Asymptotic distributions generated in a nucleation pulse

Vitaly A. Shneidman

Department of Physics
New Jersey Institute of Technology

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Overview

- experimental motivation
- classical nucleation and growth equations
- transient nucleation
- nucleation pulse
- conclusions

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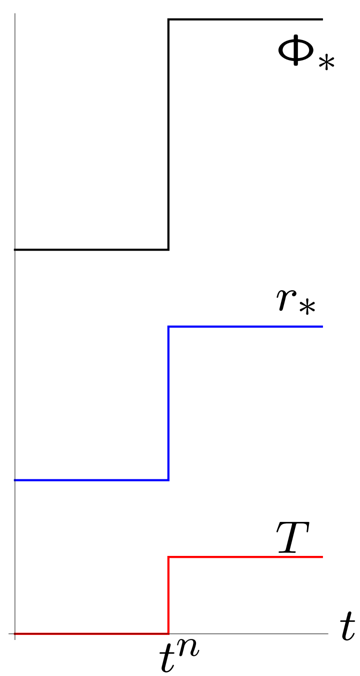
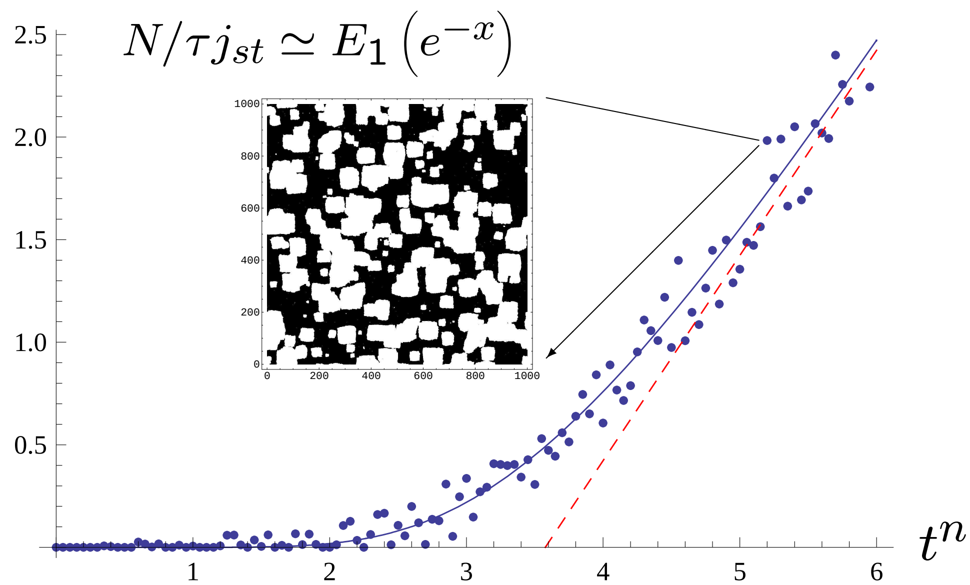
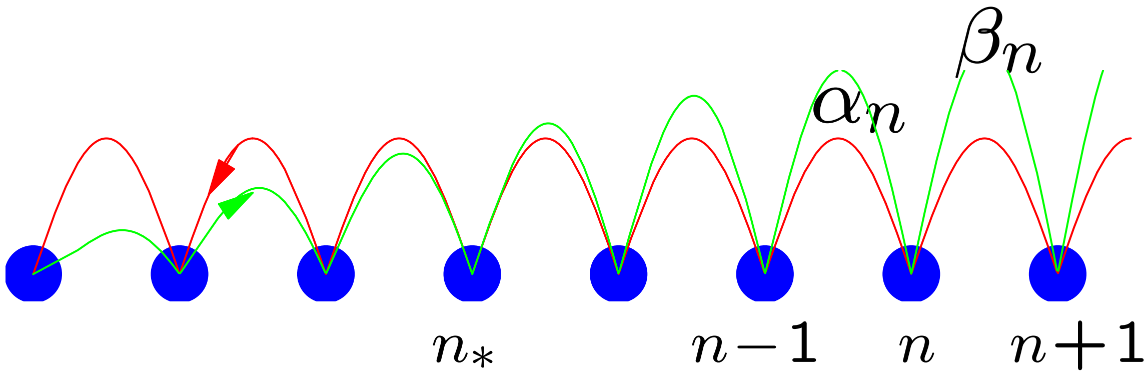
Two-step annealing in lithium disilicate

