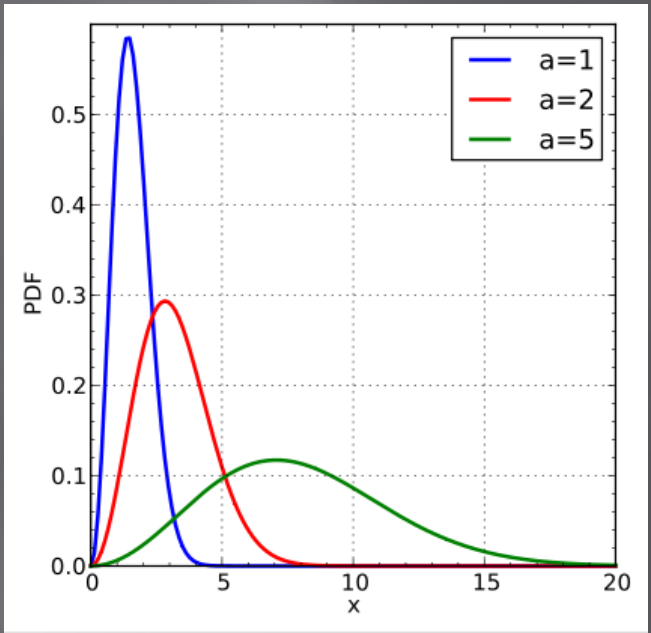
Secondary Sputtering Mechanisms

Pulsed Laser Deposition of Thin Films

Chrisey and Hubler, 1994

Secondary Sputtering Mechanisms

- Laser pulse strikes target, particles emitted in a pulse
- If density of sputtered atoms from target is low enough, particles will escape in free flight without interacting with each other
- Velocity distribution depends on Primary mechanism, i.e. thermal sputtering results in a Maxwellian distribution



Secondary Sputtering Mechanisms

- If pulse releases on the order of 0.5 monolayers per nanosecond(s) scale, particles will collide sufficiently often enough to reach an equilibrium where we treat the body of sputtered atoms as a gas.
- Equilibrium referred to as a Knudsen Layer, with an outer boundary characterized by $M = \frac{u_k}{a_k} = 1$
- $a = \frac{\gamma k_b T}{m}^{1/2}$, $u_k = a_k = (\frac{\gamma k_b T_k}{m})^{1/2}, \gamma = \frac{C_p}{C_v} = \frac{j+5}{j+3}$
- $u_k = flow\ velocity, a_k = speed\ of\ sound\ in\ gas, \gamma = ratio\ of\ heat\ capacities$
- $\rho\ \alpha\ T^{1/\gamma-1}\ \alpha\ a^{2/\gamma-1}$

Secondary Sputtering Mechanisms

- For 1-D motion we use two coupled flow equations

$$\frac{\partial a}{\partial t} + u\frac{\partial a}{\partial x} + \frac{(\gamma-1)a}{2}\frac{\partial u}{\partial x} = 0 \quad (3.1a)$$

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + \frac{2a}{\gamma-1}\frac{\partial a}{\partial x} = 0 \qquad (3.1a)$$

- Equation of state for the gas is

$$p = nk_bT = \frac{\rho k_bT}{m} = \frac{\rho a^2}{\gamma} \quad (3.2c)$$

- If laser pulse interacts with particles then we need a third flow equation

$$\rho\frac{\partial e}{\partial t} + \rho u\frac{\partial e}{\partial x} + p\frac{\partial u}{\partial x} = \frac{\partial \Phi}{\partial x} \quad (3.3)$$

- If $e = {a^2}/{\gamma(\gamma-1)}, {\partial\Phi}/{\partial x} = 0 \; and \; p = {\rho a^2}/{\gamma}$ then (3.3) reduces to (3.1)

Secondary Sputtering Mechanisms

- When KL forms, gas exhibits a shifted Maxwellian velocity distribution about $(v_x - u_k)$
- Once a KL forms the sputtered atoms lose memory of Primary Mechanism

