INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR. 628 - 28

Research workshop in Condensed Matter,
Atomic and Molecular Physics
(22 June - 11 September 1992)

Working Party on:
"Energy Transfer in Interactions with
Surfaces and Adsorbates"
(31 August - 11 September 1992)

"Multiphonons excitation in HAS from surfaces"

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He scattering for $10\,\mathrm{meV} < E_i < 100\,\mathrm{meV}$

The Trajectory Approximation and its Improvements

The Transition from Quantum to Classical Scattering

One-Phonon and Multiphonon Processes

D. Himes - Virginia

Bortolani, Franchini, Santoro - Modena

Toennies, Wöll, Zhang - MPI Göttingen

Old Wisdom: Structureless Multiphonon Background

New Wisdom: Multiphonon Features

PRL 66 (1991) 3160 ; Surf. Sci. 242 (1991) 518

JR Manson, Phys. Rev. B43 (1991) 3524

(D)ATA ANALYSIS IN THE ONE-PHONON APPROX.

PEAKS IN TOF SPECTRA → SURFACE PHONONS

SCATTERED INTENSITY → SURFACE-PROJECTED PHONON DENSITY OF STATES

(ALMOST) ONLY TOP SURFACE LAYER SAMPLED

$u_z \frac{\partial V}{\partial z} + i \vec{Q}_{\parallel} \cdot \vec{u}_{\parallel} V$ MATRIX ELEMENT

(WITH BOND CHARGES ?)

V IS A SUM OF PAIRWISE POTENTIALS

DISTORTED WAVE BORN APPROX. (DWBA)

(O)NE-PHONON INTENSITY $\sim \begin{cases} n_B & \text{ANN.} \\ n_B + 1 & \text{CR.} \end{cases}$

(M)UST BE MULTIPLIED BY

e^{-2W} WITH $2W \sim T$

DEBYE-WALLER FACTOR

NEED TO UNDERSTAND MULTIPHONON PROCESSES T(O)

- SUBTRACT "STRUCTURELESS MULTIPHONON BACKGR(OUND)"
- USE He ENERGIES $\gtrsim$ 40 meV
- DESCRIBE Ne, Ar, NO ... SCATTERING

OF EXCHANGED PHONONS = 2W

$$P_n = e^{-2W} \frac{(2W)^n}{n!}$$

$$2W \simeq \frac{24 \mu T (D + E_i \cos^2 \vartheta_i)}{k_B T_D^2} = \langle (\vec{q} \cdot \vec{u})^2 \rangle$$

$T_D \simeq$ bulk Debye temperature

D = Surface well depth

E_i = Incident energy μ = mass ratio

WHAT HAPPENS FOR $W \gtrsim 1$?

Trajectory Approximation (TA)

$$N(\Delta\vec{K}_{\parallel}, \Delta E) = \int dt\, d^2R_{\parallel}\; e^{i(\Delta E\, t - \Delta\vec{K}_{\parallel}\cdot\vec{R}_{\parallel})}\, e^{\Gamma(\vec{R}_{\parallel},t) - 2W}$$

where $\Gamma(\mathbf{R}_{\parallel},t)$ is linearly related to the correlation function

$$\langle u_\alpha(\vec{R}_\ell, t)\; u_\beta(\vec{0}, 0)\rangle$$

and $2W = \Gamma(\mathbf{0},0)$ is the DW factor.

For 1-d hard-wall collision:

$$\Gamma(\vec{R}_{\parallel},t) = \langle u_z(\vec{R}_{\parallel},t)\; u_z(0,0)\rangle\, q_z^2$$