James '74, Filipowich et al. '76-'80, Deubener et al. '93





CLASSICAL KINETICS



$$\dot{n} \simeq \beta_n - \alpha_n$$

(*Becker&Döring'35 (discrete), Zeldovich'42 (cont.)*):

$$\frac{d\,f_n}{d\,t} = j_n - j_{n+1} \,, \quad j_n = \beta_{n-1} f_{n-1} - \alpha_n f_n$$

Detailed Balance : $f_n^{eq} \propto \exp\left\{-\frac{W(n)}{T}\right\} \,, \quad \beta_{n-1} f_{n-1}^{eq} = \alpha_n f_n^{eq}$

$$\frac{\partial f}{\partial t} = -\frac{\partial j}{\partial R} \,, \quad j = -\beta f^{eq} \frac{\partial}{\partial R} \frac{f}{f^{eq}}$$

Growth and Steady-State Nucleation

Zeldovich'42

$$\dot{R} = -\frac{\beta}{T}\frac{d\,W}{d\,R}\,, \;\; \tau^{-1} = \left.\frac{d\dot{R}}{dR}\right|_*$$

$$\dot{R} = \frac{R_*}{\tau}\left(\frac{R_*}{R}\right)^\theta\left(1 - \frac{R_*}{R}\right)$$

$\theta = 0/1/-1$ – ballistic/diffusion/cavitation

$$j_{st} \simeq \frac{\Delta}{2\tau\sqrt{\pi}} f^{eq}(R_*)\,,\;\Delta^{-2} = -\left.\frac{1}{2T}\frac{d^2W}{dR^2}\right|_*$$

Asymptotic j_{st} and exact (*Farkas'27*) are very close;
(small corrections for $n_* \lesssim 10$ - *VS, PRL'05*)

Transient nucleation

Singular perturbation (matched asymptotic) solution of the Becker-Döring equation (*VS'87'88*). In the growth region $r = R/R_* > 1$:

$$j_0(r) = j_{st} \exp\left(-e^{-x}\right) \ , \quad x \equiv \frac{t - t_i(r)}{\tau}$$

$$t_i(r) = \mathbf{P} \int_0^r \frac{dr}{\dot{r}} + \tau \ln \frac{\Phi_*}{T} + const$$

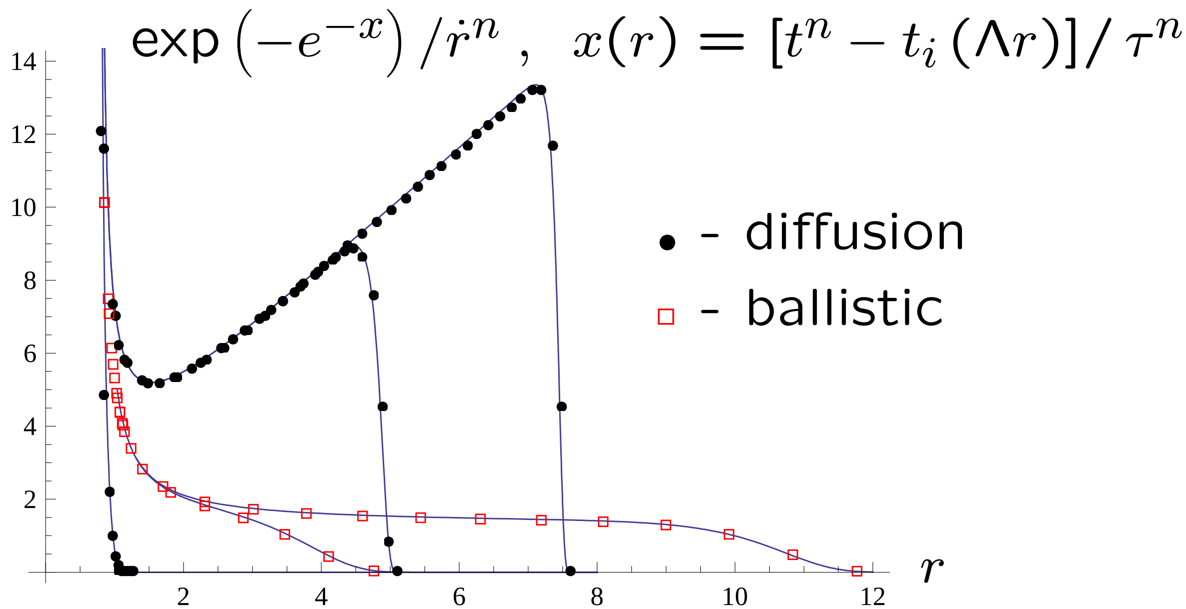
$$\frac{1}{\tau} t_i(r) = \ln \frac{6\Phi_*(r-1)}{T} + r - 2 + \theta\left(\frac{r^2}{2} - 1\right), \ \theta = 0, 1$$

