Analytical formula for interpretation of time-of-flight distributions of neutral particles under pulsed laser evaporation into vacuum

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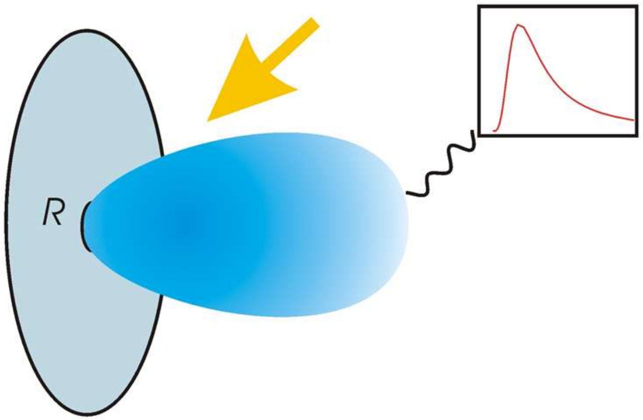
Motivation

- Time-of-flight (TOF) distributions is one of the main instruments for study of mechanisms and dynamics of pulsed laser ablation.
- Usually TOF detector with small size (*h* ~ 0.1 mm) is located at the normal to the target at a large distance (*L* > 5 cm) and allows to get temporal evolution of the number of particles, passing through the detector.
- For effective application of TOF distributions it is important to correctly interpret them, i.e. to identify the regime of ablation and determine:
  - — the surface temperature;
  - — the amount of the evaporated material;
  - — the ionization degree;
  - — the composition of mixture during evaporation;
  - — the mechanism of ablation (evaporation, phase explosion, etc…)



- Previously it was shown that TOF distributions for neutral particles can be interpreted based on results of the direct Monte Carlo simulation.

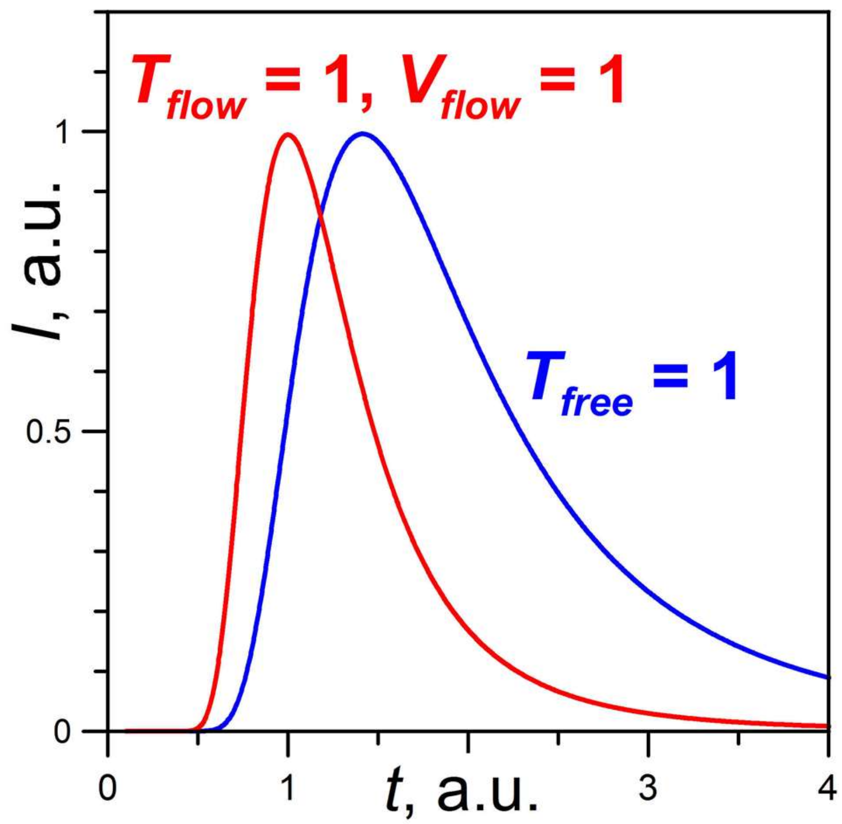
A. A. Morozov. *Interpretation of time-of-flight distributions for neutral particles under pulsed laser evaporation using direct Monte Carlo simulation* // J. Chem. Phys. 139 (2013) 234706.

Maxwell-Boltzmann distribution

Collisionless expansion

$$I(t) \sim \frac{1}{t^4} \exp\left\{ -\frac{(L/t)^2}{2kT_{free}/m} \right\}$$

T_{free} – the evaporating surface temperature
L – distance to the detector
m – molecular mass
k – the Boltzmann constant



Collisional expansion

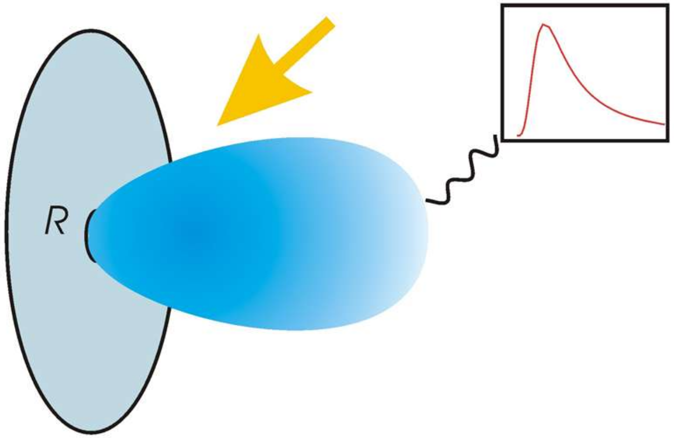
$$I(t) \sim \frac{1}{t^4} \exp\left\{ -\frac{(L/t - V_{flow})^2}{2kT_{flow}/m} \right\}$$

T_{flow}, V_{flow} are fitting parameters without clear physical sense (sometimes velocity V_{flow} even is negative)

Usually TOF distributions are approximated by the Maxwell-Boltzmann equation, however ground for such an approximation is lacking.