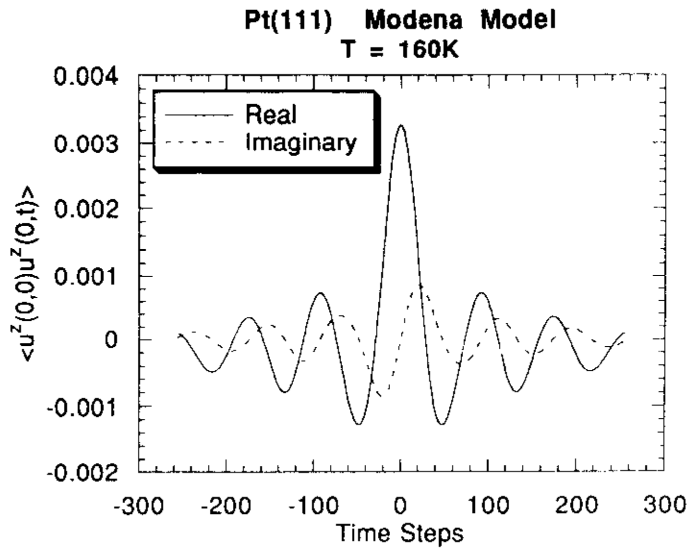
where q_z is the $\perp$ momentum transfer

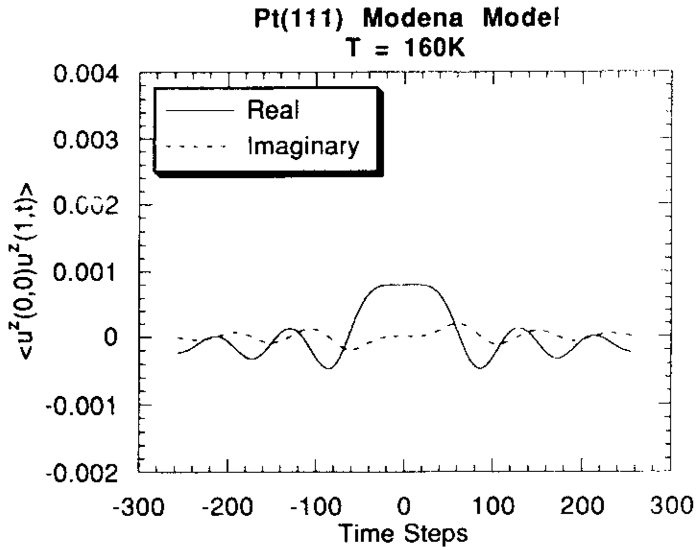
$$q_z u_z \Rightarrow \sum_{\ell} \int d\tau\, \vec{F}(\vec{r}(\tau) - \vec{R}_\ell)\cdot\vec{u}(\vec{R}_\ell, t)$$

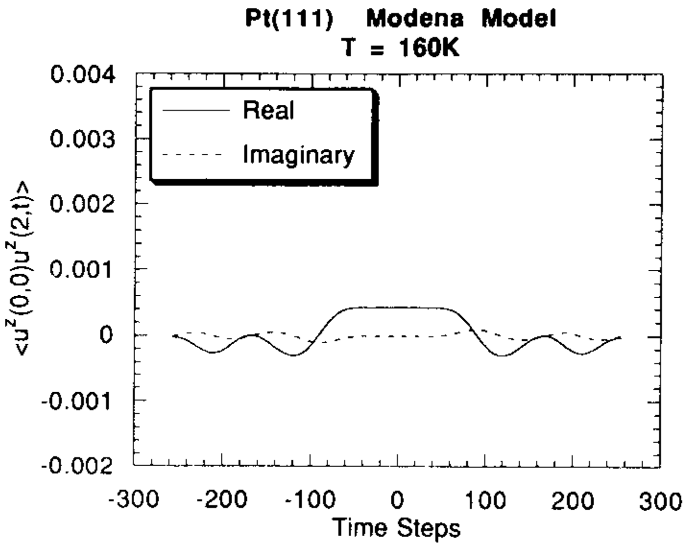
re
nerally

F is the He-surface atom force along the trajectory **r**(t)

Typical correlation functions







TIME OF FLIGHT

Kinematics - Scan Curves

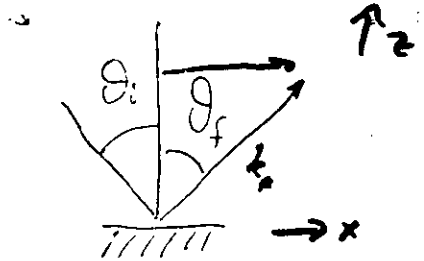
Conservation laws:

Energy. $\hbar\omega_f = \hbar(\omega_i + \omega) = E_i + \Delta E$

Parallel Momentum $K_{f_x} = K_{i_x} + \Delta K_x$

Geometry:

