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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

ATOMIC AND MOLECULAR SCATTERING FROM SURFACES (EXPERIMENTAL)
Part I

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Atomic scattering from Surfaces

— Interactions of gas-phase atoms and molecules with surfaces play a basic role in a wide range of phenomena:

- Sticking
- Adsorption
- Oxidation
- Catalysis
- Film growth
- ⋮

— For surface study the experimental techniques are based on {atom/mol. | electron} scattering which are intrinsically complex:

a) Exp.ly, we have to use vacuum conditions to keep a surface clean and avoid beam attenuation

b) Th.ly, we have to develope new approx. and models to perform a comparison with exp. results.

— The At./mol. scattering and electron scattering are complementary technique with "probes" having different behaviour:

- no penetration for At./mol. at thermal energy
- few atomic layers for el. in energy range 10 ÷ 200 eV.

- Considering He beams, the most used in surface studies, the relevant characteristic are:

a) He is a noble gas and interacts only physically with the surface atoms. It can be used with stable as well as reactive surfaces

b) The low mass enhances elastic scattering

c) Energy range $18 \div 64$ meV

wave lenght " λ_{He} $1 \div 0.5$ Å

wave vector " k $6 \div 12$ Å^{-1}

d) Energy spread $\frac{\Delta E}{E} \sim 2 \div 4\%$ (FWHM)

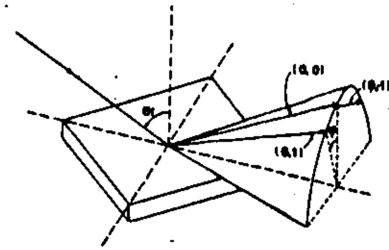
Atomic scattering history

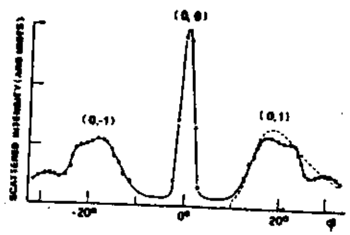
- Pioneer experiments were carried out by Stern and coworkers in order to test the wave nature of atomic beams (H and He).
- For the first time they observed the diffraction peaks of He and H atoms from LiF and NaCl surfaces confirming the wave nature of an atomic beam.

a) Estermann, Stern Z. Phys. 61 (1930) 95

b) Estermann, Frisch, Stern " 73 (1931) 348

c) Frisch, Stern Z. Phys. 84 (1933) 430

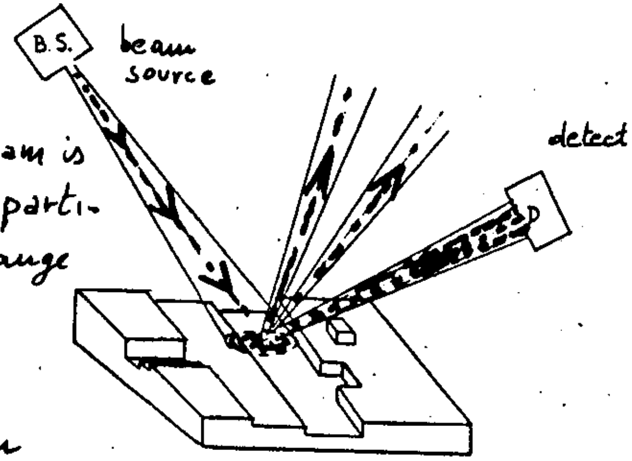




- About 20 years ago, by the developement of a new vacuum technology and quasi-monochromatic beam sources, atomic scattering became a reliable and accurate surface technique.

Scattering experiments

<u>Real exp.</u>



- Incident beam is composed of particles with a range of directions and speeds.
- In a quantum mechanical language each particle is described by a wave packet
- The detector has a finite angular acceptance and a finite energy window.
- The surface presents defects (steps, domain, adatoms, ...)