Objective

- Presently analytical formula for interpretation of TOF distributions is absent, that considerably reduce efficiency of this method.

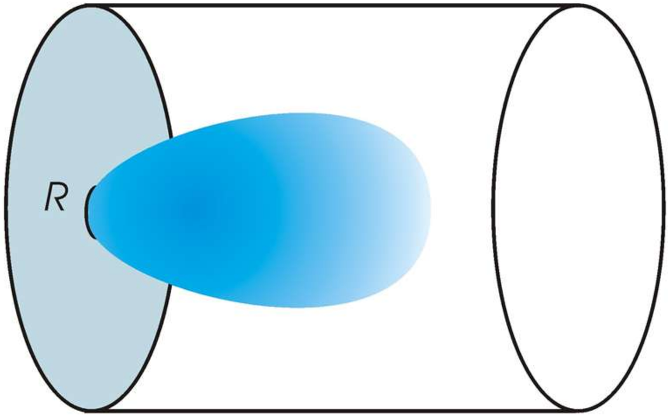


The objective of work is to elaborate an analytical formula for interpretation of TOF distributions based on analysis of results of direct Monte Carlo simulation.

Model assumptions

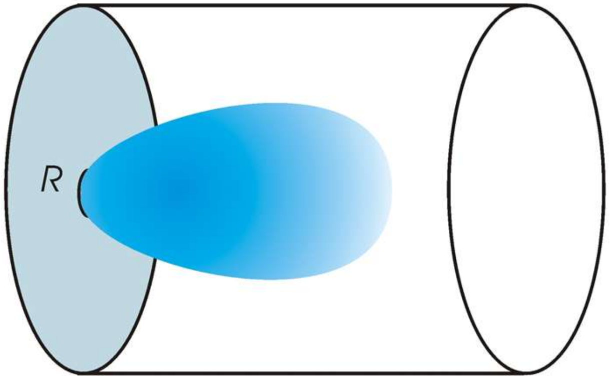
The following assumptions are used both in simulation and in the analytical model:

- one-component gas
- no ionization
- no absorption of laser irradiation within the plume
- the mechanism of ablation: thermal evaporation
- constant temperature at the evaporating surface
- constant flux of particles from the surface during evaporation
- internal degrees of freedom of molecules



Formulation of the problem

For numerical simulation of cloud expansion into vacuum under pulsed laser ablation we used the direct simulation Monte Carlo (DSMC) method.



Θ is the number of evaporated monolayers

$$\Theta = \frac{N\sigma}{4S}$$ **, where**

N is the total number of evaporated particles,
σ is the collision cross-section,
S is the square of the evaporating spot.

R is the evaporating spot radius

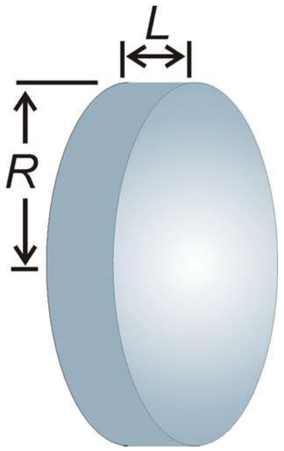
Units:

$$u_0 = \sqrt{\frac{2kT_0}{m}} \quad \lambda_0 = \frac{1}{n_0\sigma\sqrt{2}} \quad t_0 = \frac{\lambda_0}{u_0}$$