$K_{f_x} = k_f \sin\vartheta_f$



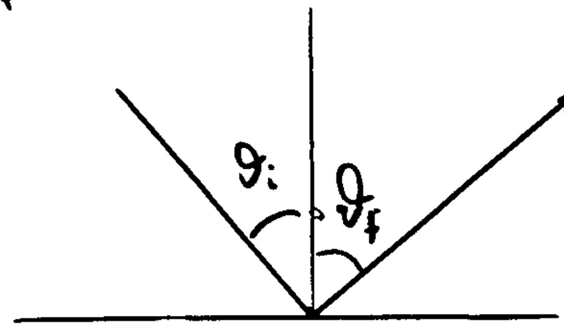
Algebra:

$$k_f = \frac{K_{fx}}{\sin\vartheta_f} = \frac{(K_i+\Delta K)_x}{\sin\vartheta_f}$$

$$\frac{\omega_f}{\omega_i} = \frac{k_f^2}{k_i^2} = \frac{(K_i+\Delta K)_x^2}{k_i^2 \sin^2\vartheta_f} \qquad \text{x-comp.}$$

$$\boxed{\frac{\Delta E}{\hbar\omega_i} = \frac{(K_i+\Delta K)_x^2}{k_i^2 \sin^2\vartheta_f} - 1}$$ a parabola

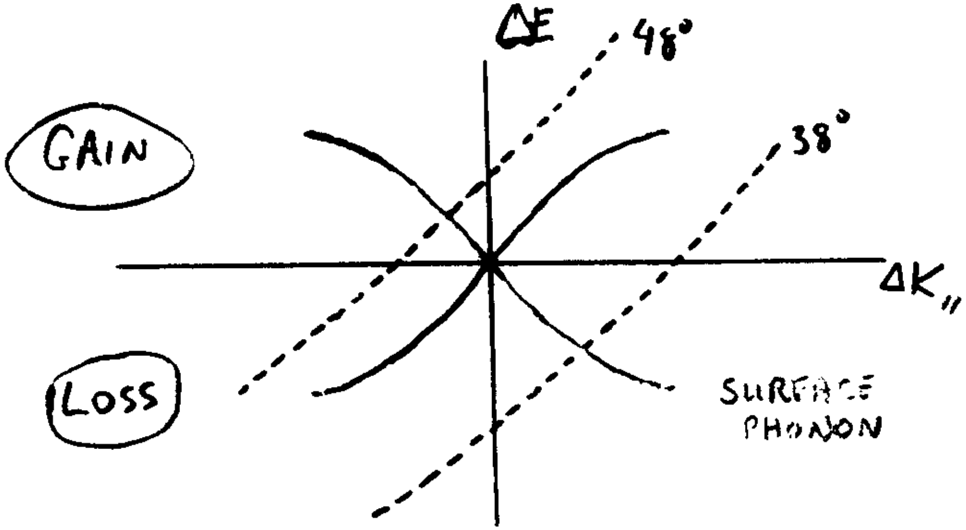
$$\vartheta_i + \vartheta_f = 90^\circ$$



