Path-integral approach to anharmonic vibration of solids and solid surfaces

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Quantum-statistical perturbation theory

Eigenstate representation based on the Schrödinger equation
Analytical representation of the EXAFS cumulants

First-order  
- polyatomic  T. Yokoyama and T. Ohta et al. (1996);
- solid  T. Yokoyama (XAFS-IX in Grenoble, 1996)

Second-order  diatomic  T. Yokoyama (XAFS-X in Chicago, 1998)

Heavy computational load for large systems such as solids
Complicated derivation for higher-order perturbation

Path-integral effective classical potential (PI-ECP) theory

Real-space representation based on the Feynman’s path-integral theory
First application of PI-ECP to EXAFS
Two-body systems

Comparison with experiments  
- Diatomic Br₂ and solid fcc Kr and Ni  

Easier handling for large anharmonic systems, 
large dimensional systems, many-body forces, etc.
No analytical formula of the EXAFS cumulants
Difficulty in quantum anharmonicity at low T
Melting transition

Melting transition has been known from ancient. Its thermodynamics is well understood. Microscopic origin is however still an open question.

M. Faraday: Melting starts from the surface. Recent UHV techniques allows us to investigate surface melting.

Key issues

- **Anharmonicity**: to account for partial bond dissociation. No melting transitions take place with the harmonic potential.
- **Surface anisotropy**: to account for pre-melting at the surface.
- **First-order transition**: short-range studies essential from the microscopic point of view.

Much effort in terms of long-range order using diffraction technique.

Few short-range studies using EXAFS.

Importance of anisotropic and anharmonic vibration enhanced at the surface at $T << T_c$.
Introduction

Scope of today’s talk

Anharmonic and anisotropic vibration of metal thin films

Experimental
Temperature-dependent EXAFS measurements and analysis of ultrathin Ni and Cu (111) epitaxial films grown on HOPG
Anisotropy studied via polarization dependent measurements
Anharmonicity analyzed by the cumulant-expansion formula

Theoretical
Path-integral effective classical potential (PI-ECP) calculations of an ultrathin Cu(111) film
Embedded-atom method (EAM): suitable semi-empirical method to describe the bonding (many-body force) of metals

Contents
I. Introduction
II. Experimental
   (i) Sample preparation and spectroscopic measurements
   (ii) Experimental results
   (iii) Anisotropy and anharmonicity of the surface bonds

III. Theoretical
   (i) Brief description of the PI-ECP method
   (ii) Introduction of EAM for the Monte-Carlo simulations
   (iii) Computational details
   (iv) Results of bulk Cu: Comparison with the experiments
   (v) Results of the thin Cu film: Comparison with the experiments

IV. Concluding remarks
Experimental setup

Sample manipulator

Q-mass
Evap.

ion. chamber

SSD

Sample manipulator

X-ray

SSD

at KEK-PF BL7C
Sample preparation

**Preparation**
1) annealing HOPG at 800 K
2) Cu or Ni deposition at 120 K
3) anneal to 300 K or 470 K

120-K deposition results in disordered Cu clusters

300-K annealing gives clear 1x1 LEED spots, implying thin layer formation

470-K annealing leads to large 3D islands

Use 300-K annealing for the temperature-dependent EXAFS for thin Cu and Ni films

Thickness
- Ni 4 ML
- Cu 4 ML, 8 ML
EXAFS $k^2\chi(k)$ of thin Cu and Ni films

Wave number $k$ (Å$^{-1}$)

EXAFS oscillation function $k^2\chi(k)$ (Å$^{-2}$)

- Ni 4 ML
- Cu 4 ML
- Cu 8 ML

$120$ K
$300$ K
FT of thin Cu and Ni films

Fourier Transform (arb. units) vs. Distance R (Å)

- Ni 4 ML
- Cu 4 ML
- Cu 8 ML

Temperature:
- 120 K
- 300 K

Angles: 90°, 30°
Extracted $k^2\chi(k)$ of the 1st-NN shells

EXAFS oscillation function $k^2\chi(k)$ (Å$^{-2}$)

Ni 4 ML
- 90°
- 30°

Cu 4 ML
- 90°
- 30°

Cu 8 ML
- 90°
- 30°

Wave number $k$ (Å$^{-1}$)

Graph showing EXAFS oscillations for Ni 4 ML, Cu 4 ML, and Cu 8 ML at different wave numbers $k$ and temperatures (120 K and 300 K).
**Experimental results**