$$N = \tau j_{st} E_1\left(e^{-x}\right)$$

$$f(r) = j_0(r)/\dot{r}$$

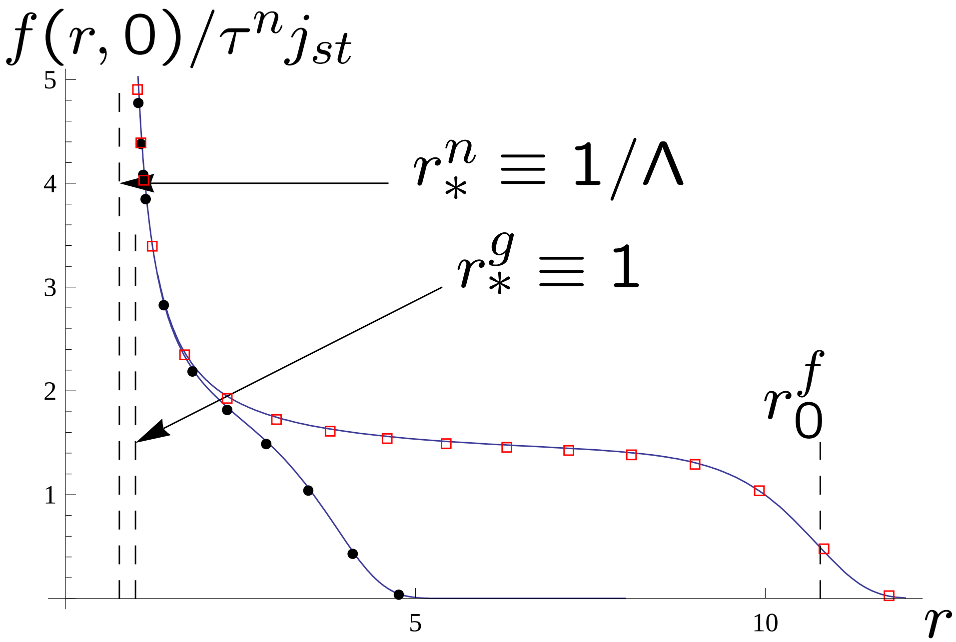
Nucleation pulse

- deep quench, large supersaturation, small R_*^n
- nucleation during a *finite* time t^n (thus transient effects)
- rapid decrease of supersaturation
- growth with a larger R_*^g during time t
- Units: main control parameter $\Lambda = R_*^g/R_*^n > 1$, $r = R/R_*^g$, $\tau^g = 1$.



