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"Debye-Waller Factor in Atom-Surface Scattering"

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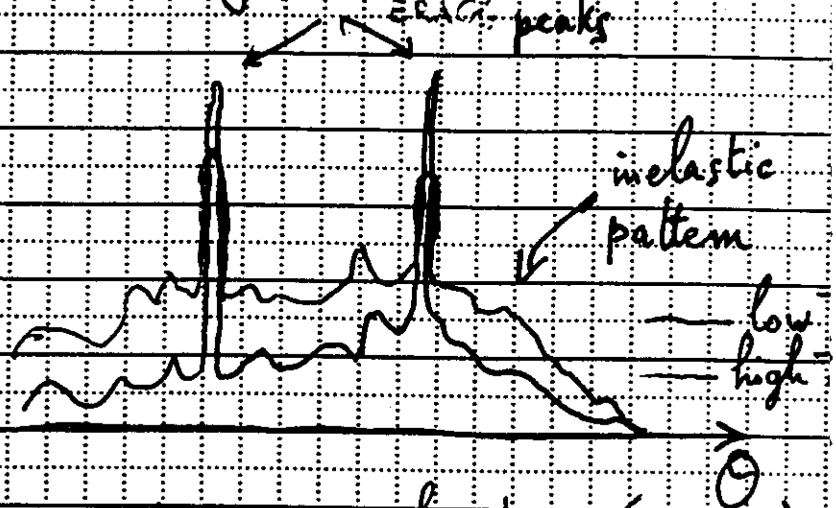
DEBYE-WALLER FACTOR
IN ATOM-SURFACE SCATTERING

It was shown by DEBYE (1914) and WALLER (1923) that the effect of vibrations on X-ray scattering from a crystal
is to reduce (without broadening) the BRAGG diffraction intensities:
the missing intensity goes into the inelastic pattern



The resulting DEBYE-WALLER factor (DWF) $F = \frac{I}{I_{static}}$ is written as an exponential,