### Results of the curve-fitting analysis

<table>
<thead>
<tr>
<th>Sample angle</th>
<th>N*</th>
<th>R (Å)</th>
<th>$C_2^\text{so}$ (10^{-3} Å²)</th>
<th>$\Delta C_2^\text{so}$ (10^{-3} Å²)</th>
<th>$\Delta C_3^\text{so}$ (10^{-4} Å³)</th>
<th>$\Theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni 4 ML</td>
<td>90°</td>
<td>9.2(7)</td>
<td>2.47(2)</td>
<td>5.8(3)</td>
<td>3.4(4)</td>
<td>366(20)</td>
</tr>
<tr>
<td></td>
<td>30°</td>
<td>8.4(3)</td>
<td>2.47(1)</td>
<td>5.8(2)</td>
<td>4.0(4)</td>
<td>345(15)</td>
</tr>
<tr>
<td>Ni bulk</td>
<td></td>
<td>12</td>
<td>2.47</td>
<td>3.2</td>
<td>2.6</td>
<td>416</td>
</tr>
<tr>
<td>Cu 4 ML</td>
<td>90°</td>
<td>10.2(3)</td>
<td>2.54(1)</td>
<td>5.6(3)</td>
<td>4.4(4)</td>
<td>325(15)</td>
</tr>
<tr>
<td></td>
<td>30°</td>
<td>8.6(3)</td>
<td>2.53(1)</td>
<td>5.8(3)</td>
<td>5.0(5)</td>
<td>307(15)</td>
</tr>
<tr>
<td>Cu 8 ML</td>
<td>90°</td>
<td>10.9(3)</td>
<td>2.54(1)</td>
<td>5.2(2)</td>
<td>4.3(4)</td>
<td>328(15)</td>
</tr>
<tr>
<td></td>
<td>30°</td>
<td>10.4(4)</td>
<td>2.54(1)</td>
<td>5.8(3)</td>
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<td>Cu bulk</td>
<td></td>
<td>12</td>
<td>2.54</td>
<td>4.0</td>
<td>4.0</td>
<td>338</td>
</tr>
</tbody>
</table>

$N^*, R, \text{ and } C_2$ for 120 K, $\Delta C_2$ and $\Delta C_3$ for 120 and 300 K

### Estimation of surface Debye temperature

$$C_2(m,\theta) = \frac{(C_2^{\text{so}}+6C_2^{\text{si}})\sin^2\theta+4C_2^{\text{so}}\cos^2\theta+4C_2^{\text{b}}(m-2)}{4m-4+3\sin^2\theta}$$

$m$ thickness (ML)

$C_2^{\text{so}}$ $C_2$ for surface out-of-plane bond

$C_2^{\text{si}}$ $C_2$ for surface in-plane bond

$C_2^{\text{b}}$ $C_2$ for other bond
Effective classical potential method for the two-body system

Basic formula of the Feynman path integral

\[ \rho(x) = \frac{1}{Z} \langle x | e^{-\beta \hat{V}} | x \rangle = \frac{1}{Z} \int_{(x,0) \Rightarrow (x,y)} Dx(u) e^{-A[x(u)]/\hbar} \]

Trial Euclidean action \( A_0[x(u)] \)

\[ A_0[x(u)] = \int_0^{\beta \hbar} du \left[ \frac{1}{2} \mu \dot{x}^2 + \frac{1}{2} \mu \omega^2 (\bar{x}) x^2 + w(\bar{x}) \right] \]

\( \bar{x} = \frac{1}{\beta \hbar} \int_0^{\beta \hbar} du x(u) \) : average path \( \omega^2, w \) : variational parameters

Resultant density matrix \( \rho_0 \)

\[ \rho_0(\bar{x}) = \frac{1}{\sqrt{2 \pi \hbar^2 \beta}} e^{-\beta V_{\text{eff}}(\bar{x})} \frac{1}{\sqrt{2 \pi \alpha(\bar{x})}} \int_{-\infty}^{\infty} dx \exp \left( -\frac{(x - \bar{x})^2}{2\alpha(\bar{x})} \right) \]

\[ \alpha(\bar{x}) = \frac{\hbar}{2 \mu \omega(\bar{x})} \left( \coth f(\bar{x}) - \frac{1}{f(\bar{x})} \right), \quad f(\bar{x}) = \frac{1}{2} \beta \hbar \omega(\bar{x}) \]

\[ V_{\text{eff}}(\bar{x}) = w(\bar{x}) + \frac{1}{\beta} \ln \frac{\sinh f(\bar{x})}{f(\bar{x})} \] : effective classical potential

Optimization of \( w \) and \( \omega^2 \)

\[ F \leq F_0 + \frac{1}{\beta \hbar} < A - A_0 >_0 \] : Jensen-Feynman inequality

\( F \) : true free energy \( F_0 \) : trial free energy

\[ w(\bar{x}) + \frac{1}{2} \omega^2 (\bar{x}) \alpha(\bar{x}) = \frac{1}{\sqrt{2 \pi \alpha(\bar{x})}} \int_{-\infty}^{\infty} dx V(\bar{x} + x) e^{-\frac{(x - \bar{x})^2}{2\alpha(\bar{x})}} \]

\[ \omega^2 (\bar{x}) = \frac{1}{\mu \sqrt{2 \pi \alpha(\bar{x})}} \int_{-\infty}^{\infty} dx \frac{d^2 V(\bar{x} + x)}{dx^2} e^{-\frac{(x - \bar{x})^2}{2\alpha(\bar{x})}} \]
(1) **Low-coupling approximation**

Assume the variational parameters of $w$ and $\omega$ are independent of $\bar{X}$.

