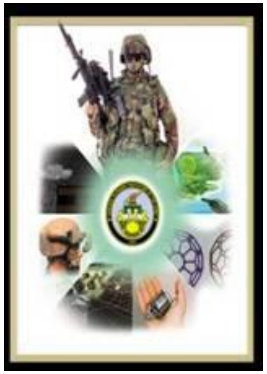
Field Theory of Nucleation at Large Driving Forces

Alex Umantsev

Fayetteville State University,
Fayetteville, NC

CHiMaD

National Science Foundation
WHERE DISCOVERIES BEGIN



Nucleation: old phase → new phase

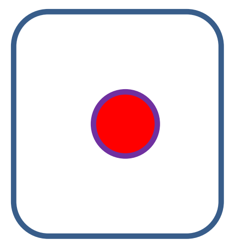
Classical Approach

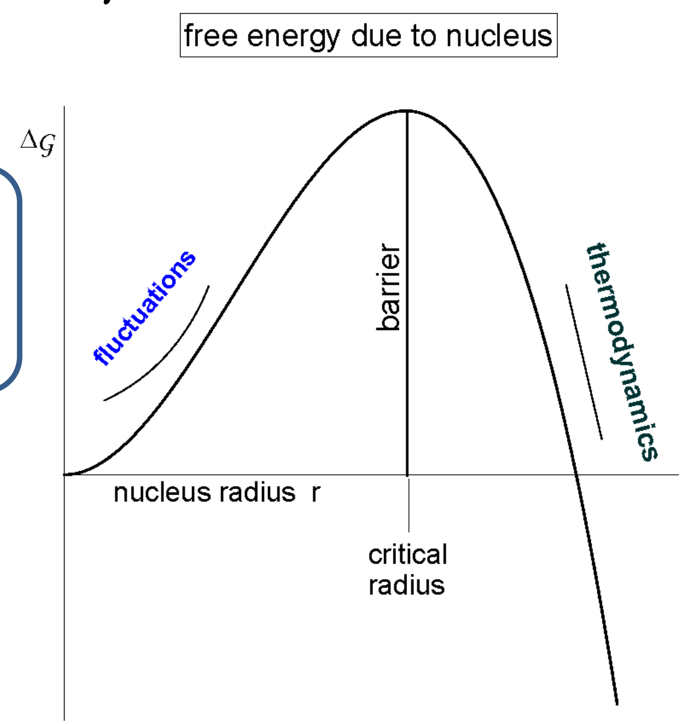
Gibbs, 1879

$$\Delta \mathcal{F} = -V_n \cdot \Delta\mu + S_n \cdot \sigma$$

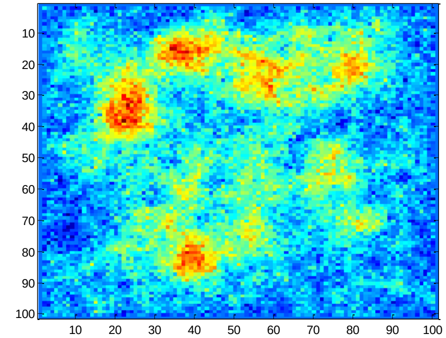
$$R_* = \frac{2\sigma}{\Delta\mu} \qquad \Delta \mathcal{F}_* = \frac{16\pi\sigma^3}{3\Delta\mu^2}$$

1. Supercooled water is stable but not completely-metastable
2. Potential barrier between the supercooled water and ice
3. Nucleation is activated by shaking, noise, thermal fluctuations
4. Nucleus: small piece of new phase in the ocean of old phase





Field Theory of Nucleation



$$I = K \cdot Z \cdot e^{-\frac{\Delta G}{k_B T}} = \frac{1}{V\tau}\left[\frac{\#cr}{vol * time}\right]$$

1. Volmer, circa 1920—activation process, Arrhenius factor
2. Bekker-During—first quantitative model of nucleation
3. Kramers, 1940—a particle in a potential well, Fokker-Plank equation, escape time
4. Zeldovitch, 1942—classical nucleation as a stochastic process, Fokker-Plank equation, Zeldovitch factor
5. Langer, 1967—field method, shape and position of the nucleus , concept of a lifetime as a function of system's parameters
6. Patashinski, et al, late '70—consistent field theory of nucleation
7. Klein, early '80—Langer's method, close to the loss of stability (spinodal point)
8. Mazenko, mid '80—numerical method, domain growth dynamics, structure factor