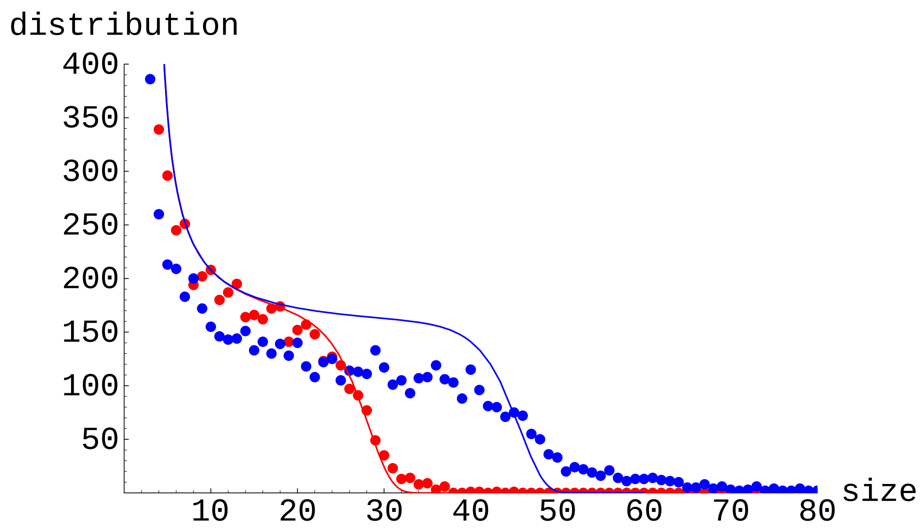
Typical reduced distribution $f(r,0)/j_{st}\tau^n$ at the end of nucleation pulse (initial conditions for growth). Lines - analytics, symbols - numerics. Reduced pulse durations t^n/τ^n are: (from left to right, ballistic) 10 and 20; (diffusion) 2.45, 30.6 and 61.2. Numbers of nuclei (area for $r > 1$) $N \simeq \tau^n j_{st} E_1\left(e^{-X}\right)$ with $X = x(1)$, E_1 - exp. integral (*VS'88*).

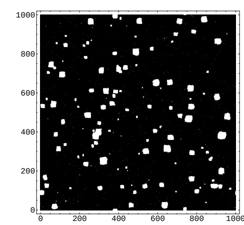
$f(r,0)$ for ballistic nucleation and growth in the *Zeldovich-Frenkel* equation, and explanation of notations

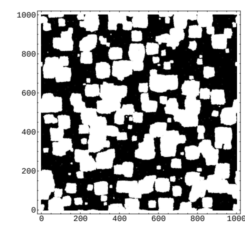


Note: The small-r part is insensitive to t^n, which affects only the length of the tail (the initial location of the front, r_0^f, shown for the longer pulse). In the deterministic approximation the distribution has a singularity at $r = r_*^n$ which disappears after a short time t_d during the growth stage.

Becker-Döring vs Lattice Gas







Lines :

$$f(r,0) = \frac{j_{st}}{\dot{r}} \exp\left\{ - \exp\left[- \frac{t^n - t_i(r)}{\tau^n} \right] \right\}$$

Points: MC data for a 2000 × 2000 lattice, $T \simeq 0.35\,T_C$, $h = 0.22$ at two different times

Nucleation pulse.

Result:

$$f(r,t) = j_0\,(\Lambda r_0)\,\frac{\dot{r}_0^g}{\dot{r}_0^n\,\dot{r}^g}$$

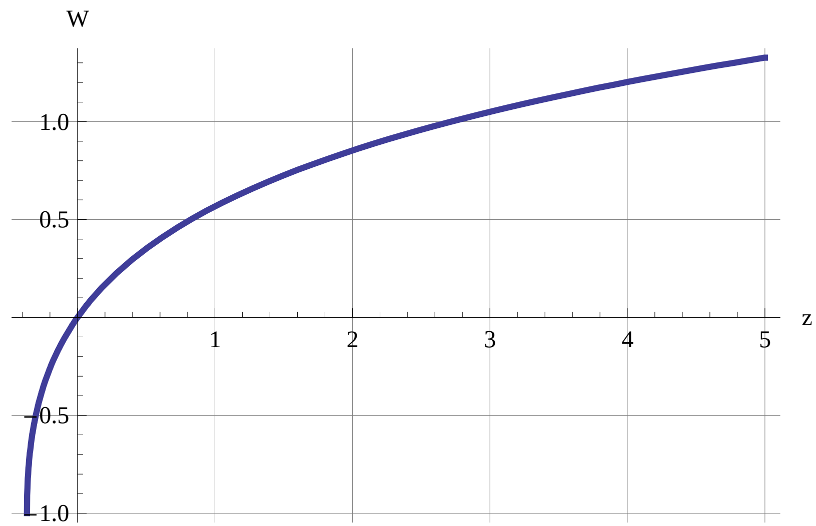
$$\int_{r_0}^{r} \frac{dr}{\dot{r}^g} = t$$