⟹ too complex is the situation to be described

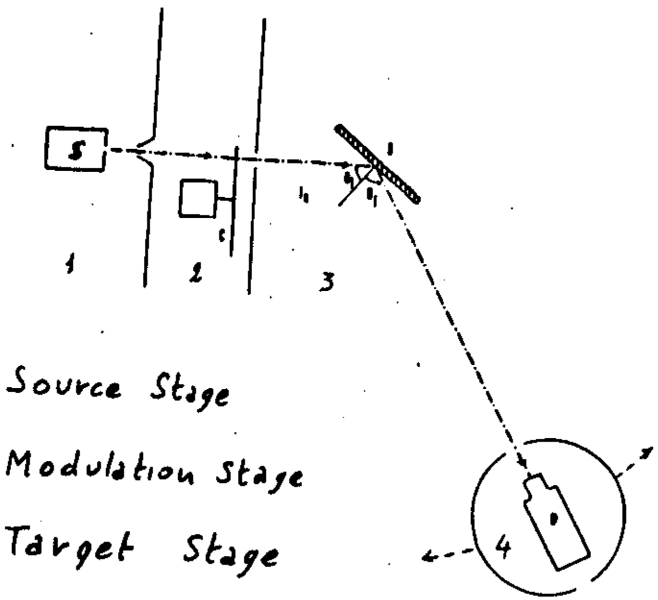
- Ideal (theoretical) Experiments

- Incident plane wave (precisely defined $\underline{k}$, direction, infinite lateral extension)
- Perfect surface with infinite 2D periodicity.

→ Experimental challenge is:

- to obtain Real condition as close as possible to the idel one
- to develope methods of data analysis which correct the exp. yields to compare with theoretical predictions.

Experimental set-up



1) Source Stage
2) Modulation Stage
3) Target Stage
4) Detector stage

Beam Sources

- Starting with a source pressure P_0 and a source temperature T_0 two cases are possible

a) $\frac{\lambda}{d_0} > 1$ effusive source

b) $\frac{\lambda}{d_0} < 1$ supersonic source

(During the gas expansion, in continuum flow regime, the gas cools down and the local sound speed decreases so that the beam becomes supersonic.)

(λ = mean free path, d_0 = source orifice diameter)

Effusive sources

- They were the first ones used in scattering experiments

- From kinetic theory of gases the velocity distribution along the axis of the source is

$$f(v) \propto v^3 \exp\left\{-\frac{mv^2}{2k_B T_0}\right\}$$

- The intensity of an effusive beam along its axis, 1 m away from the source, is $\sim 5 \cdot 10^{12}$ atoms/cm²s at $T_0 = 300K$

- The energy spread is too great ($\approx k_B T_0$) to resolve diffraction peaks or to resolve inelastic structure.

- Velocity selectors give narrow velocity distribution with a loss in intensity

Supersonic Sources

- Supersonic sources are also called nozzle sources because the gas expansion is similar to that one in a converging-diverging rocket nozzle.
- The flow crossing the nozzle is continuum, but at some distance away from nozzle a transition occurs, the flow is molecular, now, and no collision occurs between beam atoms.
- During the free jet expansion, since the flow time is short, no energy exchange occurs, so that along any stream line:

$h + \frac{V^2}{2} = h_0$ where h is the enthalpy per unit mass, V is hydrodynamics or flow velocity and h_0 is the gas enthalpy in the source where $V=0$. For ideal gas ($dh = C_p\,dT$)

$V^2 = 2\int_T^{T_0} C_p\,dT$ with T = final temperature

If C_p is constant and since, generally, $T_0 \gg T$ $V_\infty = \sqrt{2 C_p T_0}$ terminal velocity

- Knowing the total flux $\dot{N}$ through the nozzle, the intensity I along the source axis can be expressed by

$I = \frac{k\,\dot{N}}{\pi}$ the peaking factor $\begin{cases} 1 & \text{ideal effusive source} \\ 2 & \text{supersonic source monoatomic gas.} \end{cases}$

- For a supersonic He source with

$T_0 = 300\,K$, $P_0 = 30\,Atm$, $d_0 = 5\,\mu m$ } $I \sim 2 \cdot 10^{15}\,at/cm^2 s$ 1 m away along source axis.

- There is an intensity gain of ~ 3 order of magnitude with respect to the effusive source.
- This is only due to the higher value of total flux $\dot{N}$.
- Source pumping stages need of pumps with great pumping speed (usually greater than 1000 l/s)

- The velocity distribution along the source axis, for a supersonic beam, can be well approximated by

$$f(v) \sim v^3 \exp\left\{-\frac{m}{2k_B T}(v-V)^2\right\}$$

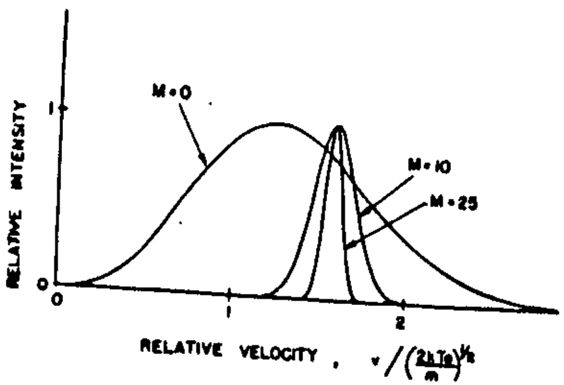
with T the final temperature and V the flow velocity.