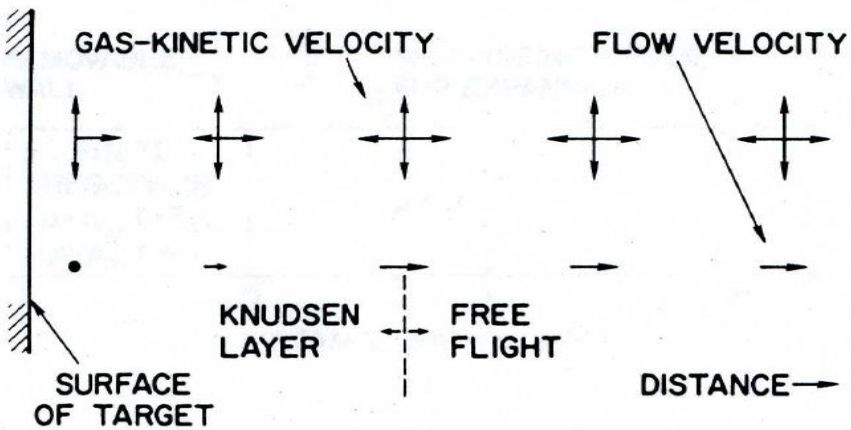


Figure 3.11. Schematic representation of a KL followed by free flight. A continuous, one-dimensional column of gas is assumed to be released from the target surface. The gas nearest the surface is characterized by $v_x > 0$ and $u = 0$, while at the KL boundary the gas shows $-\infty < v_x < +\infty$ and $u = u_K$. A surprisingly small number of collisions (~ 3; NoorBatcha et al., 1987 and 1988) is sufficient to establish the KL. The particles finally go into free flight and the velocities then persist unchanged.

Secondary Sputtering Mechanisms

- KL Theory defines $\frac{T_k}{T_s}$ and $\frac{\rho_k}{\rho_s}$ ratios for each γ as well as a backscattered ratio, F^- (assumed to re-condense)

TABLE 3.8 Parameters to Describe a Fully Developed Knudsen Layer for $M = u/a = 1$

Degrees of Internal Freedom, j	Heat–Capacity Ratio, $\gamma = C_p/C_V$ (Eq. 3.2a)	Temperature Ratio, T_K/T_s	Density Ratio, ρ_K/ρ_s	Backscattered Fraction, F^-
0	$\frac{5}{3}$	0.669	0.308	0.184
2	$\frac{7}{5}$	0.782	0.301	0.212
4	$\frac{9}{7}$	0.837	0.298	0.224
6	$\frac{11}{9}$	0.871	0.297	0.231
8	$\frac{13}{11}$	0.893	0.297	0.236
Infinity	1	1	0.296	0.257

Source: Kelly and Dreyfus, 1988a.

- We expect a TOF spectrum measurement to yield a surface temperature $k_b T_s = \frac{mv^2}{2} * \frac{T_s}{\eta T_k}$