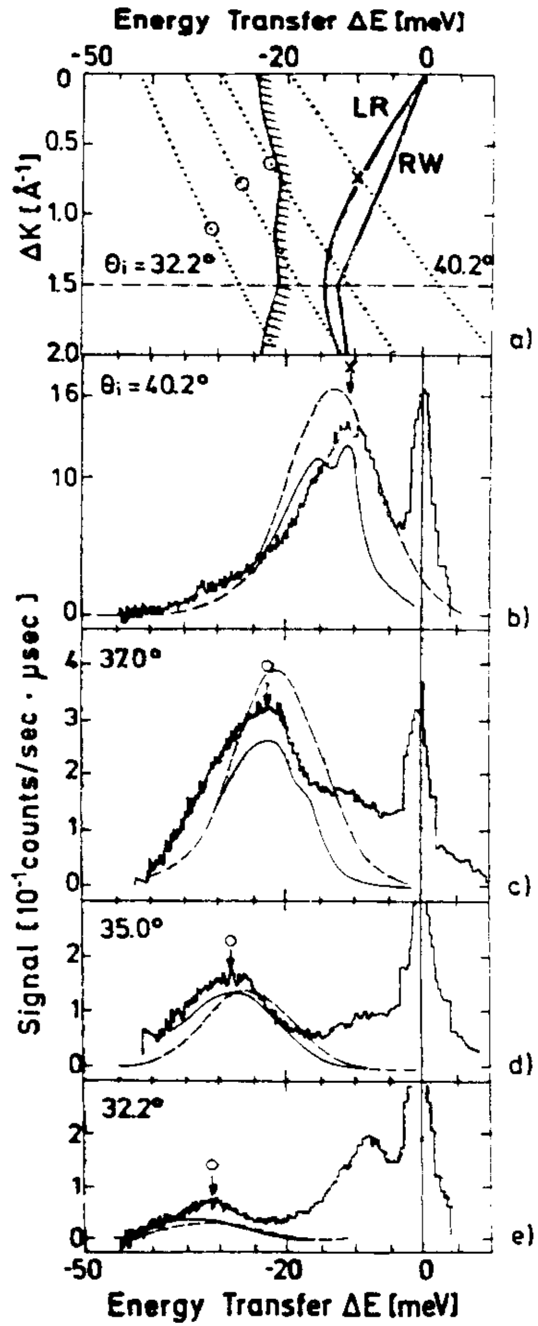
ON A GIVEN TOF RUN, THE ENERGY TRANSFER ΔE IS RELATED TO THE MOMENTUM TRANSFER ΔK BY

$$\Delta E = \hbar\omega = E_i \left[\frac{(\sin\vartheta_i + K_{\parallel}/k_i)^2}{\sin^2\vartheta_f} - 1 \right]$$

