitude associated with the top three layers of atoms, is plotted in figure 6 along with that associated with a bulk atom. We note from this figure that this quantity scales inversely with the coordination, in agreement with the scaling of the local entropy. Note also that at room temperature the mean square vibrational amplitude of the kink atom is an order of magnitude higher than that of the bulk. Since all thermodynamic quantities presented here were calculated in the harmonic approximation, the mean square vibrational amplitude scales linearly with the temperature at high temperatures. We report in table 3 the slope of the mean square vibrational amplitude (taken at temperatures between 100 and 300 K) for atoms in layers 1–9 along with that of the bulk. This slope decreases dramatically from  $2.74$  to  $0.9 \text{ \AA}^2 \text{ K}^{-1} \times 10^{-4}$  as the atomic coordination varies from 6 (kink atom) to 12 (bulk atom) and should be useful for estimations of the Debye–Waller factors for the analysis of the decrease in the intensities of diffracted beams as a function of temperature in the case of surface-sensitive experimental techniques.



**Table 3.** Slope of the local mean square vibrational amplitude ( $\text{\AA}^2 \text{K}^{-1} \times 10^{-4}$ ).

Layer no.	Slope
1	2.74
2	2.23
3	2.04
4	1.72
5	1.70
6	1.86
7	1.58
8	1.45
9	1.03
Bulk	0.90

#### 4. Conclusions

The detailed study of the structure and vibrational dynamics and thermodynamics of the chiral surface Cu(532) shows that the relaxation pattern is governed by the bond-length/bond-order correlation. The equilibrium positions of the surface atoms tend to optimize their effective coordination number, which results in an oscillatory relaxation pattern. The vibrational dynamics and thermodynamics of a kink atom are similar to those of a step atom, showing saturation in the excess quantities with coordination. As a result of the high vibrational entropy associated with the low-coordinated atoms on the chiral surface Cu(532), the contribution of the vibrational dynamics to the free energy is evaluated to be about 90 meV per surface unit cell (consisting of eight atoms), in excess of the corresponding contribution from the bulk unit cell. This is a substantial contribution that should be taken into account when the energetics of the system are considered.

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#### References

- [1] Sholl D S, Asthagiri A and Power T D 2001 *J. Phys. Chem. B* **105** 4771
- [2] Gellman A J, Horvath J D and Buelow M T 2001 *J. Mol. Catal. A* **167** 3
- [3] Schunack M, Laegsgaard E, Stensgaard I, Johannsen I and Besenbacher F 2001 *Angew Chem.* **113** 2693
- [4] Power T D and Sholl D S 2002 *Top. Catal.* **18** 201
- [5] Asthagiri A, Feibelman P J and Sholl D S 2002 *Top. Catal.* **18** 193
- [6] Ahmadi A, Attard G, Feliu J and Rodes A 1999 *Langmuir* **15** 2420
- [7] Daw M S and Baskes M I 1984 *Phys. Rev. B* **29** 6443  
Foiles S M, Baskes M I and Daw M S 1986 *Phys. Rev. B* **33** 7983  
Daw M S, Foiles S M and Baskes M I 1993 *Mater. Sci. Rep.* **9** 251
- [8] Rahman T S, Kara A and Durukanoglu S 2003 *J. Phys.: Condens. Matter* **15** S3197
- [9] Dy K S, Wu S Y and Spartlin T 1979 *Phys. Rev. B* **20** 4237  
Wu S Y, Xie Z L and Potoczak N 1993 *Phys. Rev. B* **48** 14826
- [10] Haydock R, Heine V and Kelly M J 1972 *J. Phys. C: Solid State Phys.* **5** 2845
- [11] Wu S Y, Cocks J and Jayanthi C S 1994 *Phys. Rev. B* **49** 7957  
Kara A, Jayanthi C S, Wu S Y and Ercolessi F 1994 *Phys. Rev.* **72** 2223
- [12] Durukanoglu S, Kara A and Rahman T S 1997 *Phys. Rev. B* **55** 13 894
- [13] Durukanoglu S, Kara A and Rahman T S 2003 *Phys. Rev. B* **67** 235405
- [14] Yang L and Rahman T S 1991 *Phys. Rev. Lett.* **67** 2327