Combination of parameters gives the normalized spot radius *b*

$$b = \frac{R}{u_T\tau} = \frac{R}{16\sqrt{2\Theta}}$$

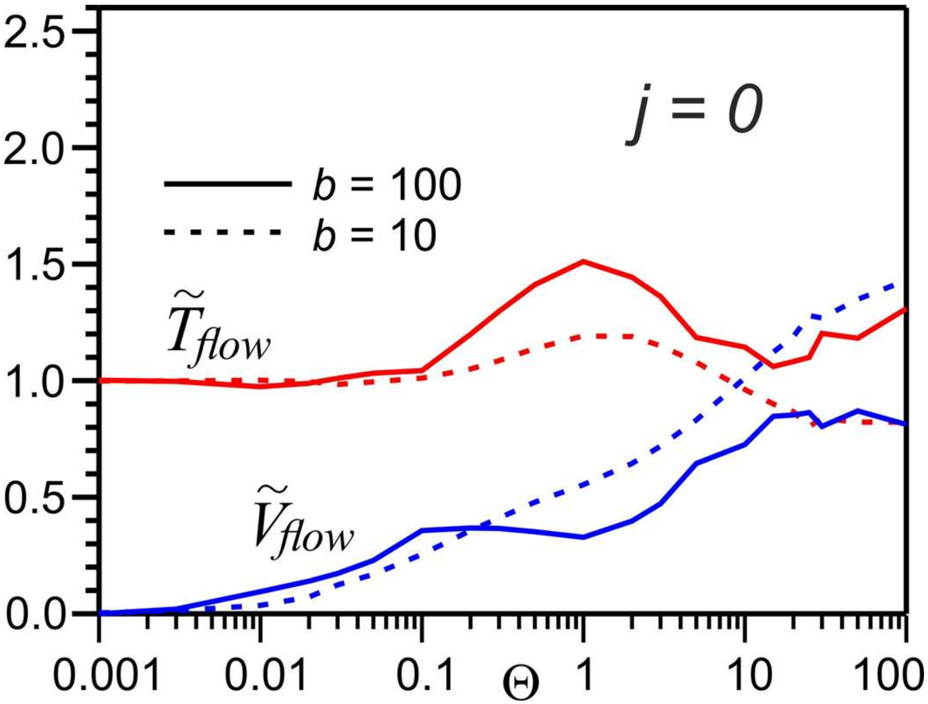
Usually *b* > 10

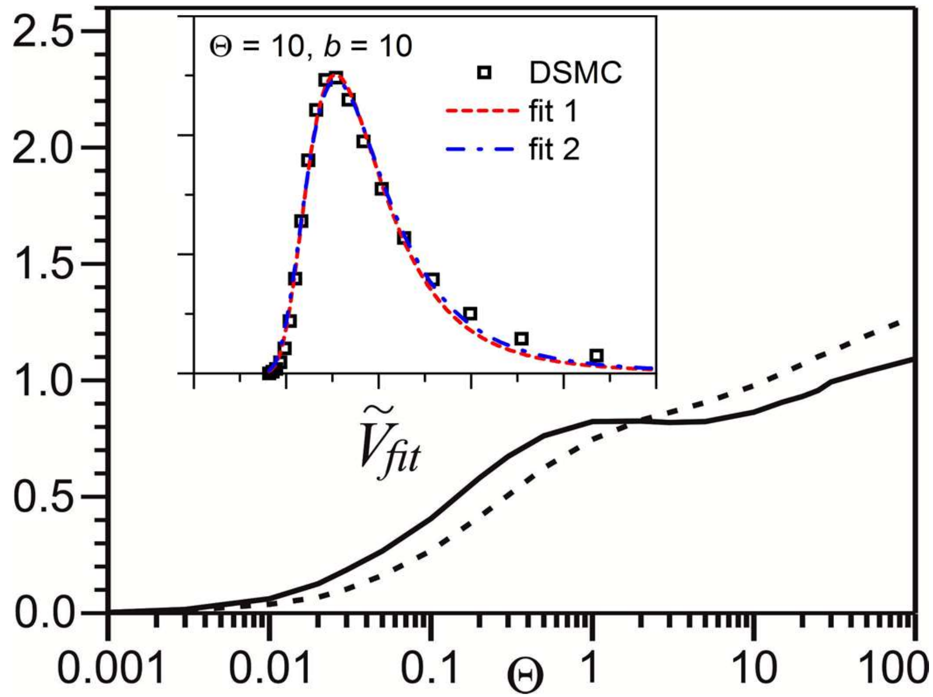


- **Hard sphere model.**
- **Larsen–Borgnakke model is used for internal degrees of freedom.**
- **$j = 0 \div 10$ is the number of internal degrees of freedom**
- **$Z = 1$ is the number of collisions for energy relaxation.**

Influence of the number of monolayers on the shape of the TOF distribution: $j = 0$

DSMC-calculated TOF distributions have been fitted by Maxwell-Boltzmann formula.





$$I(\tilde{t}) \sim \frac{1}{\tilde{t}^4} \exp\left\{ -\frac{(\tilde{L}/\tilde{t} - \tilde{V}_{flow})^2}{\tilde{T}_{flow}} \right\}$$

$$\tilde{T}_{flow} := 1 \longrightarrow$$

$$I(\tilde{t}) \sim \frac{1}{\tilde{t}^4} \exp\left\{ -(\tilde{L}/\tilde{t} - \tilde{V}_{fit})^2 \right\}$$

$\tilde{T} = T/T_0, \tilde{V} = V/u_0,\ u_0 = \sqrt{2kT_0/m}, T_0$ – the surface temperature

Let us find relation between V_{fit} **and** Θ **via component of the kinetic energy in the forward direction** $E_{\parallel} = E_{\parallel}(V_{fit}) = E_{\parallel}(\Theta)$

Kinetic energy in the forward direction $E_{||}$ as a function of velocity V_{fit}

Velocity distribution function for particles in the forward direction

$$f(\tilde{u}) \sim \tilde{u} \exp\left\{-(\tilde{u} - \tilde{V}_{fit})^2\right\}$$

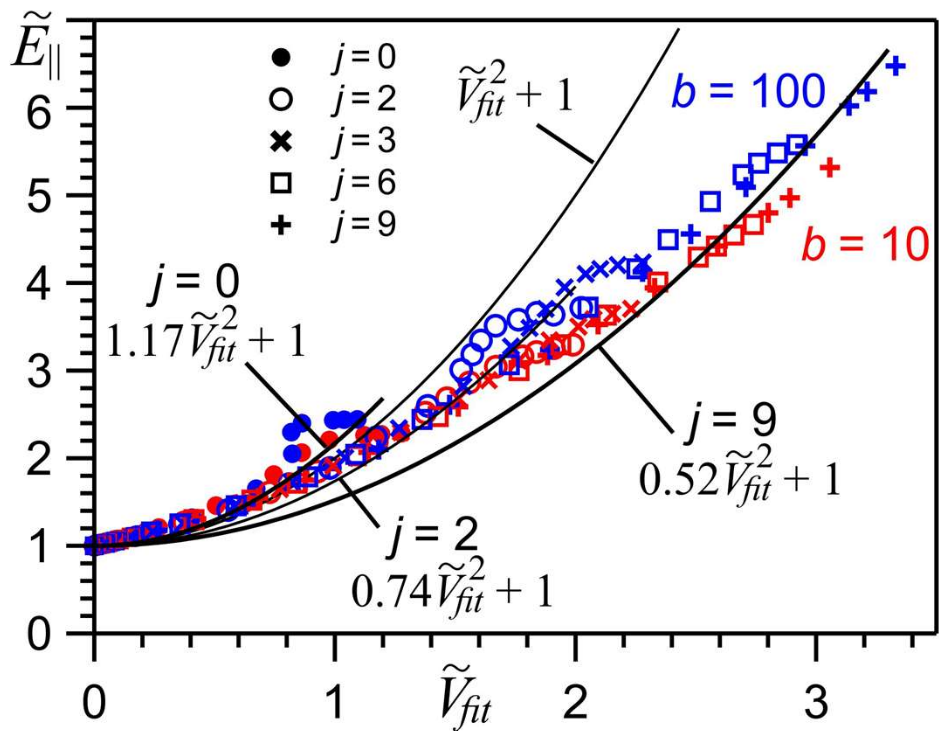
Total energy of the plume in the forward direction