(2) **Pairwise potential**

(3) **Monatomic Bravais lattice**

Resultant effective potential $V_{\text{eff}}(X)$

$$
V_{\text{eff}}(X) = \sum_{i\neq j} u(R_{ij}) + \frac{1}{\beta_{k,\lambda}} \sum \ln \frac{f_{k\lambda}}{f_{k\lambda}} + \sum_{i\neq j} \left[ u''(R_{ij}) - u''(R_{ij}^0) \right] \sigma_{ij}^{(2)L} + \left[ \frac{u'(R_{ij}) - u'(R_{ij}^0)}{R_{ij}} \right] \sigma_{ij}^{(2)T}
$$

$$
\sigma_{ij}^{(2)L} = \frac{2}{Nm_{k,\lambda}} \sum (1 - \cos k \cdot R_{ij}^0)(\hat{R}_{ij}^0 \cdot e_{k\lambda})^2 \alpha_{k\lambda}
$$

$$
\sigma_{ij}^{(2)T} = \frac{2}{Nm_{k,\lambda}} \sum (1 - \cos k \cdot R_{ij}^0)(1 - (\hat{R}_{ij}^0 \cdot e_{k\lambda})^2) \alpha_{k\lambda}
$$

$u(R_{ij})$: pairwise potential for the atom pair $i$ and $j$

$k$: phonon wave number vector; $\lambda$: phonon branch ($\lambda=1,2,3$)
**Application of EAM to PI-ECP**

**Basic formula**


Total adiabatic potential of the system $V$

$$V = \sum_i V_i = \sum_i \left( F_i(\rho_{h,i}) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(R_{ij}) \right)$$

$\rho_{h,i}$: total electron density at atom $i$ due to the host

$F_i$: embedding energy for placing atom $i$ into the electron density

$\phi_{ij}$: short-range pairwise interaction (ion-core repulsion)

$F_i$ given by the local density approximation

$\rho_{h,i}$ given by the atomic wave functions

Numerical parameters tabulated semi-empirically for many metal elements

**Harmonic approximation**

$$V \approx N[F(\bar{\rho}) - \bar{\rho} F'(\bar{\rho})] + \frac{1}{2} \sum_{i \neq j} u(R_{ij})$$

$$u(R) = \phi(R) + 2 F'(\bar{\rho}) \rho^a(\bar{R}) + F''(\bar{\rho})[\rho^a(\bar{R})]^2$$

$u_{ij}$: pairwise potential between atoms $i$ and $j$

In the harmonic approximation, the interaction is pairwise.

Effective classical potential scheme in pairwise-potential systems can be applied
**Calculational Method**

### Geometries in MC calculation

**thin Cu film**
- 48 atoms x 6 layers
- 48 atoms
- Two-dimensional periodicity is imposed.

**bulk Cu**
- 256 atoms
- (4³ unit cells)
- Three-dimensional periodicity is imposed.
- Interactions up to the 4th shell were taken into account.

**Procedures**

1. **EAM interatomic potential**
2. **Normal vibrational analysis**
   - \(\omega_{kl}, \epsilon_{kl}, \alpha_{kl} \rightarrow \sigma_{ij}^{(L)}, \sigma_{ij}^{(T)}\)
   - cubic Brillouine zone
   - \([-2\pi/a_0, 2\pi/a_0]\)
   - \(\sim 10^6\) phonons sampled
3. Classical-like \(NPT\)-MC with \(V_{\text{eff}}(X)\)
   - 10,000 MC steps after equilibrium
4. Pair correlation functions and EXAFS cumulants

**Approximation for thin films**

The vibration of thin films is assumed to be the same as that of bulk. This is crude but practically makes sense because of larger inaccuracy in the interatomic potential.