Secondary Sputtering Mechanisms

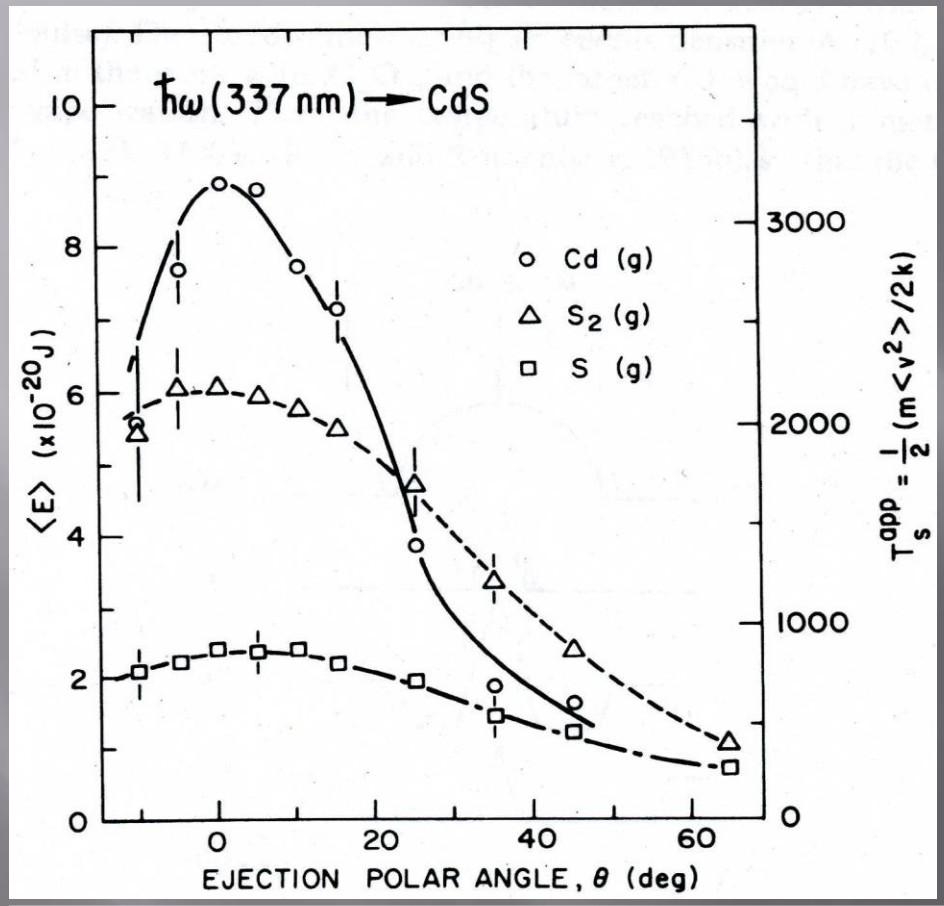


Figure 3.2. Examples of apparent TOF temperatures, T_s^{app}, vs. polar angle, θ, for t pulsed laser sputtering of CdS. Temperatures measured normally to the target a distinctly too high, those measured obliquely are distinctly too low, and the norm temperatures increase with the mass of the emitted species. These effects are characteristic of UAE, although the extent is rather greater than gas dynamics c explain. (From Namiki et al. 1986.)

Secondary Sputtering Mechanisms

- For larger quantities of sputtered atoms, gas undergoes UAE (time dependent adiabatic expansion)
- Occurs when >>1 monolayers emitted on in nanoseconds
- Flow velocity u_M increases beyond u_k, a_M drops below u_k and the $\frac{T_k}{T_s}$ evolves to $\frac{T_M}{T_s}$
- Gas exhibits more pronounced forward peaking, increases with Mach number