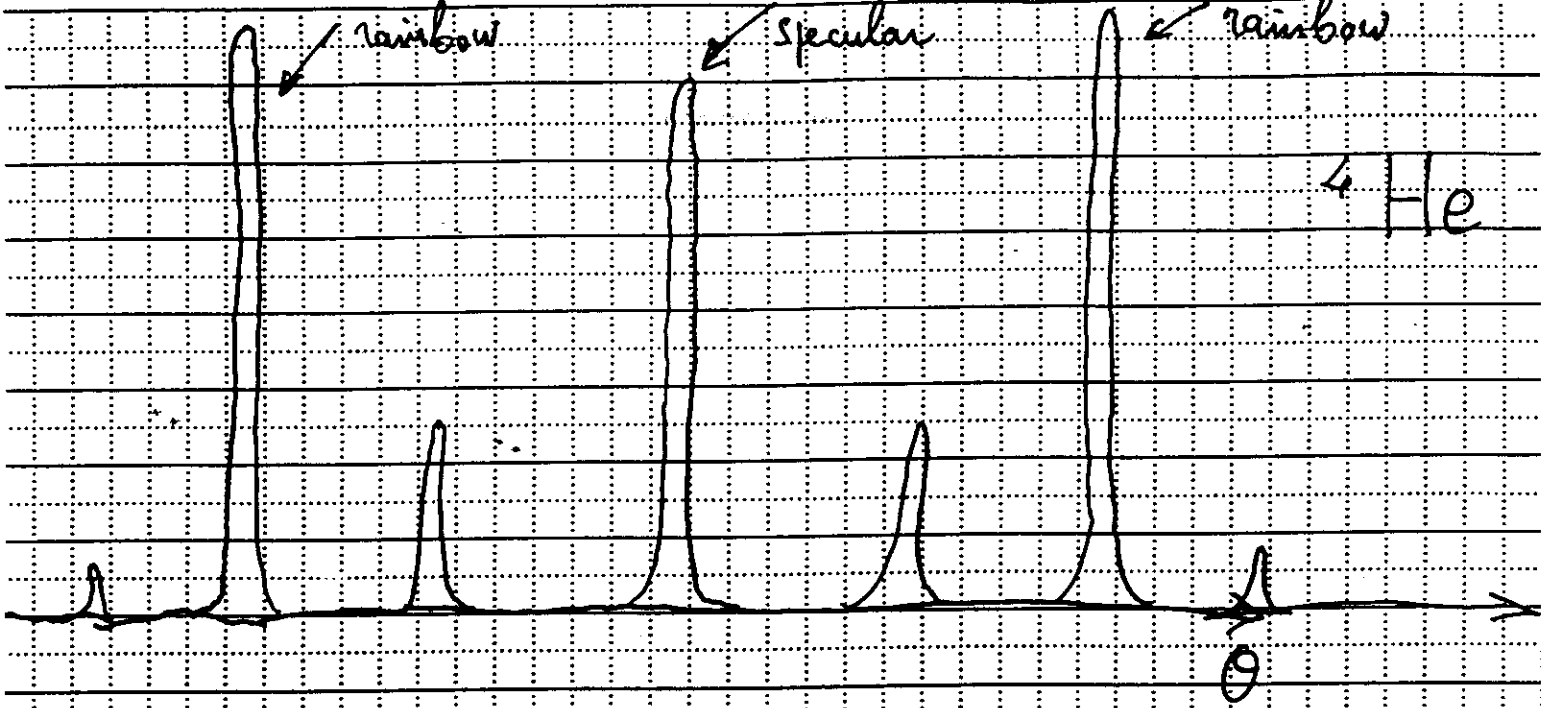
$$F = e^{-2W}$$

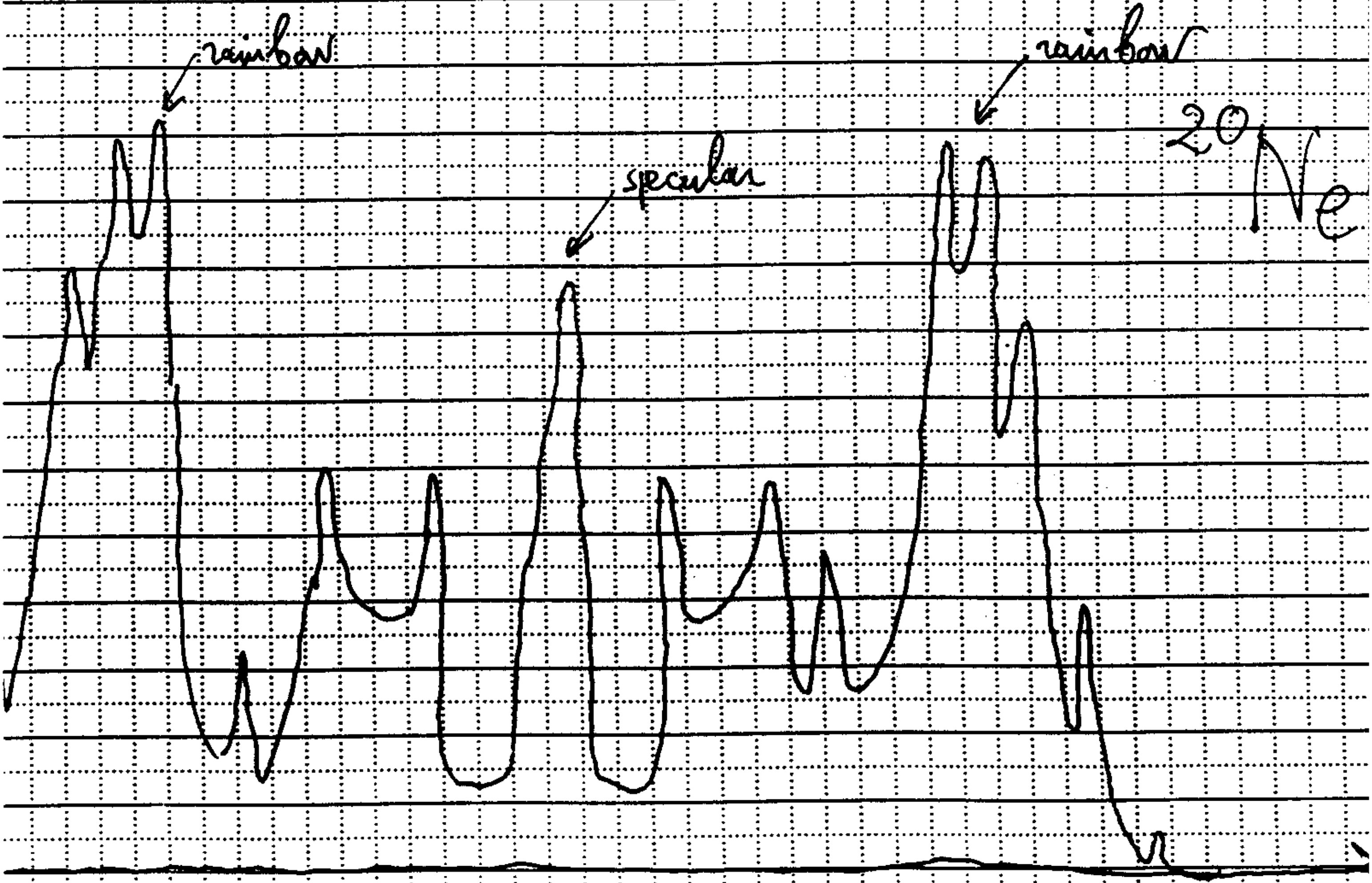
2: WALLER's correction

where in the simplest case

$$W = \frac{1}{2}\langle(\vec{q}\cdot\vec{u})^2\rangle$$

($\hbar\vec{q}$ momentum transfer, $\vec{u}$ atomic (ionic) displacement).





$$W_0 = 4.6 \quad e^{-2W_0} = e^{-9.2} = 10^{-4}$$

$$W = 1.84 \quad e^{-2W} = e^{-3.68} = .025$$

A fact
250 !

The theory was later extended to neutron, electron and atom scattering. The hypotheses on which the DW theory rested (weak, fast scattering) became more and more questionable.

Weak scattering
⇓ BA

In the BORN approximation the DW theory is exact.
But the BA strictly never holds:

X-rays – The BA (equiv. to the kinematic approximation) implies neglecting the dynamic effects (multiple scattering) important for large, perfect crystals.

neutrons – The BA is wrong in the nuclear sense, but the kinematic approximation is right (no multiple scattering): $f \gtrsim 10^{-15}$ m (scattering length) $\ll d \simeq 10^{-10}$ m (distance between scatterers)

electrons, atoms – BA wrong (for atoms DWBA reasonable).

Fast scattering

Even if the scattering is strong, the DW theory may still be right if it is fast: the ions don't move and a snapshot is taken of their instantaneous positions. True for X-rays, electrons, irrelevant for neutrons (whose scattering is very weak), questionable for H, He, H_2, false for heavier atoms.

What to do if the scattering is strong & slow?