- Remembering that $T \ll T_0$

$\rightarrow \frac{\Delta v}{v}$ is less than for effusive sources (few per cent)

Comparison between velocity distribution

M = Mach number = $\frac{V}{V_s}$ $\quad V_s$ = sound speed



- It is useful to introduce a non-dimensional velocity x and the speed ratio S

$$x = \sqrt{\frac{m}{2k_B T_0}}\, v \qquad S = \sqrt{\frac{m}{2k_B T}}\, V$$

$$f(v) \longrightarrow g(x) \propto x^3 \exp\left\{-\left(x\sqrt{\frac{T_0}{T}} - S\right)^2\right\}$$

- For a monoatomic gas the enthalpy conservation reads

$$\frac{5}{2} k_B T_0 = \frac{1}{2} m V^2 + \frac{3}{2} k_B T \quad \text{so, finally,}$$

$$g(x) \propto x^3 \exp\left\{-\left(x\sqrt{\frac{3}{5} + \frac{2}{5}S} - S\right)^2\right\}$$

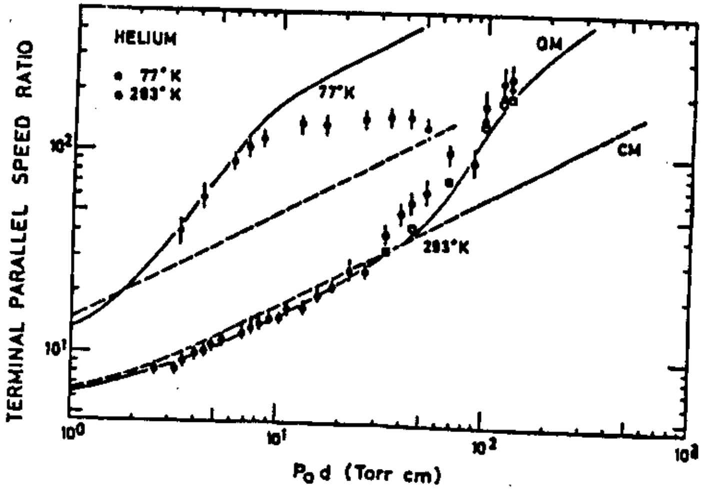
- For $S > 10$ the most probable velocity and the velocity spread are given by

$$x_{mp} \sim \sqrt{\frac{5}{2}} \longrightarrow v_{mp} = \sqrt{\frac{5k_B T_0}{m}}$$

$$\frac{\Delta x}{x} = \frac{\Delta v}{v} \simeq \frac{1.65}{S}$$

- v_{mp} depends on source temperature T_0

$\frac{\Delta v}{v}$ depends on speed ratio S

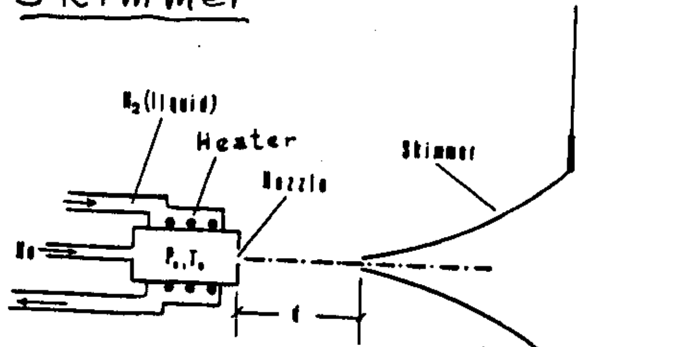


(Brusdeylins et al. Prog. Astro. and Aeronautics 51 (1977) 1047)