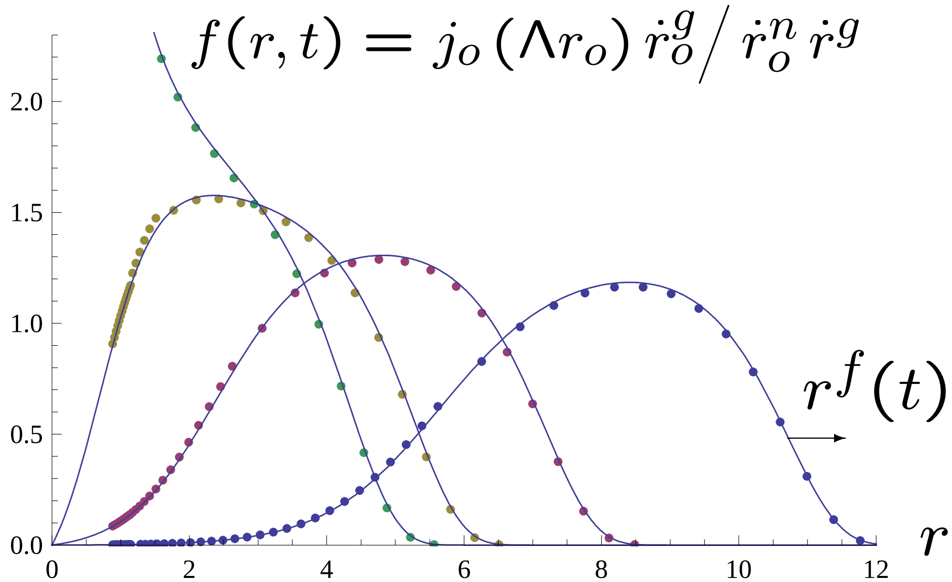
Ballistic growth (standard *Zeldovich-Frenkel* equation):

$$\dot{r} = 1 - \frac{1}{r}\,, \quad r_0(r,t) = 1 + \mathbf{W}\left[(r-1)e^{r-t-1}\right]$$

$\mathbf{W}[z]$ - the Lambert $\mathbf{W}$ function, is the root of

$$z = \mathbf{W}e^{\mathbf{W}}$$





Transformations of the distribution during growth for the Zeldovich-Frenkel equation after initial pulse with $t^n \simeq 10\,\tau^n$ and $\Lambda \simeq 1.3$. Symbols - exact numerics, lines - analytics. Dimensionless growth times, from left to right: $t/\tau^g \approx 0.6$ (descending), and (bell-shaped) 2, 4 and 8. Note the emergence of asymptotic shape at large t. Singularity at small r disappears at $t = t_d$

$$f(r,t) \simeq \tau^n j_{st} \frac{r}{r^2/2 + t - t_d}\,, \;\; r \ll 1\,,\; t \sim t_d$$