We should distinguish 2 cases: Let l be a characteristic length for the potential variation

Case a) $m\omega_D l^2 \lesssim \hbar$, case b) $m\omega_D l^2 \gg \hbar$.

Case a) (relatively light particles)

In this case at low energies ($E \lesssim m\omega_D^2 l^2$) the collision time τ_c is long or comparable to the vibration period τ_D: a time-dependent interaction occurs. Otherwise $\tau_c \ll \tau_D$ and the conventional DW theory applies.

Case b) (very heavy particles)

The crystal can adapt to the instantaneous position of the heavy atom.

This regime is essentially adiabatic, hence quasi-elastic.

Both in cases a) and b) the scattering is more elastic than according to the conventional DEBYE-WALLER theory, but the picture is different.

GENERAL EXPRESSIONS

When a projectile (atom) collides with a large system (surface) the information is contained in the T-matrix elemen

$$(\beta | T_{\vec{p} \leftarrow \vec{p}_i} | \alpha)$$

for the projectile, large system to go from $\vec{p}_i, \alpha$ to $\vec{p}, \beta$

The inelastic scattering differential probability is

$$dP = \frac{L^4 m^2 p}{4\pi^2 \hbar^4 |p_{iz}|} \sum_\alpha p_\alpha \sum_\beta \left| (\beta | T_{\vec{p} \leftarrow \vec{p}_i} | \alpha) \right|^2 \delta(E_\beta - E_\alpha - \Delta) \, d\Omega \, d\Delta =$$

(Δ energy loss)

$$= \frac{L^4 m^2 p}{8\pi^3 \hbar^5 |p_{iz}|} \int e^{-\frac{it\Delta}{\hbar}} \langle T^{\dagger}_{\vec{p} \leftarrow \vec{p}_i}(0) \, T_{\vec{p} \leftarrow \vec{p}_i}(t) \rangle dt \, d\Omega \, d\Delta$$