$$\tilde{E}_{||} = \frac{E_{||}}{kT_0} = \frac{\int_0^\infty \tilde{u}^2 f_{||}(\tilde{u}) d\tilde{u}}{\int_0^\infty f_{||}(\tilde{u}) d\tilde{u}} = \frac{\exp\left(-\tilde{V}_{fit}^2\right)\cdot\left(\tilde{V}_{fit}^2+1\right) + \tilde{V}_{fit}\sqrt{\pi}\left(1+erf\tilde{V}_{fit}\right)\cdot\left(\tilde{V}_{fit}^2+1.5\right)}{\exp(-\tilde{V}_{fit}^2) + \tilde{V}_{fit}\sqrt{\pi}\left(1+erf\tilde{V}_{fit}\right)} \approx$$

$$\approx \tilde{V}_{fit}^2 + 1$$

To better describe DSMC data, it is necessary to introduce an additional coefficient $\kappa(j)$

$$\tilde{E}_{||} = \kappa(j)\cdot\tilde{V}_{fit}^2 + 1$$



Kinetic energy in the forward direction $E_{||}$ as a function of the number of monolayers Θ

$$E_{total} = E_{||} + 2E_{\perp} + E_{\text{int}} = kT_0 + 2\frac{kT_0}{2} + j\frac{kT_0}{2} = (4+j)\frac{kT_0}{2}$$ **is the total energy of the plume**

$E_{\perp}$ **is the plume energy in the lateral direction**

Let in one collision $E_{\perp}$ is reduced by a fraction δ

Then energy decrease $E_{\perp}$ in dependence on the number of collisions *N*

$$E_{\perp,N} = E_{\perp,0}(1-\delta)^N \approx E_{\perp,0}\exp(-\delta N)$$

$$E_{\perp,0} = \frac{kT_0}{2}$$ **is the initial energy $E_{\perp}$**

Internal energy decrease E_{int}

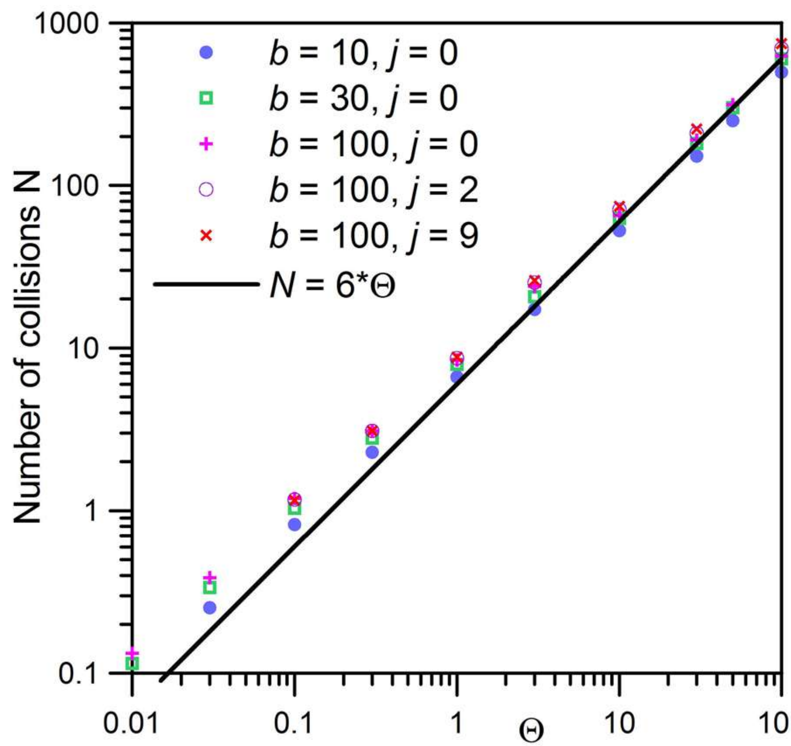
$$E_{\text{int}}(N) = E_{\text{int},0}\exp(-\delta N) = j\frac{kT_0}{2}\exp(-\delta N)$$

$$E_{||}(N) = E_{total} - 2E_{\perp} - E_{\text{int}} = \boxed{\frac{kT_0}{2}\left(4+j-(2+j)\cdot\exp(-\delta N)\right)}$$