Secondary Sputtering Mechanisms

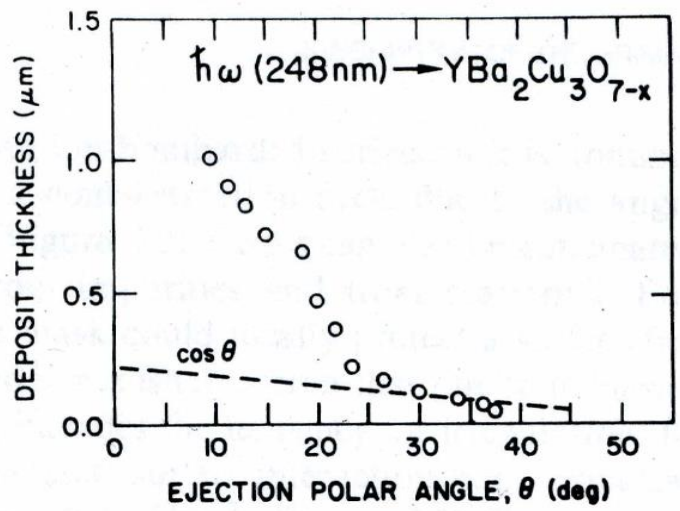


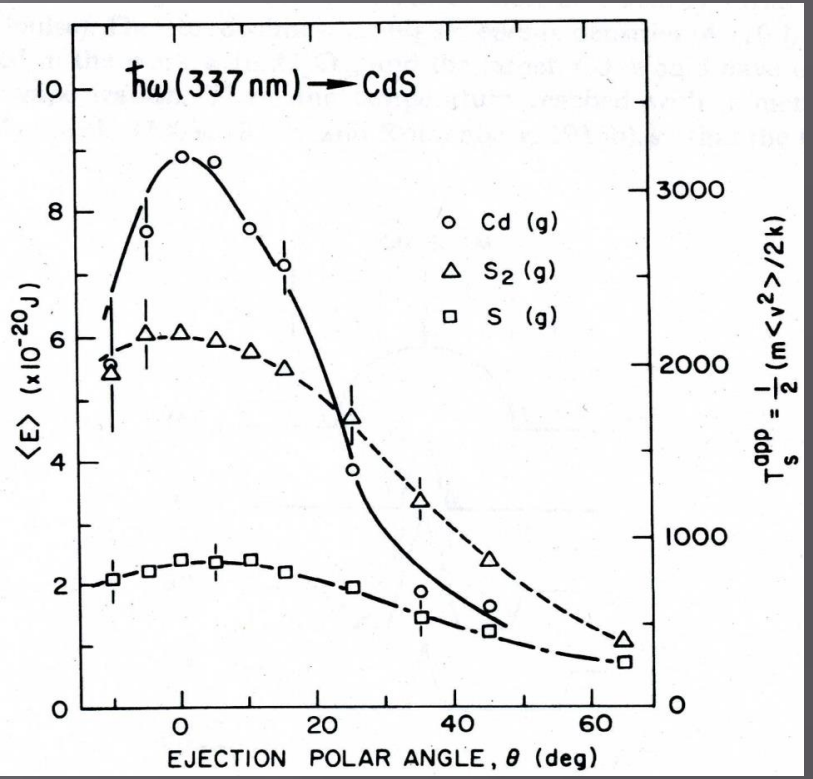
Figure 3.1. Example of strong forward peaking in the yield vs. polar angle, θ, for t
pulsed laser sputtering of $YBa_2Cu_3O_{7-x}$. The pulse length was $\sim$20 ns. The data ha
the approximate form $\cos^{11}\theta$, as for $M = u/a \approx 2.5$ (Kelly, 1990b), and from this
infer that there were both a KL and UAE. (From Venkatesan et al. 1988.)

Secondary Sputtering Mechanisms

TABLE 3.9 Values of T_M/T_s and of $\eta T_M/T_s$ for Various Combinations of $M = u/a$, θ, and j

$M = u/a$	T_M/T_s ($j = 0$)	$\eta T_M/T_s$ for $\theta = 0°$ ($j = 0$)	$\eta T_M/T_s$ for $\theta = 30°$ ($j = 0$)	$\eta T_M/T_s$ for $\theta = 60°$ ($j = 0$)	$\eta T_M/T_s$ for $\theta = 75°$ ($j = 0$)
0	1	2	2	2	2
1	0.6691	2.53	2.32	1.85	1.58
2	0.4282	2.89	2.49	1.62	1.19
3	0.2974	3.31	2.73	1.51	0.977
4	0.2185	3.74	3.00	1.47	0.842
5	0.1673	4.13	3.25	1.46	0.754
	($j = 4$)	($j = 4$)	($j = 4$)	($j = 4$)	($j = 4$)
0	1	2	2	2	2
1	0.8374	2.93	2.72	2.22	1.94
2	0.6617	3.90	3.41	2.32	1.77
3	0.5360	5.02	4.20	2.45	1.66
4	0.4429	6.20	5.03	2.61	1.58
5	0.3722	7.40	5.88	2.79	1.53

Note: The significance of $\eta T_M/T_s$ is seen in Eqs. 3.12, that is, T_s is given by the temperature-like quantity $m\hat{v}^2/2k_B$ divided by $\eta T_M/T_s$. See Kelly (1990b).



$$k_b T_s = \frac{mv^2}{2} * \frac{T_s}{\eta T_M}$$

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Outflow

- Assume target bombarded in vacuum
- Neglect passage to free flight that occurs at low densities
- Gas dynamics ceases when density is low enough
- Transition to free flight modeled with “sudden freeze” approximation
- Collisions cease abruptly at a critical gas density