In the elastic case $\Delta = 0$ and the integral is dominated by long times. Then the correlation factorizes and

$$dP_{elastic} = \frac{L^4 m^2 p}{4\pi^2 \hbar^4 |p_{iz}|} \delta(\Delta) \left| \langle T_{\vec{p} \leftarrow \vec{p}_i} \rangle \right|^2 d\Omega \, d\Delta$$

So we define the DEBYE-WALLER factor as

$$F = \frac{\left| \langle T_{\vec{p} \leftarrow \vec{p}_i} \rangle \right|^2}{\left| T^{(0)}_{\vec{p} \leftarrow \vec{p}_i} \right|^2}$$

static lattice

BORN APPROXIMATION

$$V_{\vec{q}} = v_{\vec{q}} \sum_n e^{i\vec{q}\cdot(\vec{R}_n^{(0)}+\vec{u}_n)} \qquad \hbar\vec{q} = \vec{p}_i - \vec{p}$$

In the BORN approximation $T_{\vec{p}\leftarrow\vec{p}_i} = V_{\vec{q}}$

and $\langle T_{\vec{p}\leftarrow\vec{p}_i} \rangle = \langle V_{\vec{q}} \rangle = v_{\vec{q}} \sum_n e^{i\vec{q}\cdot\vec{R}_n^{(0)}} \langle e^{i\vec{q}\cdot\vec{u}}$

$$= v_{\vec{q}} \langle e^{i\vec{q}\cdot\vec{u}} \rangle \sum_n e^{i\vec{q}\cdot\vec{R}_n^{(0)}} = v_{\vec{q}} \langle e^{i\vec{q}\cdot\vec{u}} \rangle S_{\vec{q}} =$$

$$= v_{\vec{q}}\, e^{-W} S_{\vec{q}} = \qquad W = \frac{1}{2}\langle (\vec{q}\cdot\vec{u})^2 \rangle$$

$$= e^{-W}\, T^{(0)}_{\vec{p}\leftarrow\vec{p}_i}, \qquad \text{thus} \quad F = e^{-2W},$$

which is the DEBYE-WALLER result

FAST SCATTERING

To show that for fast scattering the DEBYE-WALLER result still holds, let us consider a rather trivial model: $\vec{u}_n = \vec{u}$ (indep of n), the whole surface oscillating rigidly.

$$V_{\vec{q}} = v_{\vec{q}}\, S_{\vec{q}}\, e^{i\vec{q}\cdot\vec{u}}$$

$$T_{\vec{p}\leftarrow\vec{p}_i} = V_{\vec{q}} + \sum_{\vec{k}'} V_{\vec{k}-\vec{k}'}\left[z - \frac{\hbar^2 k'^2}{2m} - h_0(\vec{u})\right]^{-1} T_{\hbar\vec{k}'\leftarrow\vec{p}_i}$$

$h_0(\vec{u})$ is the free Hamiltonian describing the motion $\vec{u}$ of the ions. If the mass M of the latter is ∞, h_0 is neglected, and the factors $e^{i(\vec{k}_2-\vec{k}_1)\cdot\vec{u}}$ occurring in terms as $VG_0VG_0VG_0 \ldots VG_0V$ $\left(V = \left(z - \frac{\hbar^2 k'^2}{2m}\right)^{-1}\right)$ multiply to get $e^{i(\vec{k}_i-\vec{k})\cdot\vec{u}}$ every time

$$S_0 \quad T_{\vec{p}\leftarrow\vec{p}_i} = T^{(0)}_{\vec{p}\leftarrow\vec{p}_i}\, e^{i\vec{q}\cdot\vec{u}} \quad \text{and}$$

$$\left\langle T_{\vec{p}\leftarrow\vec{p}_i}\right\rangle = T^{(0)}_{\vec{p}\leftarrow\vec{p}_i}\, e^{-W}, \qquad W = \tfrac{1}{2}\langle(\vec{q}\cdot\vec{u}$$

Corrections are of the order $\sqrt{\frac{m}{M}}$.

So the DW result holds for $M \to \infty$ (fast scattering). That the surface moves as a whole is not restrictive; the same is true in the opposite limit where all ions move independently.