The number of collisions $N \approx N_1 \cdot \Theta$

$$\boxed{E_{||}(\Theta) = \frac{4+j-(2+j)\cdot\exp(-\alpha\Theta)}{2}kT_0,}$$

$$\alpha = N_1 \cdot \delta$$

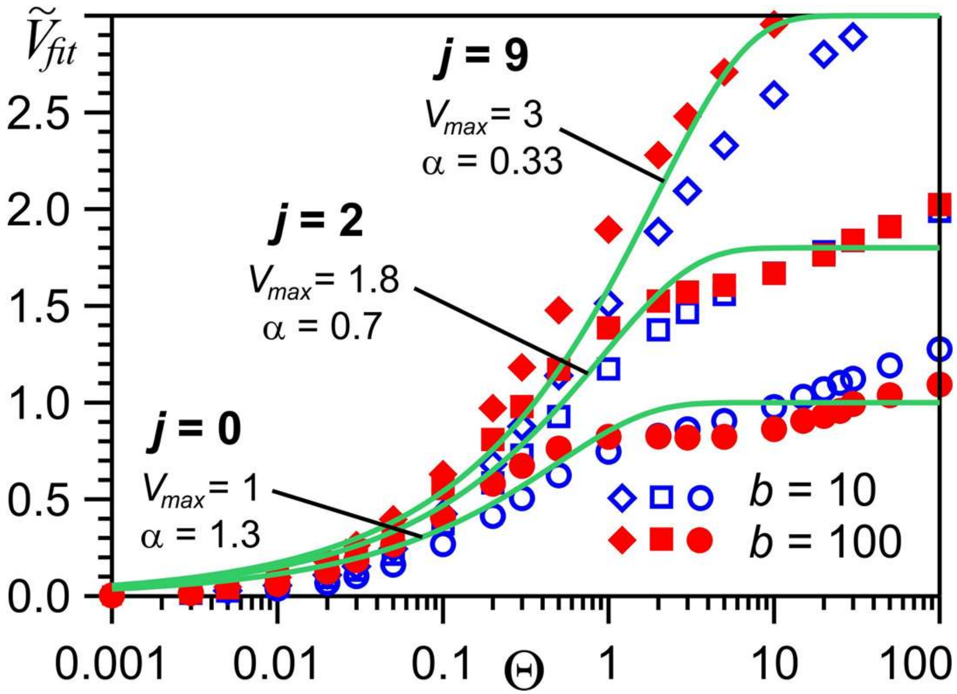


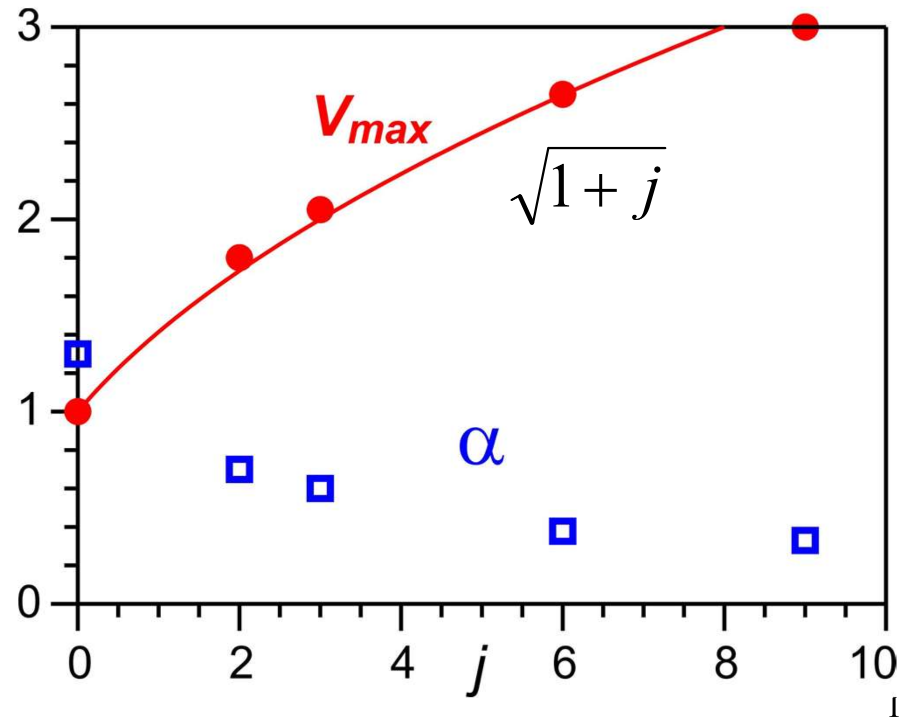
Shift velocity V_{fit}

$$\frac{E_{\parallel}}{kT_0} = \frac{4 + j - (2 + j)\cdot\exp(-\alpha\Theta)}{2} = \kappa\tilde{V}_{fit}^{2} + 1$$

$\Downarrow$

$$\boxed{\tilde{V}_{fit} = V_{\max}\sqrt{1 - \exp(-\alpha\Theta)}}\ , \quad V_{\max} = \sqrt{\frac{1 + j/2}{\kappa}} = \sqrt{1 + j}, \quad \Longrightarrow \quad \kappa = \frac{1 + j/2}{1 + j}$$