Transition to asymptotic shape

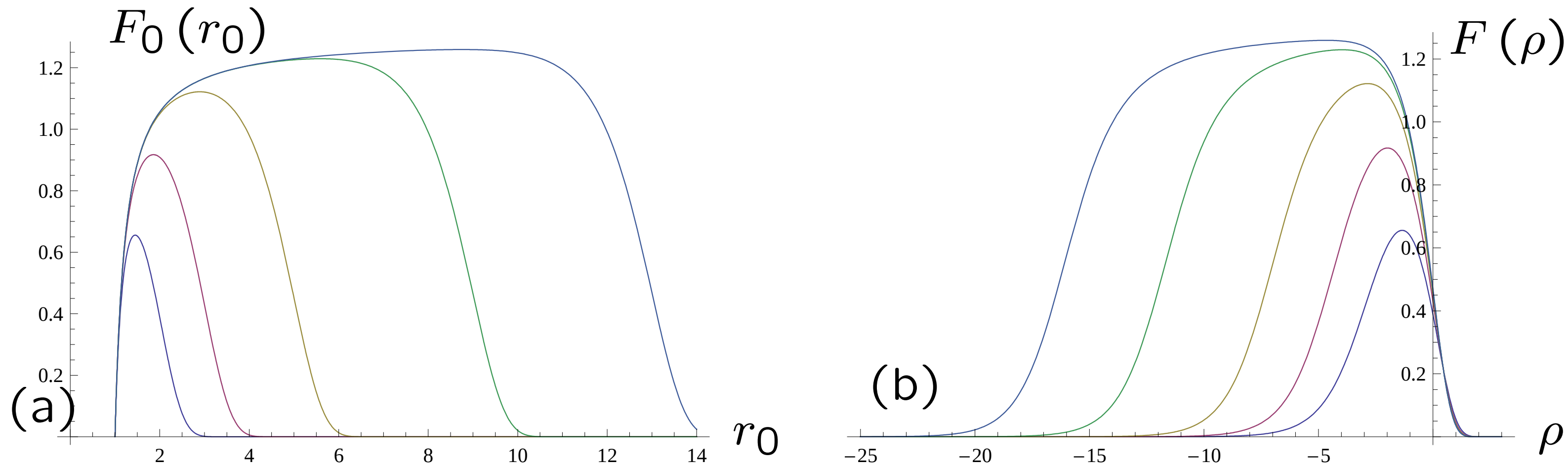
$$r_0(r,t) \;\to\; r_0(\rho)$$

$\rho \propto r - r^f$, distance from the front.

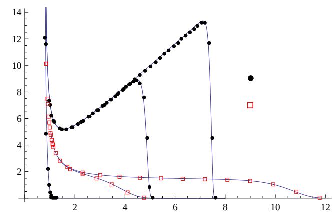
Equation for $r_0(\rho)$

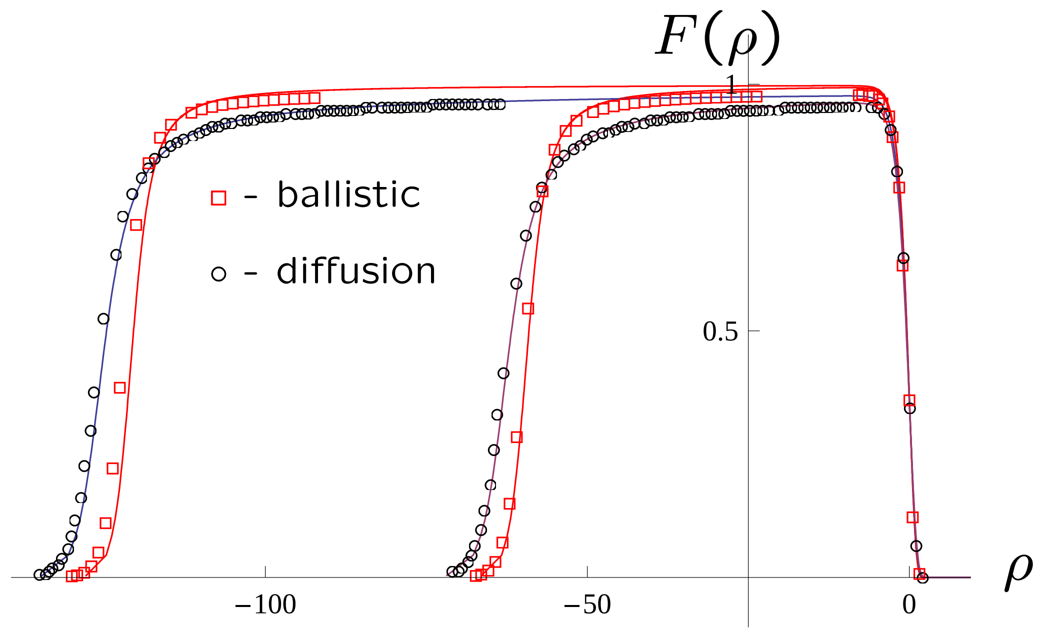
$$\int_{r_0^f}^{r_0} \frac{dr}{\tau^g \dot{r}^g} \sim \rho$$

r_0^f, initial position of the front, is determined by t^n, the duration of a nucleation pulse.