A <u>SCAN CURVE</u> IS A PLOT OF ΔE VS. $\Delta K_{\parallel}$



Pt (111)
Göttingen data
PRL '91



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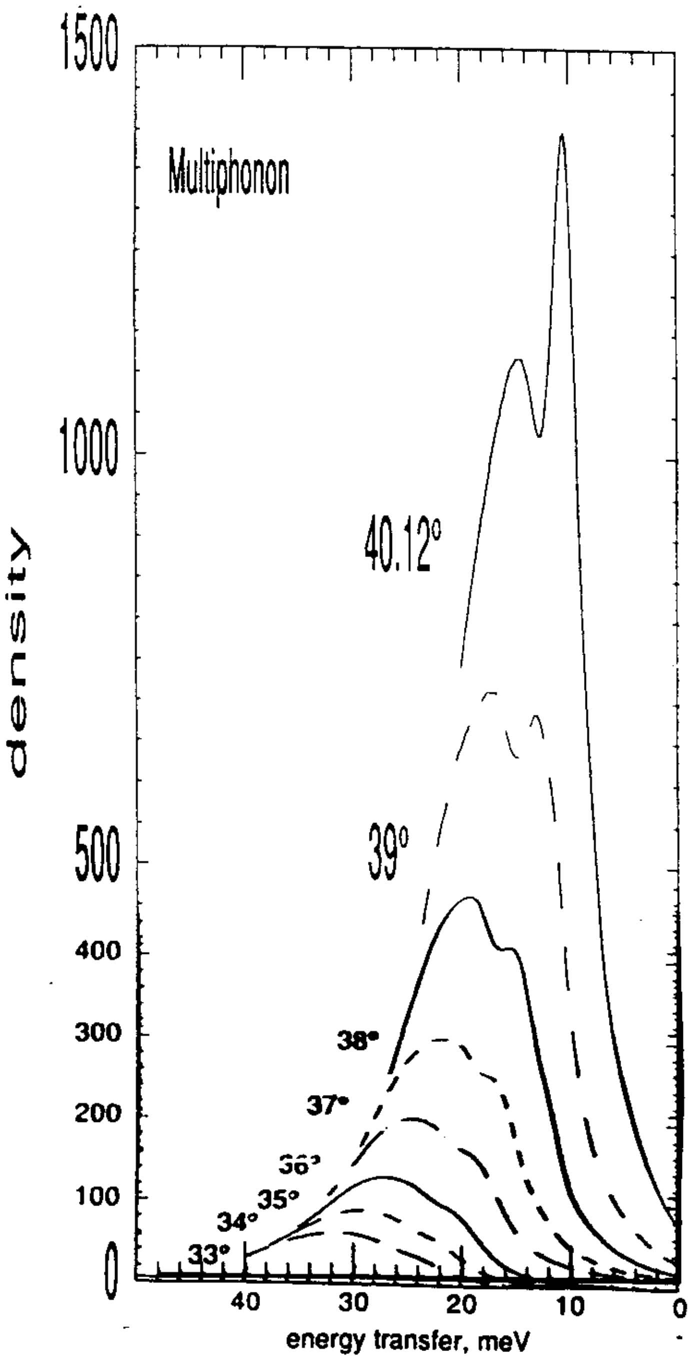
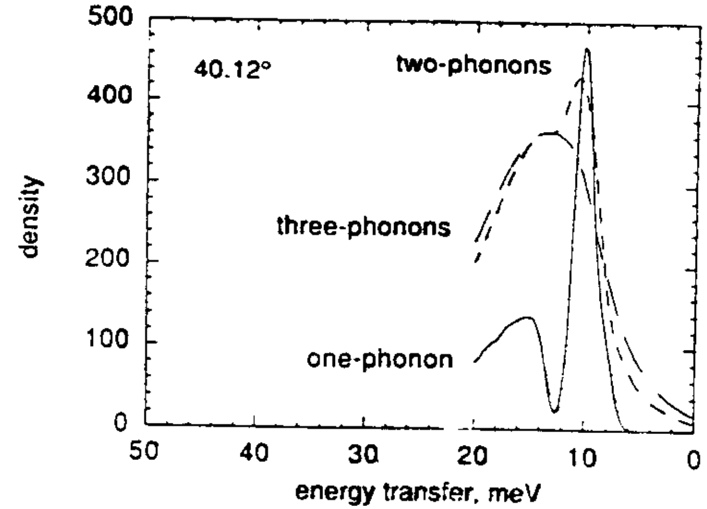
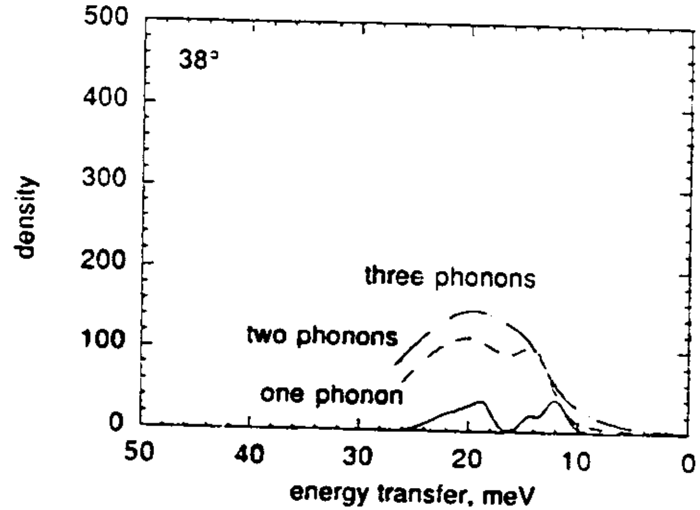
Pt(111)
Himes