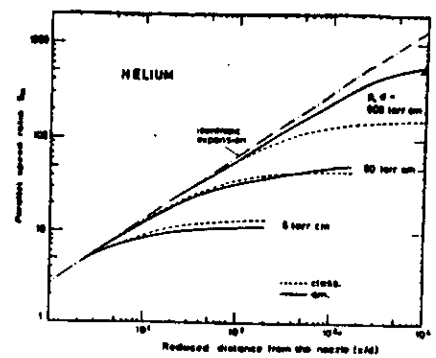
- Limits to S

- Condensation of atoms in clusters especially for heavy atoms
- Very high flow to pump
- Mechanical limit to work with high value of P_0

Skimmer



- The skimmer selects the central part of a beam
- The design of a skimmer is critical. Especially the entrance hole has to be very sharp to avoid skimmer interferences which can broaden the velocity distribution
- The nozzle-skimmer distance has to be chosen beyond the transition from continuum to molecular regime.
- Generally the n.-S. distance is chosen in order to limit the flow entering the following stage.



(Toennies, Winkelmann J. Chem. Phys. 66 (1977) 3965)

Detectors

Ionization detectors	Bolometers
a) flow-through type in which density is measured	a) Semiconducting Bol.
b) Stagnation type in which flux is measured	b) Superconducting Bol.
	a) and b) are sensitive to the energy of impinging particles

Sensitivity $\sim 10^7$ part/S

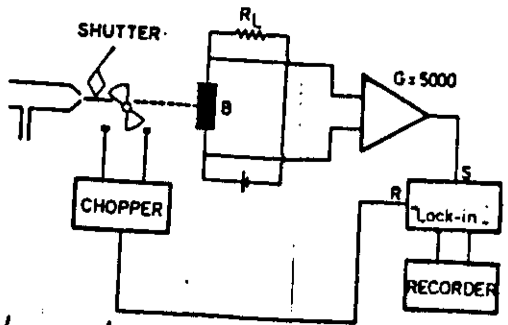
- To perform a measurements it is important to have a good Signal to Noise ratio

- This ratio can be raised

  1) lowering the background pressure (and I.R. source for bolometers)

  2) using beam modulation

Beam modulation

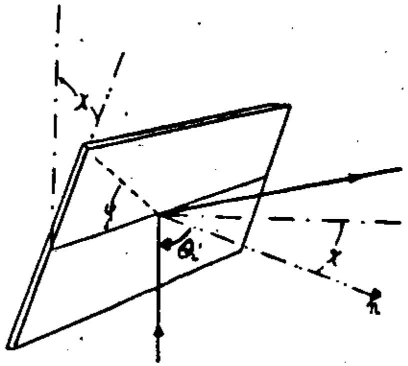


- The beam is chopped by a rotating slotted disk. A reference signal (R) is generated synchronously with beam pulses.

- The detected signal (S) is amplificated by a lock-in amplifier which mixes the two signal (S and R) and averages out the fluctuating signal (noise)

- The averaged signal depends on the relative phase of S and R, this phase can be changed to maximize the output.

Surface movements



- To perform scattering measurements manipulators must allow the surface to rotate about two surface axis, one of them is along the incident beam projection on the surface, the other one is perpendicular to the previous one; then a rotation about the surface normal must be allowed.

These rotations change the incident angle θ_i, the tilt angle χ and the azimuthal angle φ, respectively.

Surface temperature

- The surface temperature is an important parameter of a scattering experiment. Infact, the exp. yields are sensitive to this temperature. Furthermore the crystal heating or annealing is used in the surface cleaning or ordering procedure.

Surface Preparation

LiF(001): - The surface is cleaved in air

- heating at 400÷500 K for some hours is sufficient to remove adsorbed water and to clean the surface before any measurements

Ag(110): - the surface is obtained cutting a mono crystalline bar within $\pm\left(\frac{1}{2}\right)^{\circ}$ the right direction to expose (110) plane

- Several cycles of ion sputtering at 1 keV, followed by annealing at ~750 K for few minutes must be used in order to obtain ordered and clean surface.

- After the annealing, exposure to an oxygen flux helps to remove chemisorbed carbon compounds.

(Frankl, Prog. in Surf. Sci. 13(1983)265)

LiF(001)

Typical cleaved LiF surface
Crystal is about 5 mm square.
Rough appearance is exaggerated by photographic technique.

- The order of the surface can be tested with the He diffraction itself.