SLOW SCATTERING, LOW ENERGY

$$E \ll m\omega_D^2 \ell^2 \qquad (\tau_c \gg \tau_D)$$

$$E \ll \hbar\omega_D \qquad \text{(single phonon)}$$

This case can be treated semiclassically; recoil neglected.

Eikonal approximation for T:

$$T_{\vec{p}_f \leftarrow \vec{p}_i} = -i \frac{\hbar |p_{iz}|}{m L^3} \int e^{i\eta(\vec{R},t)} \, d^2R$$

$$\eta(\vec{R},t) = \eta_1 + \eta_2 + \eta_3$$

$\eta_1 = \vec{Q}\cdot\vec{R}$, $\eta_2(\vec{R})$ contains the static corrugation $(\eta_2 = q_z \zeta(\vec{R}))$

$\eta_3(\vec{R},t)$ the dynamic corrugation (phonons) $(\eta_3 = q_z \delta\zeta(\vec{R},t))$

$$\langle e^{i\eta_3}\rangle \approx e^{-\frac{1}{2}\langle\eta_3^2\rangle} = e^{-W(\vec{R})}$$

The diffraction intensity corresponding to the reciprocal lattice vector $\vec{G}$ is

$$\sim \vec{A}^2 \left| \int_{\text{unit cell}} e^{i\vec{G}\cdot\vec{R}+i\eta_2(\vec{R})-W(\vec{R})}\, d^2R \right|^2 .$$

W depends on $\vec{R}$, but by the stationary phase principle may be evaluated at $\vec{R}_{\vec{G}}$, $\qquad (\nabla\eta_2(\vec{R}_{\vec{G}}) = -\vec{G})$

so the DEBYE-WALLER factor is

$$F_{\vec{G}} = e^{-2W_{\vec{G}}}, \qquad W_{\vec{G}} = \frac{1}{2}\langle\eta_3^2(\vec{R}_{\vec{G}})\rangle$$

To evaluate explicitly η_3 we can relate it to the work $\mathcal{L}$ done by the atom on the crystal ions. It was shown by BRENIG (Z. Phys. B36 (1979) 81) that the operator $Q(t) = S^{\dagger}(0)\,S(t)$ (related to the phase shift) evolves with $\mathcal{L}$:

$$\frac{dQ}{dt} = \frac{i}{\hbar}\, Q\, e^{\frac{i}{\hbar}tH_s}\, \mathcal{L}\, e^{-\frac{i}{\hbar}tH_s} \qquad (H_s\text{: phonon Hamiltonian}$$

η_3 may be written

$$\eta_3 = \frac{1}{\hbar}\,\delta\, S_{cl} = \qquad S_{cl}\ \text{action}$$

$$= -\frac{1}{\hbar}\int \sum_n \vec{F}_n(t)\cdot\vec{u}_n(t)\,dt$$

where $\vec{u}_n$ is the displacement of ion n,
and $\vec{F}_n$ is the force with which it acts on the atom.
Therefore

$$W_6 = \frac{1}{2\hbar^2}\sum_{mn}\int \vec{\vec{A}}_{mn}(\tau) : \vec{\vec{B}}_{mn}(\tau)\,d\tau$$

where $\vec{\vec{A}}_{mn}(\tau)$ is the force correlation:

$$\vec{\vec{A}}_{mn}(\tau) = \int \vec{F}_m(t)\,\vec{F}_n(t+\tau)\,dt .$$

and $\vec{\vec{B}}_{mn}(\tau)$ is the displacement correlation:

$$\vec{\vec{B}}_{mn}(\tau) = \langle \vec{u}_m(0)\,\vec{u}_n(\tau)\rangle$$

Neglecting recoil, the forces may be evaluated along the trajectory of the atom as scattered
off a static crystal.