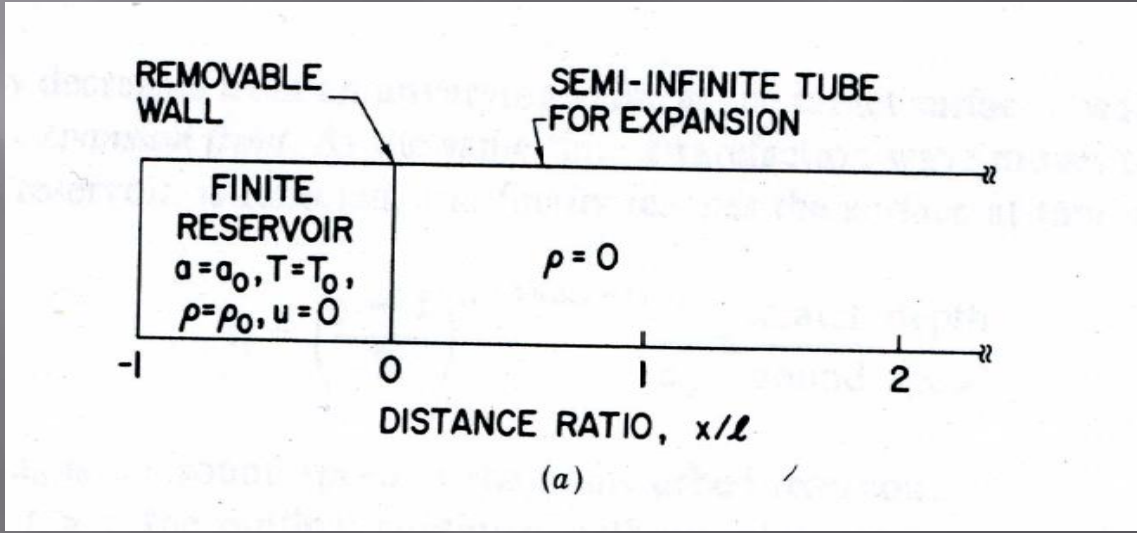
Outflow

- In real systems there tends to be an ambient gas
- Expansions terminate at a contact front where densities are equal
- Also approximate as one dimensional
- Information of 3-D expansion limited but authors claim not necessary

Outflow

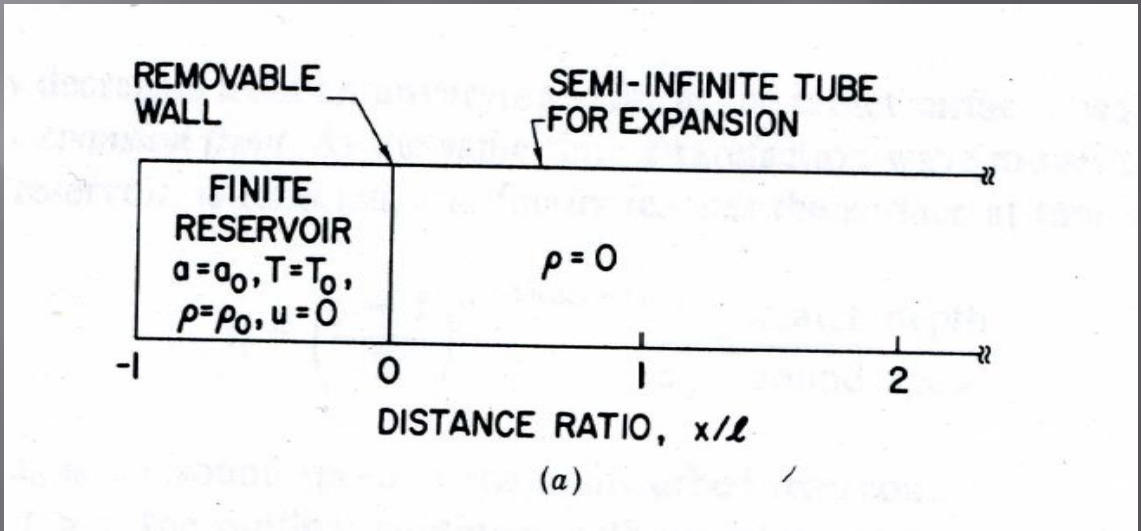
- Features a finite reservoir and removable wall
- Particles backscattered toward target surface are either reflected or absorbed and re-condensed
- Gas exhibits shifted Maxwellian velocity distribution

$$k_b T_s = \frac{mv^2}{2} * \frac{T_s}{\eta T_M}$$



Outflow with Reflection

- Behaves as if wall (x=0) removed at t=0
- Could occur if laser pulse caused rapid passage to gas-like condition where $T > T_{ct}$
- Boundary condition for reflection is u=0 at back of reservoir (x=-l)
- Resembles gun problem (solved 1960)