- The intensity I of a scattered wave is the result of superposition of wave, scattered by each surface atom,
  The waves have different phases so that

$$I \propto \left| \sum_{ij} \exp\{-i\,(\Delta \underline{K} \cdot \underline{R}_{ij})\} \right|^2 \quad \text{interference function}$$

$\underline{R}_{ij} = i\,\underline{A}_1 + j\,A_2$ atomic position

$\hbar \Delta \underline{K} = \hbar(\underline{K}_f - \underline{K}_i)$ parallel momentum exchange

- Summing up

$$I \propto \frac{\sin^2\{\frac{1}{2} N_1\, \Delta\underline{K}\cdot \underline{A}_1\}}{\sin^2\{\frac{1}{2}\, \Delta\underline{K}\cdot\underline{A}_1\}} \cdot \frac{\sin^2\{\frac{1}{2} N_2\, \Delta\underline{K}\cdot\underline{A}_2\}}{\sin^2\{\frac{1}{2}\, \Delta\underline{K}\cdot\underline{A}_2\}}$$

where N_1 and N_2 are the number of surface atoms along the two surface directions.

- The maxima of I are for

$\Delta\underline{K}\cdot\underline{A}_1 = 2\pi h$
$\Delta\underline{K}\cdot\underline{A}_2 = 2\pi l$ (h, l integer) Bragg condition

- The widths of the peaks are proportional to $\frac{1}{N_2}$ and $\frac{1}{N_1}$: Greater the ordered surface region → Narrower the diffraction peaks

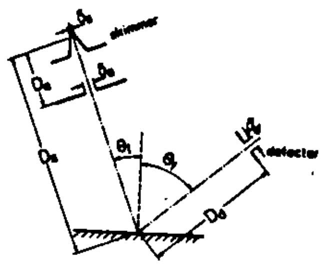
- For in-plane scattering along $\underline{A}_1$ direction

$$\Delta K = k_i \left(\sin\theta_f - \sin\theta_i \right)$$

and the Bragg condition becomes

$$\sin\theta_f = \sin\theta_i + \frac{2\pi h}{k_i A_1}$$

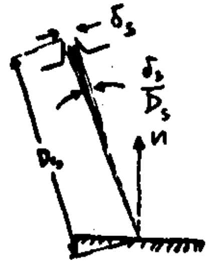
- Considering the geometry of scattering, we have a broadening of diffracted peaks due to the finite dimension of source, beam, and detector opening.



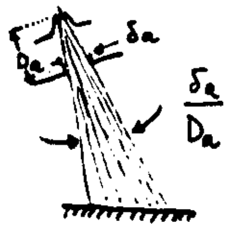
Angular Broadening

- The contribution of instrumental geometry to angular width is given by

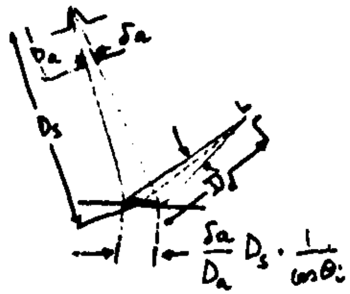
$$\left(\Delta_\theta \theta_f\right)^2 \approx \left(\frac{\cos\theta_i}{\cos\theta_f}\,\frac{\delta_s}{D_s}\right)^2 +$$



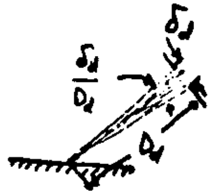
$$+\left(\frac{\cos\theta_i}{\cos\theta_f}\,\frac{\delta_a}{D_a}\right)^2 +$$



$$+\left(\frac{\cos\theta_f}{\cos\theta_i}\,\frac{D_s}{D_d}\,\frac{\delta_a}{D_a}\right)^2 +$$



$$+\left(\frac{\delta_d}{D_d}\right)^2$$



- The energy distribution of incident beam gives the last contribution to the angular width

From the Bragg condition

$$\Delta_E \theta_f = \frac{|\sin\theta_f - \sin\theta_i|}{\cos\theta_f}\sqrt{\frac{\overline{(\Delta E^2)}}{E^2}}$$

- The total angular broadening is given by

$$\Delta\theta_f = \sqrt{(\Delta_0\theta_f)^2 + (\Delta_E\theta_f)^2 + (\Delta_s\theta_f)^2}$$

where $\Delta_s\theta_f$ is the contribution due to surface disorder.

For the experimentalist

The surface is ordered !

it is negligible the

$\Delta_s\theta_f$ contribution to $\Delta\theta_f$