Energy redistribution in collision

$$E_{\text{int},0} = j\frac{kT_0}{2}$$ **initial internal energy (at evaporation)**

$$E_{\|} = kT_0 = E_{\|,V} + E_{\|,T}$$ **kinetic energy in forward direction**

$$E_{\|,V}$$ **energy of directed motion**

$$E_{\|,T} = \beta E_{\|}$$ **energy of thermal motion**

$$E_{\perp} = \frac{kT_0}{2}$$ **kinetic energy in lateral direction**

$$\Delta E = E_{\text{int},0} + 2\cdot E_{\perp} + \beta\cdot E_{\|} = \frac{kT_0}{2}\left(j+2+2\beta\right)$$ **energy redistributed in one collision**

$$E'_{\text{int}} = j\cdot\frac{\Delta E}{j+3} = \frac{kT_0}{2}\frac{j}{j+3}\left(j+2+2\beta\right)$$ **internal energy after a collision**

$$E'_{\text{int}} = E_{\text{int},0}\cdot\left(1-\delta\right) = j\frac{kT_0}{2}\left(1-\delta\right)$$

$$\delta = \frac{1-2\cdot\beta}{j+3}$$

Let us find β:

$$\beta = \frac{E_{\|,T}}{E_{\|}}$$

Energy of thermal motion: continuum expansion

K. P. Stanukovich, Unsteady motions of continuous media. London, 1960.

$$\begin{cases} u(x') = u_K\left(1 + \dfrac{3+j}{4+j}x'\right) \\ n(x') = n_K\left(1 - \dfrac{x'}{4+j}\right)^{3+j} \\ T(x') = T_K\left(1 - \dfrac{x'}{4+j}\right)^{2} \end{cases}$$

u_K, n_K, T_K **are parameters at the boundary of the Knudsen layer**

$$x' = \frac{x}{u_K t},$$

$$x'_{\max} = 4 + j$$

$$E_{\parallel,T} = \frac{\int_0^{x'_{\max}} n(x')\dfrac{kT(x')}{2}dx'}{\int_0^{x'_{\max}} n(x')dx'} = \frac{4+j}{2(6+j)}kT_K$$

$$E_{\parallel,V} = \frac{\int_0^{x'_{\max}} n(x')\dfrac{mu^2(x')}{2}dx'}{\int_0^{x'_{\max}} n(x')dx'} = \frac{(4+j)(21+5j)}{2(3+j)(6+j)}kT_K$$

$$E_{\parallel} = E_{\parallel,T} + E_{\parallel,V} = \frac{3(4+j)^2}{(3+j)(6+j)}kT_K$$

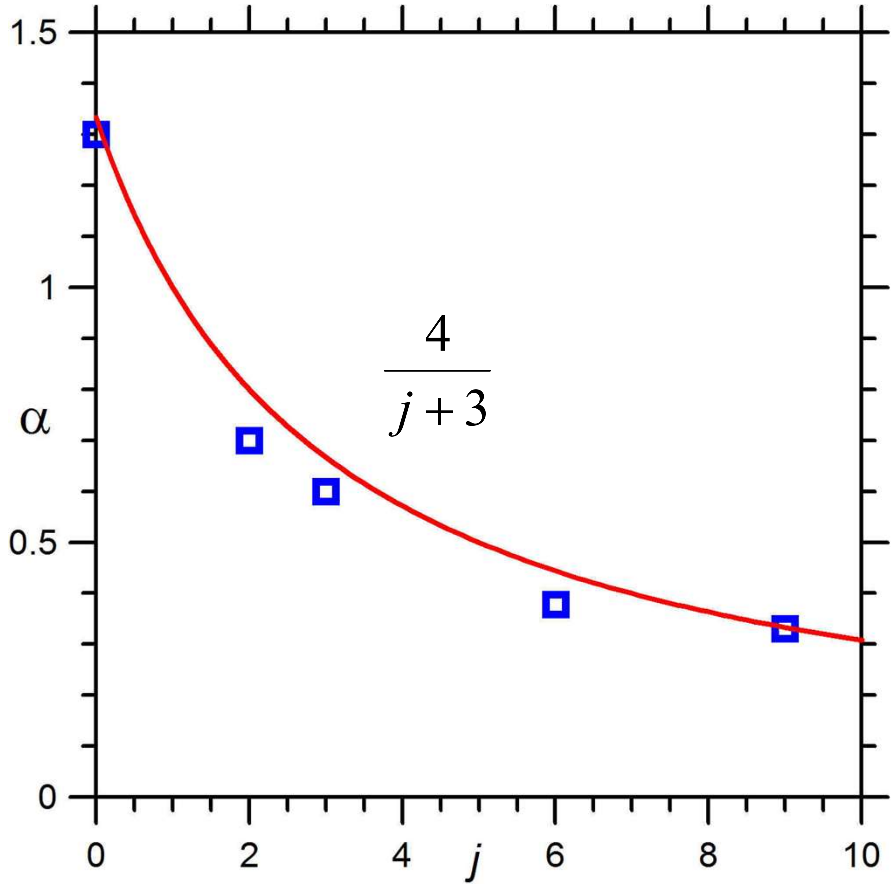
$$\beta = \frac{E_{\parallel,T}}{E_{\parallel}} = \frac{3+j}{6(4+j)}$$

$j = 0 \qquad \beta = 0.125$

$j = 3 \qquad \beta = 0.143$

Relaxation rate α

$$\alpha = N_1\delta = N_1\frac{1-2\beta}{j+3} = N_1\frac{2j+9}{3(j+3)(j+4)} = \frac{N_1}{3(j+3)}\left\{2+\frac{1}{j+4}\right\} \approx \frac{2N_1}{3(j+3)} = \frac{4}{j+3}$$



Final formula

$$I(t) \sim \frac{1}{t^4} \exp\left\{-\frac{\left(L/t - V_{fit}\right)^2}{u_0^2}\right\} = \frac{1}{t^4} \exp\left\{-\left(\frac{L}{u_0 t} - \tilde{V}_{fit}\right)^2\right\},$$

$$\tilde{V}_{fit} = V_{\max}\sqrt{1-\exp(-\alpha\Theta)} = \sqrt{(1+j)\cdot\left(1-\exp\left(-\frac{4}{j+3}\Theta\right)\right)}$$