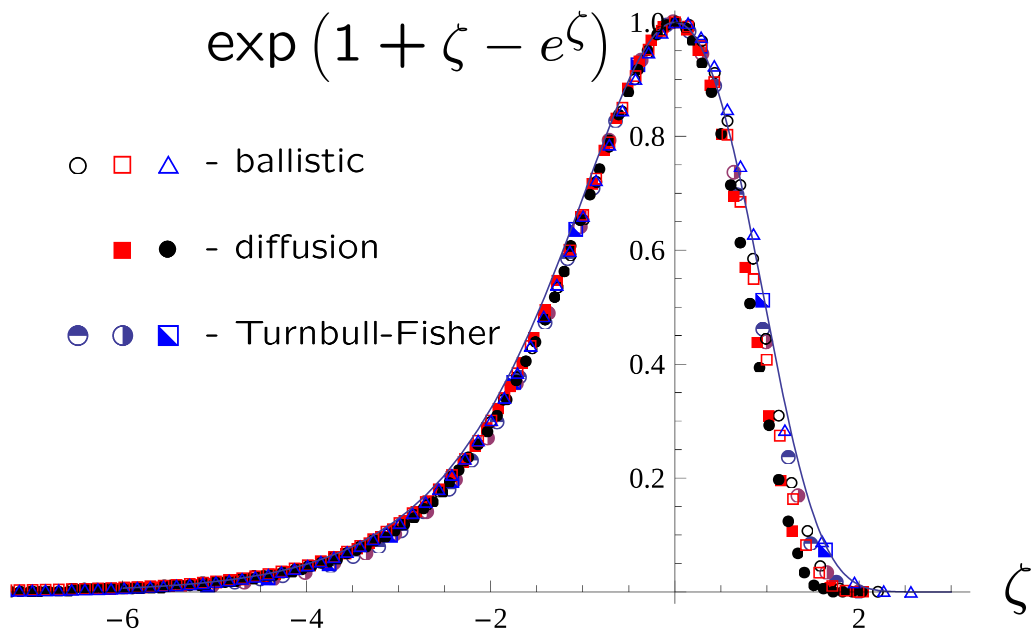


Dimensionless asymptotic distribution in terms of (a) initial size r_0 and (b) in terms of $\rho = r - r^f(t)$, with $r^f(t)$ locating the front. For the Zeldovich-Frenkel model the dependence $F_0(r_0)$ is elementary; $F(\rho)$ involves a special function. For all curves $\Lambda = 1.3$ and, from left to right for (a) [from right to left for (b)], $r_0^f - 1 = 1, 2, 4, 8, 12$.





Box-like asymptotic distributions originating from long nucleation pulses t^n ; ρ - distance from the front. Shorter pulses: $t^n/\tau^n \approx 60$; longer pulses: $t^n/\tau^n \approx 120$.



Universal distribution $F(\zeta)/F^{\max}$ formed in short nucleation pulses of different durations t^n ; the dimensionless distance from maximum, ζ and width are t^n-independent(!). Symbols - exact numerics. From left to right (legend): $t^n/\tau^n \simeq 1$, 2 and 3 (ballistic); 1.22 and 2.45 (diffusion); 0.75, 1 and 2.5 (Turnbull-Fisher).

Conclusions

- The problem of a nucleation pulse has been solved analytically. Solution is accurate in a singular perturbation sense, and is very accurate numerically.
- The resulting distribution of nuclei is not of any standard form (Gauss, log-normal, etc), but is strongly asymmetric, ranging in shape from a trapezoid to a bell-shape, depending on the duration of the pulse
- In the extremes of long and short pulses, respectively, the shapes of the distribution become remarkably universal, with additional insensitivity of either the height or the width of the distribution to the duration of the pulse
- although the problem was discussed in context of a two-step annealing crystallization experiment, the solution should have a broader applicability due to generality of the nucleation pulse technique.