ARMAND effect

Let me go back and apply the general formulae to fast scattering. The force correlation is short-lived i.e. $\vec{A}_{mn}(\tau)$ vanishes unless τ is very small. So we replace $\vec{\vec{B}}_{mn}(\tau)$ by $\vec{\vec{B}}_{mn}(0) = \langle \vec{u}_m \vec{u}_n \rangle$

$$W_{\vec{G}} = \frac{1}{2\hbar^2} \sum_{mn} \int \vec{\vec{A}}_{mn}(\tau)\, d\tau : \langle \vec{u}_m \vec{u}_n \rangle =$$

$$= \frac{1}{2} \sum_{mn} \langle \vec{q}_m \cdot \vec{u}_m \; \vec{q}_n \cdot \vec{u}_n \rangle$$

(because $\int \vec{F}_m(t)\, dt = \hbar \vec{q}_m$, the momentum transfer to the ion m). If p ions are involved in the scattering $q_m \sim \frac{q}{p}$ and $W_G \propto \frac{1}{p} W_0$ if the ionic motions are uncorrelated. This ARMAND effect makes the scattering more elastic

BEEBY effect

$$W \sim \frac{1}{2\hbar^2} \iint \vec{F}(t)\,\vec{F}(t+\tau) : \langle \vec{u}(0)\,\vec{u}(\tau) \rangle \, dt\, d\tau$$

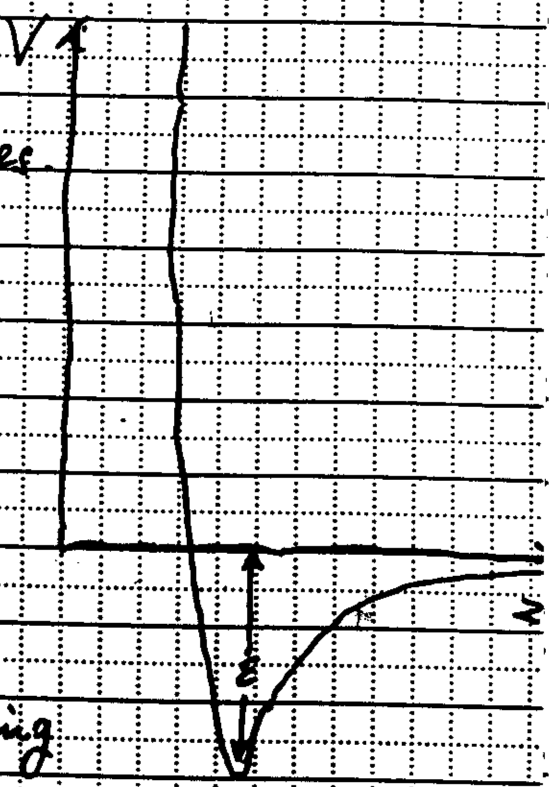
One may distinguish attractive from repulsive forces. Attractive forces are slowly varying. On their time scale $\langle \vec{u}(0)\vec{u}(\tau)\rangle \sim 0$. Considering only repulsive forces (fast varying) $W \sim \frac{1}{2} \langle (\vec{q}_{rep} \cdot \vec{u})^2 \rangle$

where $\hbar \vec{q}_{rep}$ is

the momentum transfer by repulsive forces.

$\vec{q}_{rep} > \vec{q}$ because it is measured

from the well bottom



(roughly $\frac{q_{rep}}{q} \approx \sqrt{\frac{E_z + \varepsilon}{E_z}}$)

The BEEBY effect makes the scattering more inelastic

(statistical) Heavy atoms (Ne)

$$B(\tau) = \frac{\hbar}{M}\int \frac{g(\omega)}{\omega}\left[n(\omega)\cos\omega\tau + \frac{1}{2}e^{i\omega\tau}\right]d\omega \approx$$

$$\approx \text{ at high } T \qquad \frac{kT}{M}\int \frac{g(\omega)}{\omega^2}\cos\omega\tau\, d\omega$$

For a MORSE potential, $V = 4\varepsilon\left(e^{-2\alpha z} - e^{-\alpha z}\right)$

$$F(t) = \frac{1}{2\pi}\int \tilde{F}(\omega)\, e^{i\omega t}\, d\omega$$

$$\tilde{F}(\omega) = 2\sqrt{2mE_z}\,\frac{\pi s}{\sinh \pi s}\cosh \pi\beta s$$

$$s = \omega\tau_c = \frac{\omega}{\alpha v_z} \qquad \beta = 1 - \frac{\arctan\sqrt{K}}{\pi} \qquad K = \frac{E_z}{\varepsilon}$$

$$\tilde{A}(\omega) = |\tilde{F}(\omega)|^2 = \int A(\tau)\cos\omega\tau\, d\tau$$

$$W = \frac{kT}{2\hbar^2 M}\int \frac{g(\omega)}{\omega^2}|\tilde{F}(\omega)|^2 d\omega =$$

$$= \frac{2\pi^2 m^2 kT}{\hbar^2 M \alpha^2}\int \frac{\cosh^2(\pi\beta\omega/\alpha v_z)}{\sinh^2(\pi\omega/\alpha v_z)}\, g(\omega)\, d\omega$$