Let us determine dependence of the number of monolayers Θ on the surface temperature T:

$$\Psi = \frac{1}{4} n u_T = \frac{1}{4}\frac{p}{kT}\sqrt{\frac{8kT}{\pi m}}$$

$$N = \Psi\tau = \Theta N_1 = \Theta\frac{1}{\Sigma} \quad \Rightarrow \quad \Theta = \Psi\tau\Sigma = \frac{p(T)\tau\sigma}{4\sqrt{2kT\pi m}}$$

$$p(T) = p_b \exp\left\{\frac{L_V}{k}\left(\frac{1}{T_b} - \frac{1}{T}\right)\right\}$$

$u_0 = \sqrt{2kT/m}$

L is the distance to the TOF detector

T is the surface temperature

Ψ is flux of particles from the surface

N is the number of evaporated particles

N_1 is the number of molecules in 1 monolayer

τ is the evaporation duration

Σ is an area occupied by one molecule on the surface

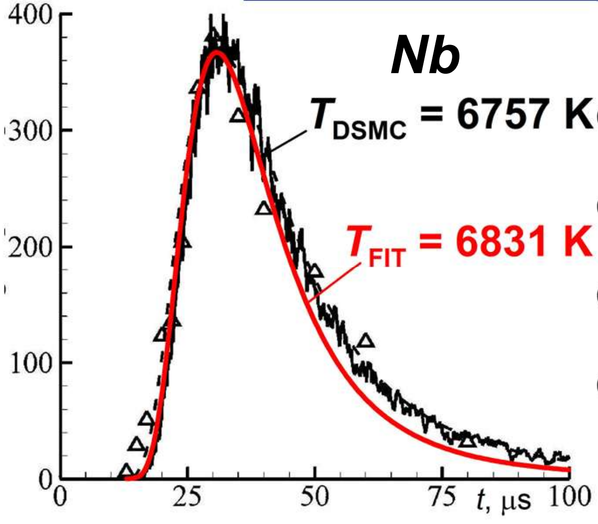
$\sigma = 4\Sigma$ is the collision cross-section

T_b is the boiling temperature under pressure p_b

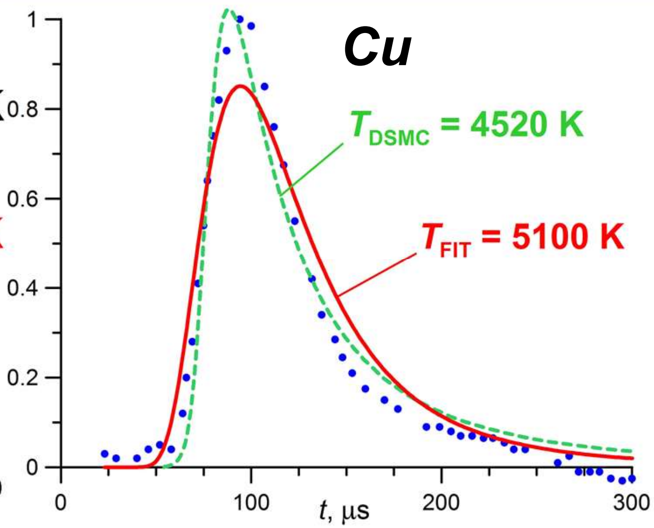
L_V is the latent heat of evaporation

$$I(t) \sim \frac{1}{t^4} \exp\left\{-\left(\frac{L}{t\sqrt{2kT_{fit}/m}} - \sqrt{(1+j)\cdot\left(1-\exp\left(-\frac{\tau\sigma p_b}{(j+3)\sqrt{2kT_{fit}\pi m}}\exp\left\{\frac{L_V}{k}\left(\frac{1}{T_b}-\frac{1}{T_{fit}}\right)\right\}\right)\right)}\right)^2\right\}$$

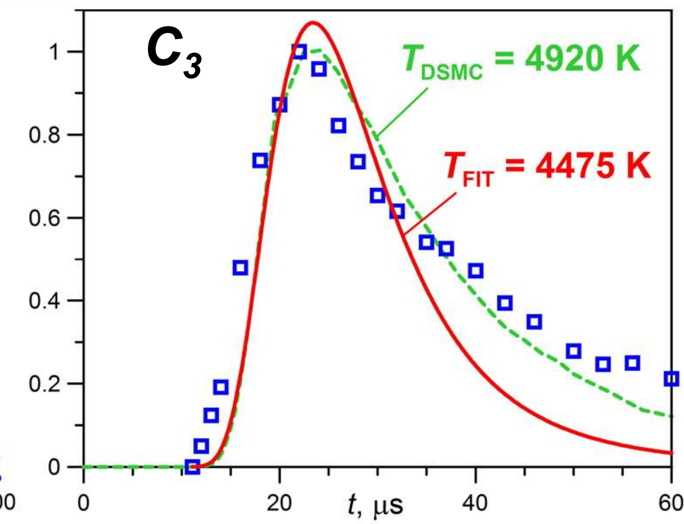
Analysis of experiments



N.Y.Bykov, N.M. Bulgakova, A.V. Bulgakov, G.A. Loukianov, **Appl. Phys. A** 79 (**2004**) 1097