Pt(111) $\beta = 1.83\ \text{Å}^{-1}$ $Q_c = 0.58\ \text{Å}^{-1}$
Himes

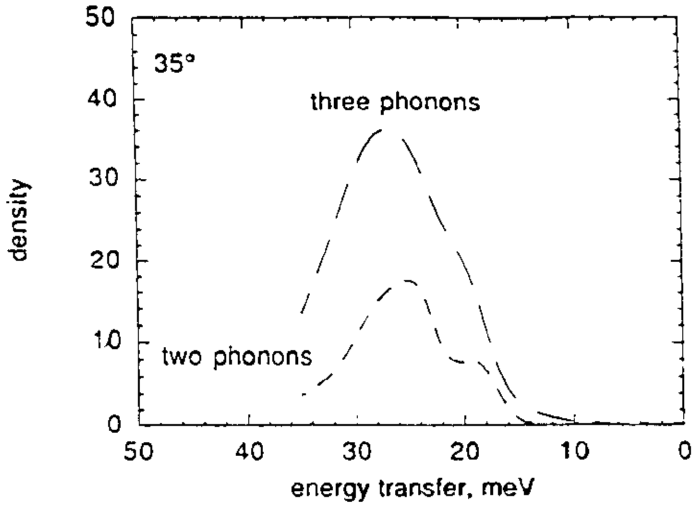
11

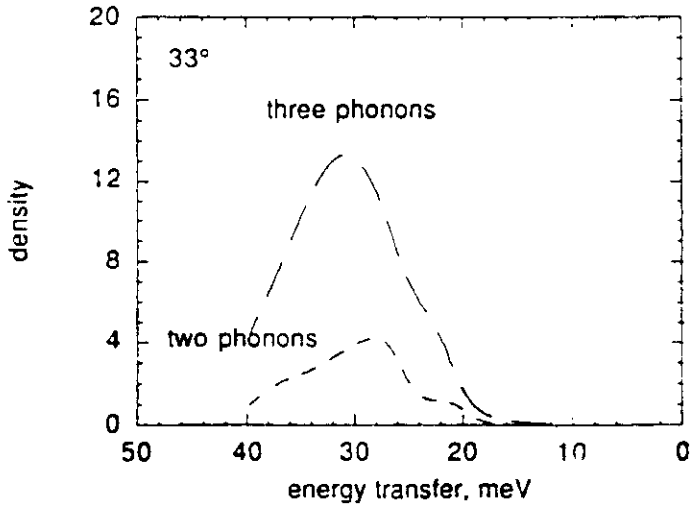




t (111)

limes





BRAKO - NEWNS:

$$N(\Delta \vec{K}_{//}, \Delta E) \simeq \frac{1}{T^{3/2}} \, e^{-\frac{(\Delta E - \overline{\Delta E})^2}{4 k_B T \overline{\Delta E}}} \, e^{-\frac{\hbar^2 v^2 (\Delta K_{//})^2}{2 k_B T \overline{\Delta E}}}$$

WITH BAULE FORMULA FOR AVERAGE ENERGY TRANSFER

$$\overline{\Delta E} = -\frac{4\mu}{(1+\mu)^2}\left[E_i \cos^2\vartheta_i + D\right]$$

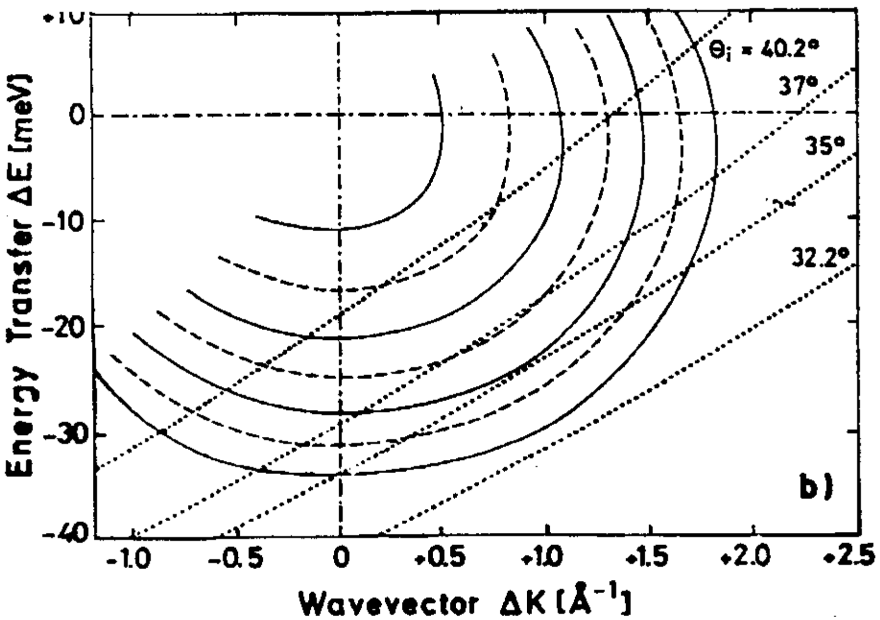
- IT IS A GAUSSIAN IN ΔE, $\Delta \vec{K}_{//}$
- IT IS CENTERED AT $\overline{\Delta E} = (\overline{\Delta E})_{Baule}$
- IT IS CENTERED AT $\overline{\Delta K_{//}} = 0$