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Radial distribution of bulk Cu

Calculation
Monte-Carlo: PI-ECP or Classical (NPT)

Radial distribution function
Results of bulk Cu

Bulk Cu

$R$ (Å)

Temperatur $T$ (K)

$C_2 \times 10^{-2}$ Å$^2$

$C_3 \times 10^{-3}$ Å$^3$
Classical distribution along surface normal

Thin Cu film (Classic MC)

Temperature (K): 400, 350, 300, 250, 200, 150, 100, 50, 10

Density (Å⁻¹): 4000, 3000, 2000, 1000, 0

Distance Z (Å): 0, 2, 4, 6, 8, 10, 12

bulk surface
Radial distribution around surface atoms

Thin Cu(111) film (Quantum)

Radial Density (Å\(^{-1}\)) vs. Distance (Å)

Temperature (K): 400, 350, 300, 250, 200, 150, 100, 50, 10

Surfaces:
- Surface in-plane
- Surface out-of-plane
$C_2$ of thin Cu(111)

Temperature $T$ (K)

Thin Cu(111) film
1st-NN $C_2$

$C_2 (10^{-2} \text{ Å}^2)$

0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6

0 100 200 300 400

012 o12
i11 o23
o34 i22
i33 bulk
Thermal expansion of thin Cu(111)

<table>
<thead>
<tr>
<th>Distance R (Å)</th>
<th>Temperature T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.54</td>
<td>0</td>
</tr>
<tr>
<td>2.55</td>
<td>100</td>
</tr>
<tr>
<td>2.56</td>
<td>200</td>
</tr>
<tr>
<td>2.57</td>
<td>300</td>
</tr>
<tr>
<td>2.58</td>
<td>400</td>
</tr>
</tbody>
</table>

Thin Cu(111) film
1st-NN distance
C₂ of thin Cu(111)

Temperature T (K)

Thin Cu(111) film
1st-NN C₂

C₂ (10⁻² Å²)

out-of-plane 12 PI-ECP
out-of-plane 12 Classical
in-plane 11 PI-ECP
in-plane 11 Classical
$C_3$ of thin Cu(111)

Thin Cu(111) film
1st-NN $C_3$

$C_3$ (10^{-3} \text{ Å}^3)

Temperature $T$ (K)

bulk

i11

i22

o23

o34

i33

o12
Comparison between experiment and calculation

Results of thin film and bulk Cu

<table>
<thead>
<tr>
<th></th>
<th>surface out-of-plane</th>
<th>surface in-plane</th>
<th>bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta C_{2}^{\text{so}} ) (10^{-2} \text{ Å}^2)</td>
<td>( \Theta_D ) (K)</td>
<td>( \Delta C_{2}^{\text{b}} ) (10^{-2} \text{ Å}^2)</td>
</tr>
<tr>
<td>Exptl.</td>
<td>7.0(1.4)</td>
<td>262(25)</td>
<td>4.5(0.9)</td>
</tr>
<tr>
<td>Calc.</td>
<td>6.287</td>
<td>272</td>
<td>5.495</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<tr>
<td></td>
<td>( \Delta C_{3}^{\text{so}} ) (10^{-3} \text{ Å}^3)</td>
<td>( \Delta C_{3}^{\text{b}} ) (10^{-3} \text{ Å}^3)</td>
<td></td>
</tr>
<tr>
<td>Exptl.</td>
<td>3.8(8)</td>
<td>3.1(6)</td>
<td>1.62</td>
</tr>
<tr>
<td>Calc.</td>
<td>3.645</td>
<td>2.465</td>
<td>1.477</td>
</tr>
</tbody>
</table>

\( \Delta C_2 \) and \( \Delta C_3 \) for 120 and 300 K, and experimental \( \Delta C_3 \) for 4 ML
Concluding remarks

Theoretical
PI-ECP method is practically useful to simulate thermal vibration. EAM is available to describe many-body interatomic potentials of metals not only for PI-ECP calculations but for classical MC simulations, where no long-range order is required.

Experimental
Thin metal epitaxial films allow us to investigate surface anisotropic and anharmonic vibration. Thin metal epitaxial films are also useful for SEXAFS of adsorbate-substrate systems because of much smaller elastically scattered x rays when low-Z substrates such as HOPG and Si are used.

Anisotropic and anharmonic vibration of surface atoms
Vibrational amplitude and anharmonicity of the surface metal-metal bonds are greater in the surface normal direction than in the lateral direction, although the surface-normal layer spacing is significantly contracted.

Although the absolute displacements are well known to be enhanced along surface normal by the diffraction studies, this conclusion concerning the relative motions is not trivial.

cf. c(2x2)S/Ni(110) (T. Yokoyama et al. Surf. Sci. 313 (1994) 197.)
p4g(2x2)N/Ni(001) (L. Wenzel et al., Phys. Rev. Lett. 60 (1988) 2327; 64 (1990) 1765.) the surface normal S-Ni or N-Ni bonds are significantly stiffer than the lateral ones.

Vibrational enhancements along surface normal should induce roughnening transition if any (roughnening should occur along the surface normal direction), which leads consequently to surface melting, and consequent bulk melting.

Relative motions directly related to the chemical bonds is essentially important to describe melting from the microscopic point of view.