Outflow with Reflection

- Results for $\gamma = 5/3$ in terms of density ratio vs distance ratio. Characterized by a_0, T_0, ρ_0 *and* $u = 0$. Curve parameter set to $a_0 t / l$

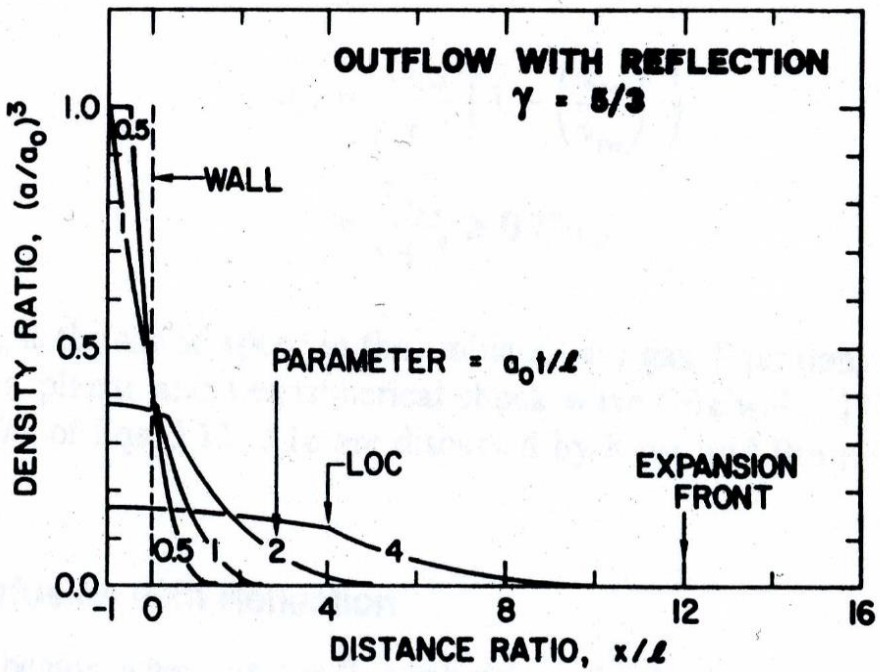


Figure 3.13. Calculated values of the density, $\rho/\rho_0 = (a/a_0)^3$, vs. the distance, x/l, for *outflow with reflection.* The problem is equivalent to that of a finite reservoir of gas as in Figure 3.12*a*. It is characterized initially by a_0, T_0, ρ_0, and $u = 0$, and is able to escape into vacuum when the wall is removed at $t = 0$. The indicated *expansion front* is that of the curve for $a_0 t/l = 4$.

Outflow with Reflection

- Density decreases from initial value at target surface (wall at x=0) to zero at expansion front

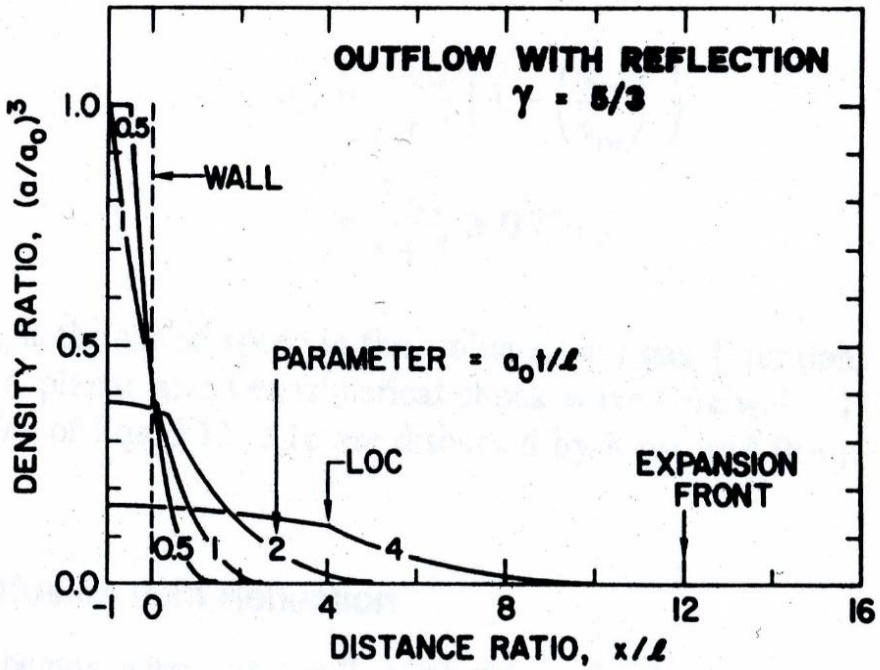
- Simultaneously, a rarefaction wave moves to back of reservoir, is reflected and reaches surface (x=0) at τ_s