  (CONSISTENT WITH BAULE FORMULA FOR $\overline{\Delta E}$ AND HARD CUBE MODEL)

- IT ASSUMES THAT THE SURFACE PHONON SPECTRUM IS DOMINATED BY A BRANCH

$$\omega = v K_{//}$$

He / Pt (111) at $E_i = 69$ meV



THE CALCULATIONS REPORTED SO F

USED THE CLASSICAL SPECULAR TRAJEC

DEFECTS OF STA

- IT GIVES AN AVERAGE ENERGY LOSS ALWAYS INDEPENDENT OF SURFACE TEMPERATURE
- IN THE CLASSICAL LIMIT, IT GIVES A GAUSSIA CENTERED AT THE AVERAGE ENERGY LOS

- INCLUDE He RECOIL WITH

EXPONENTIATED DISTORTED WAVE BORN

$$\overline{\Delta E}(T) = 4\mu\left[E_i \cos^2\theta_i + D - k_B T\right]$$

$$N(\Delta K_{\parallel}, \Delta E) \sim \frac{1}{T^{3/2}}\, e^{-\frac{(\Delta E - \overline{\Delta E}(T))^2}{4k_B T|\overline{\Delta E}(0)|}}\, e^{-\frac{\hbar^2 v^2 \Delta K}{2k_B T|\overline{\Delta E}}}$$

IT GIVES A GAUSSIAN CENTERED AT $\overline{\Delta E}(T)$, Where the Exponentiated Distorted Wave Born Approximation gives

$$\sum_j \frac{n(\omega(Q,j))}{\omega(Q,j)} \; |\mathbf{e}(Q,j)\cdot\mathbf{F}(\mathbf{k}_f,\mathbf{k}_i)|^2 \; e^{-i\omega(Q,j)t}$$

the Trajectory Approximation gives:

$$\sum_j \frac{n(\omega(Q,j))}{\omega(Q,j)} \; |\mathbf{e}(Q,j)\cdot\mathbf{F}(Q,j)|^2 \; e^{-i\omega(Q,j)t}$$

The explicit expressions for $\mathbf{F}$ in the two cases are

$$\mathbf{F}(\mathbf{k}_f,\mathbf{k}_i) = \int dz \; \chi(k_{fz}|z)^* \; \mathbf{F}(Q|z) \; \chi(k_{fi}|z)$$

$$\mathbf{F}(Q,j) = \int_{-\infty}^{\infty} dt \; \mathbf{F}(Q|z(t)) \; e^{-i(\mathbf{V}\cdot Q+\omega(Q,j))t}$$

The wave functions χ are normalized to unit incoming current. Semiclassically $\mathbf{F}(\mathbf{k}_f,\mathbf{k}_i)$ is

$$\int_0^{\infty} dz \; \frac{e^{i\int^z [k_{iz}(z')-k_{fz}(z')]dz'}}{\frac{h}{m}\sqrt{k_{iz}(z)k_{fz}(z)}} \; \mathbf{F}(z) \; +$$

$$\int_{\infty}^{0} dz \; \frac{e^{i\int^z [k_{fz}(z')-k_{iz}(z')]dz'}}{\frac{h}{m}\sqrt{k_{iz}(z)k_{fz}(z)}} \; \mathbf{F}(z)$$

which resembles $\mathbf{F}(Q,j)$, as can be seen by replacing dt with $\frac{dz}{[illegible]}$.