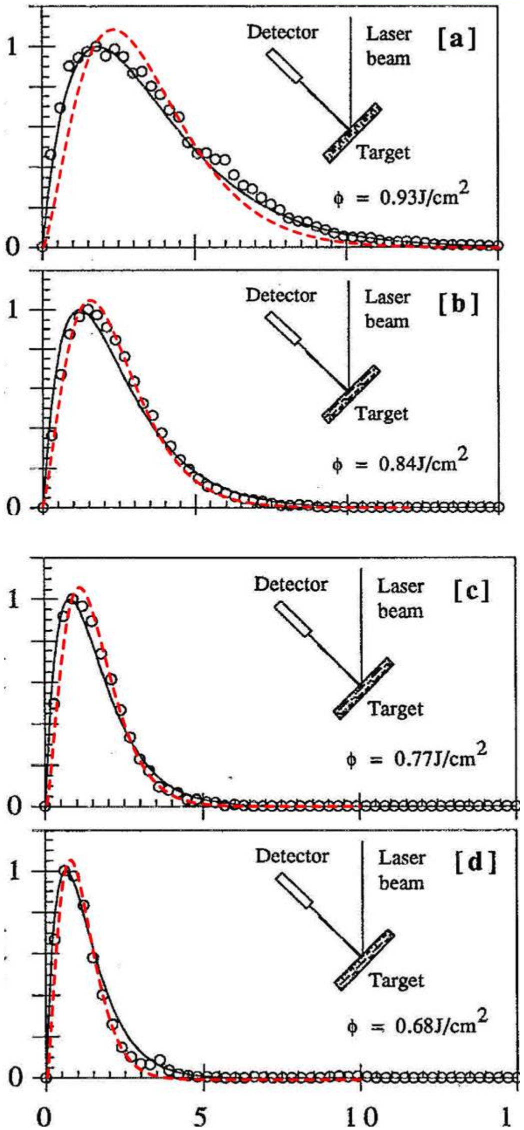
R.Viswanathan, I. Hussla, **J. Opt. Soc. Am. B** 3 (**1986**) 796



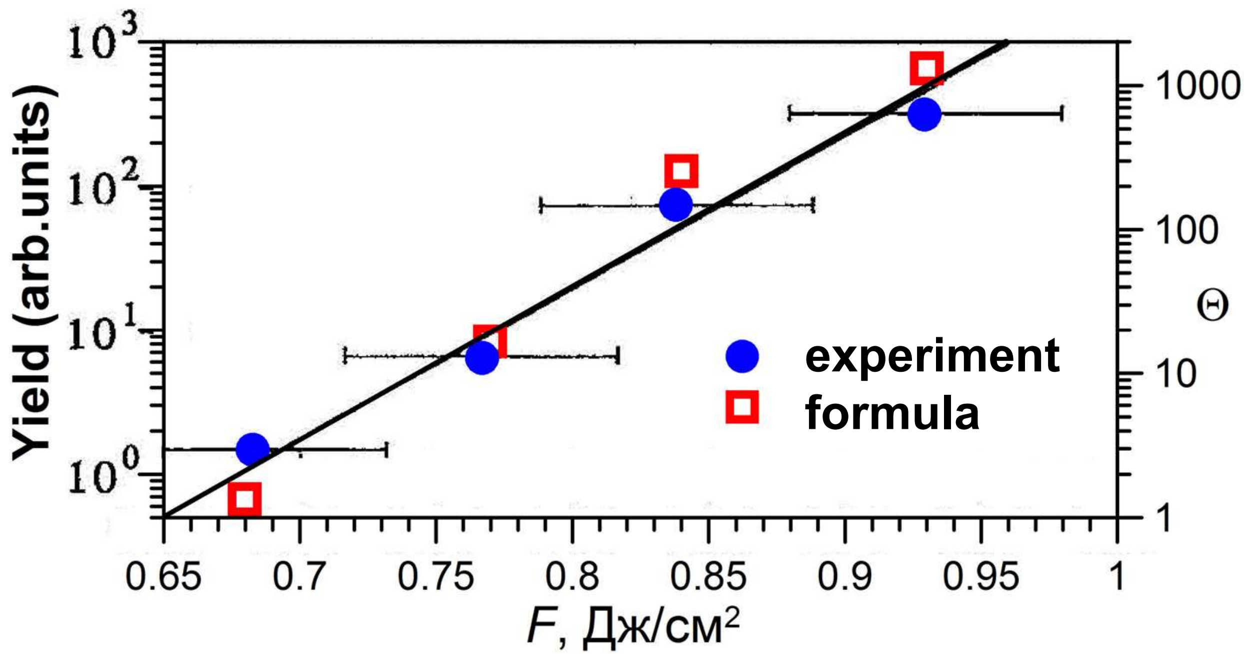
A.A. Morozov, A.B. Evtushenko, A.V. Bulgakov, **Appl. Phys. A** 110 (**2013**) 691

	T_{DSMC}	Temperature from formula			Error of the formula		
		T_{FREE}	T_{FLOW}	T_{FIT}	Δ_{FREE}	Δ_{FLOW}	Δ_{FIT}
Nb	6757	13160	10200	6831	95%	51%	1%
Cu	4520	10280	2750	5100	123%	-40%	13%
C_3	4920	13290	13290	4475	170%	170%	-9%

Analysis of experiments: gold



τ = 16 нс



1 arb. unit = 2 monolayers

T.D. Bennett, C.P. Grigoropoulos, D.J. Krajnovich, **J. Appl. Phys.** 77 (**1995**) 849

Conclusion

- Based on analysis of results of DSMC calculations, a new formula for interpretation of time-of-flight distributions for neutral particles under pulsed laser evaporation into vacuum has been proposed.
- Coefficients of the formula have clear physical meaning.
- Good agreement with different experimental data has been obtained.
- It is shown that the new formula allows to determine the surface temperature with error of 10% instead of error of 50-150% for commonly used formulas.