$$\tau_s = \left(\frac{\gamma+1}{2}\right)^{\left(\gamma+1/2(\gamma-1)\right)} \frac{l}{a_0} \approx \frac{crater\ depth}{sound\ speed}$$

- As t>τ_s, outflow continues without interruption

Outflow with Reflection

- Disturbance from rarefaction wave causes LOC (line of contact)- abrupt change of slope in density profile
- Density profile consists of nearly flat section then exponential decrease (with LOC at junction)



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Outflow with Reflection

- Photograph typically does not differentiate between reflection and re-condensation effectively

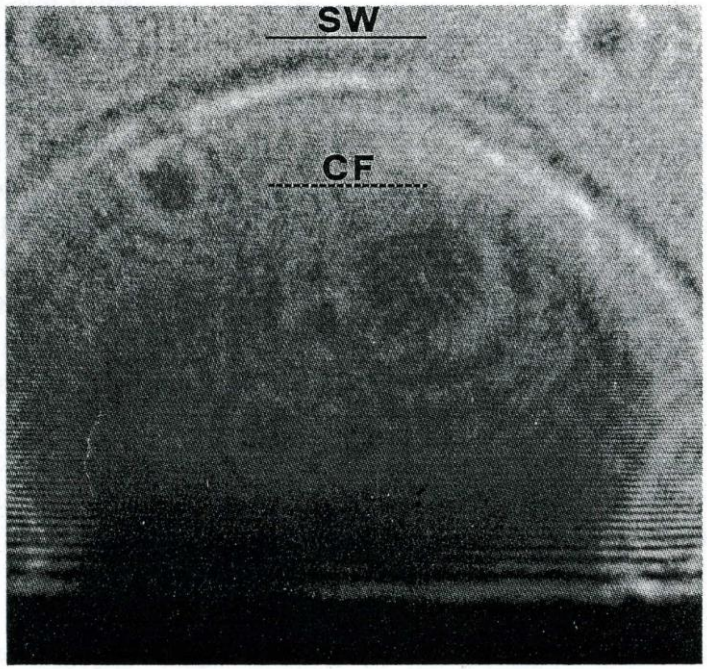

Figure 3.14. $YBa_2Cu_3O_{7-x}$ targets with a thickness of 5 mm were exposed to a single laser pulse (248 nm, ~20 ns, diameter ~800 μm, 1.5–2 J/cm^2, normal incidence) in 0.07 atm (50 torr) of air. The released particles and shock wave were photographed by firing parallel to the target surface a second ("probe") laser pulse with a delay of 500 ns. The contact front is marked CF and the shock wave, SW. (From Kelly et al., 1992a and Gupta et al., 1991.)

Outflow with Reflection

- Expansion front velocity in vacuum

$$\hat{u} = \frac{2a_0}{\gamma - 1}$$

- Expansion front in ambient gas becomes contact front

$$u_{cf} = \frac{2a_0}{\gamma - 1}\left(1 - \frac{a_{cf}}{a_0}\right) < \hat{u}$$

- At lower pressure a_{cf} approaches 0 due to cooling and we get $u_{cf} \sim \hat{u}$.
- At high pressure, cf expends energy heating and moving ambient gas. Contact front decelerates as a result.
- With ambient pressure the shockwave travels ahead of contact front.

Outflow with Reflection

- Previous equations not useful analyzing data from pulse laser sputtering
- T_{cf} (a_{cf}) is difficult to measure on relevant distance scale (0-3mm)
- We utilize relation between contact front and shockwave velocities

$$u_{cf} = \frac{2u_{sw}}{\gamma + 1}(1 - \left(\frac{a_{am}}{u_{sw}}\right)^2$$

$$\approx \frac{2u_{sw}}{\gamma + 1} \geq 0.75u_{sw}$$

- Valid for both planar and hemispherical shockwaves