RATIONALE FOR THE EDWBA

$$e^{\Gamma} = 1 + \Gamma + \cdots$$

ONE-PHONON TERM $\Rightarrow$ DWBA

PRESCRIPTION

$$\text{DWBA} \xrightarrow[(F.T.)^{-1}]{} \Gamma(R_{\parallel},t) \rightarrow e^{\Gamma} \xrightarrow[F.T.]{} N(\Delta K_{\parallel},\Delta E)$$

THIS IS A TRAJECTORY APPROXIMATION, IN THE SENSE THAT

$$N(\Delta K_{\parallel},\Delta E) = \int d^2R \, dt \; e^{\Gamma(\vec{R}_{\parallel},t)-2W} \; e^{i(\Delta E t - \Delta\vec{K}_{\parallel}\cdot\vec{R}_{\parallel})}$$

WHERE $\Gamma(\vec{R}_{\parallel},t)$ DOES NOT DEPEND ON ΔE, $\Delta\vec{K}$

THERE ARE RELATED APPROXIMATIONS IN WHICH Γ (AND 2W) <u>DO</u> DEPEND ON $\Delta\vec{K}_{\parallel}$, ΔE

THE SIMPLEST IS THE EICOVA. FOR A VIBRATION [illegible] ([illegible])

"RIPPLING WALL"

$$\nu(\Delta E) = \int dt\, e^{\Gamma(t,\Delta E) - 2W(\Delta E)}\, e^{i\Delta E t}$$

$$\Gamma(t,\Delta E) = \langle u_z(t)\, u_z(0)\rangle\, [p_i + p_f(\Delta E)]$$

$$p_f^2(\Delta E) = p_i^2 + 2m\Delta E/\hbar^2$$

THE EDWBA HAS $\int d\omega' [p_i + p_f(\omega')]\, u_\ell^2(\omega')\, e^{-i\omega' t}$

INSTEAD OF $[p_i + p_f(\Delta E)]\, u_\ell^2(t)$

ADVANTAGES OF RWA

$\overline{\Delta E}(T) = 4\mu [E_i \cos^2\theta_i + D - k_B T]$ (same as EDWBA)

CLASSICALLY, IT DOES <u>NOT</u> GIVE A GAUSSIAN CENTERED AT $\overline{\Delta E}(T)$, BUT AN ASYMMETRIC DISTRIBUTION PEAKED AT $\overline{\Delta E}(0)$.

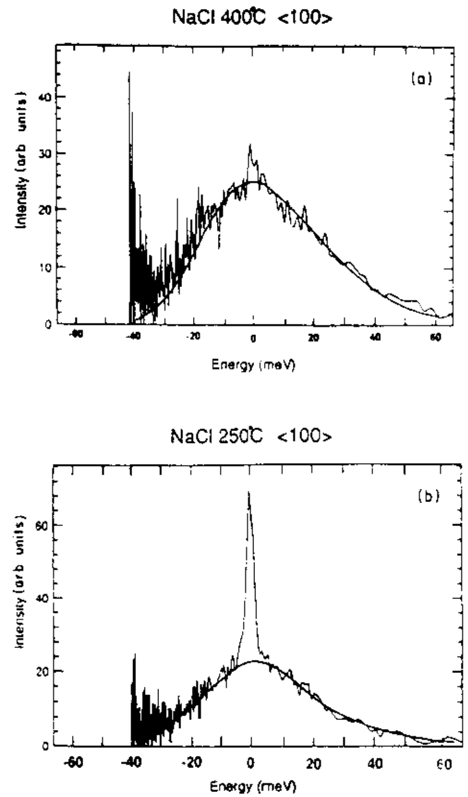


FIG. 1. The scattered intensity as a function of energy exchange for He on a NaCl(001) surface in the ⟨100⟩ direction. The incident beam wave vector is 9.2 Å^{-1}, and the angle of incidence and the detector angle are both 45°, measured from the surface normal. The solid curve is the calculation. (a) Surface temperature of 673 K. (b) Surface temperature of 523 K.

The cutoff parameter is $Q_c = 5$ Å^{-1} and the range parameter is ...

CONCLUSIONS:

- IN He TOF SPECTRA, MULTIPHONON PROCESSES HAVE A CHARACTERISTIC SIGNATURE
- WE UNDERSTAND BETTER THE TRANSITION FROM QUANTUM TO CLASSICAL BEHAVIOR FOR He AND Ne SCATTERING
- (HOPEFULLY) THIS UNDERSTANDING CAN BE EXPORTED TO STICKING AND REACTIVE SCATTERING.