Take a DEBYE spectrum and let $p_0 = p\sqrt{K}$,

$$p = \frac{\pi}{2}\omega_D\tau_c, \qquad p_0^2 = \frac{\pi^2}{8}\frac{m\omega_D^2}{\alpha^2\varepsilon}, \qquad p_0 = 19 \text{ for Ne on LiF}$$

$$W = W_0\, C, \qquad C = \frac{1}{2p}\int_0^{2p}\frac{\cosh^2\beta x}{\sinh^2 x}\, x^2\, dx$$

At high p (slow collisions) $C = \frac{\varphi(E_z/\varepsilon)}{p}$

$K = E_z/\varepsilon$	$\varphi(K)$
0	∞
1	8.7
3	4
∞	$\frac{\pi^2}{6} = 1.6$

Enhancement of diffraction takes place for $C < 1$,

i.e. $p \gtrsim \varphi$; this requires both

a collision time longer than $2\pi/\omega_D$

and an energy high in comparison to ε

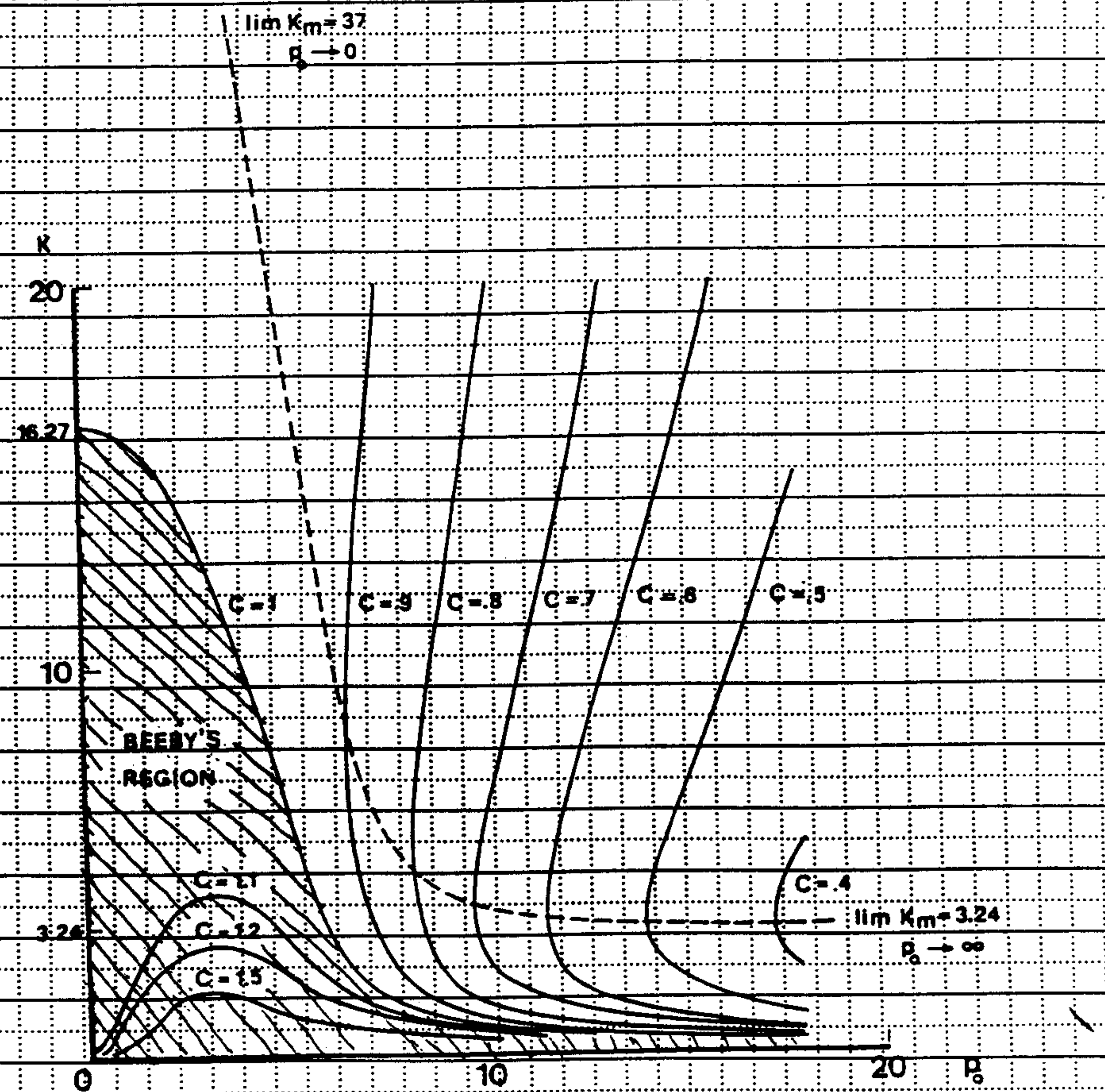


Fig. 4. Constant C lines drawn in the (p_0, K) plane. The dashed line connects the K values yielding a minimum value of C for each p_0. The shaded area in the lower left corner is "Beeby region", where $C > 1$ and diffraction is reduced.

HEAVY ATOMS

If $m \gg M$, then

during the slow collision
the phonons adjust themselves to the position of the (slowly moving) projectile.

In zeroth order the adjustment is perfect, ~~the system is always~~ the total Hamiltonian is to be diagonalized, the system samples the eigenstates ~ according to their statistical weight, and the scattering is elastic

Inelastic scattering (and the DEBYE–WALLER factor) arise from anharmonic effects (~~arising from~~ produced by the atom-surface interactions), terms like $\frac{1}{3!}\sum_j (u_j^* \cdot \nabla)^3 V(r - r_j)$.
These are cubic and a rough estimate gives

$$W \sim \frac{1}{9} W^{(0)^3},$$

i.e. $W \sim q^6 \langle u^2 \rangle^3$ at low q

"DYNAMIC" EFFECTS

The DEBYE-WALLER factor gives the inelastic drain imposed on elastic processes by phonon emission and absorption. In "kinematic" theory (i.e. for large $\vec{k}$) it depends on the momentum transfers $\vec{q}$ (or $\vec{q}_j$) in the elastic process, i.e. when the phonons are not exchanged. This is a paradox and leads to a wrong normalization (not everything lost in elastic scattering is recovered in the inelastic intensity).

In reality the inelastic momenta should appear.

An <u>exact</u> treatment for the vibrating hard wall was given by GARCÍA, MARADUDIN & CELLI. ~~They apply~~ They impose $\psi = \psi_i + \sum_{\substack{\text{reflected}\\ \text{waves}}} \psi\, R$, where

source function

including evanescent waves

R obeys the eq.

$$\frac{1}{8\pi^3}\int e^{i\vec{K}'\vec{R} + ik_z' u_z(\vec{R},t) - i\omega' t}\, R(\vec{K}\omega|\vec{K}'\omega')\, d^2K'\, d\omega' = -\, e^{i\vec{K}\cdot\vec{R} - ik_z u_z(\vec{R},t) - i\omega t}$$

where $k_z' = k_z(\vec{K}',\omega')$, $k_z(\vec{K},\omega) = \begin{cases} \sqrt{k^2-K^2} & \text{if } |\vec{K}| \le k \\ i\sqrt{K^2-k^2} & \text{otherwise} \end{cases}$

and find

$$W = \frac{1}{4\pi^2}\, k_z\left(\vec{K}_0, \frac{E_0}{\hbar}\right) \mathrm{Re}\left\{ \int d^2Q \int d\omega\, k_z\left(\vec{K}_0 - \vec{Q}, \frac{E_0}{\hbar} - \omega\right) \int d^2R \int dt\, e^{i\vec{Q}\cdot\vec{R} - i\omega t} \left\langle u_z(\vec{R}, t)\, u_z(0,0) \right\rangle \right\}$$

The appearance of $k = k_z\left(\vec{K}_0, \frac{E_0}{\hbar}\right)$ (before phonon exchange) and $k' = k_z\left(\vec{K}_0 - \vec{Q}, \frac{E_0}{\hbar} - \omega\right)$ (after phonon exchange) instead of $q \approx k + k'$ leads to the correct limiting behaviour at small k

(Further generalized by CELLI & MARADUDIN and LAPUJOULADE).