Requirements

Phase Transition

1. First order, not symmetry breaking
2. Away from the critical region

Hamiltonian

1. athermal driving force
2. no external fields
3. anharmonic interaction

Large driving force

Nucleation rate is not the right quantity to calculate

3D as opposed to 2D

Correlation properties of the fluctuations are very different

Quantitative modeling

The method should be calibrated against a reliable theory

Method

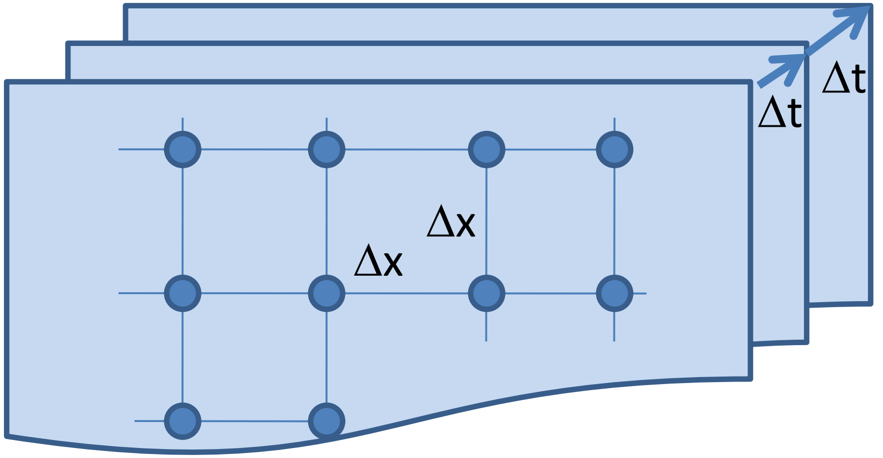
Lifetime (instead of Nucleation rate)

Definition: time for the first supercritical nucleus to appear in the system.

1. more reliable theory 2. free-energy landscape

Numerical simulations

Stochastic Integration



Calibration strategy

Δx, Δt are not just grid parameters.

These are physical quantities–the noise correlation length and time.

Field Method in Phase Transitions

Homogeneous system:

$$H(\Delta,\eta) = H_{\alpha}(T) + \frac{1}{2}W\left\{(1-\Delta)\eta^2 + \frac{2}{3}(3-\Delta)\eta^3 + \frac{1}{4}\eta^4 + \cdots\right\}$$

Inhomogeneous system:

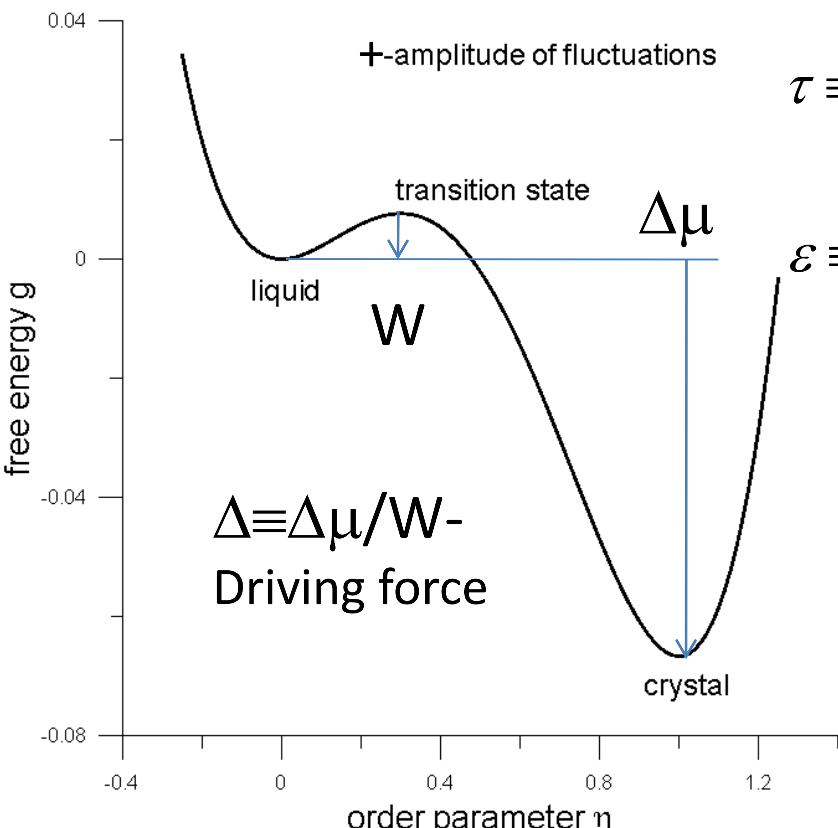
'penalty' ↓

$$\mathcal{H} = \int\left[H(\Delta,\eta) + \frac{1}{2}\kappa(\nabla\eta)^2\right]d^3x$$

$$R_0 \equiv \sqrt{\frac{\kappa}{W}}$$

$$\tau \equiv \frac{1}{\gamma W}$$

$$\varepsilon \equiv \frac{k_B T}{W R_0^3}$$



Dynamics: time-dependent Ginzburg-Landau equation

$$\frac{d\eta}{dt} = -\gamma\frac{\delta\mathcal{H}}{\delta\eta}$$

Internal fluctuations: Langevin force

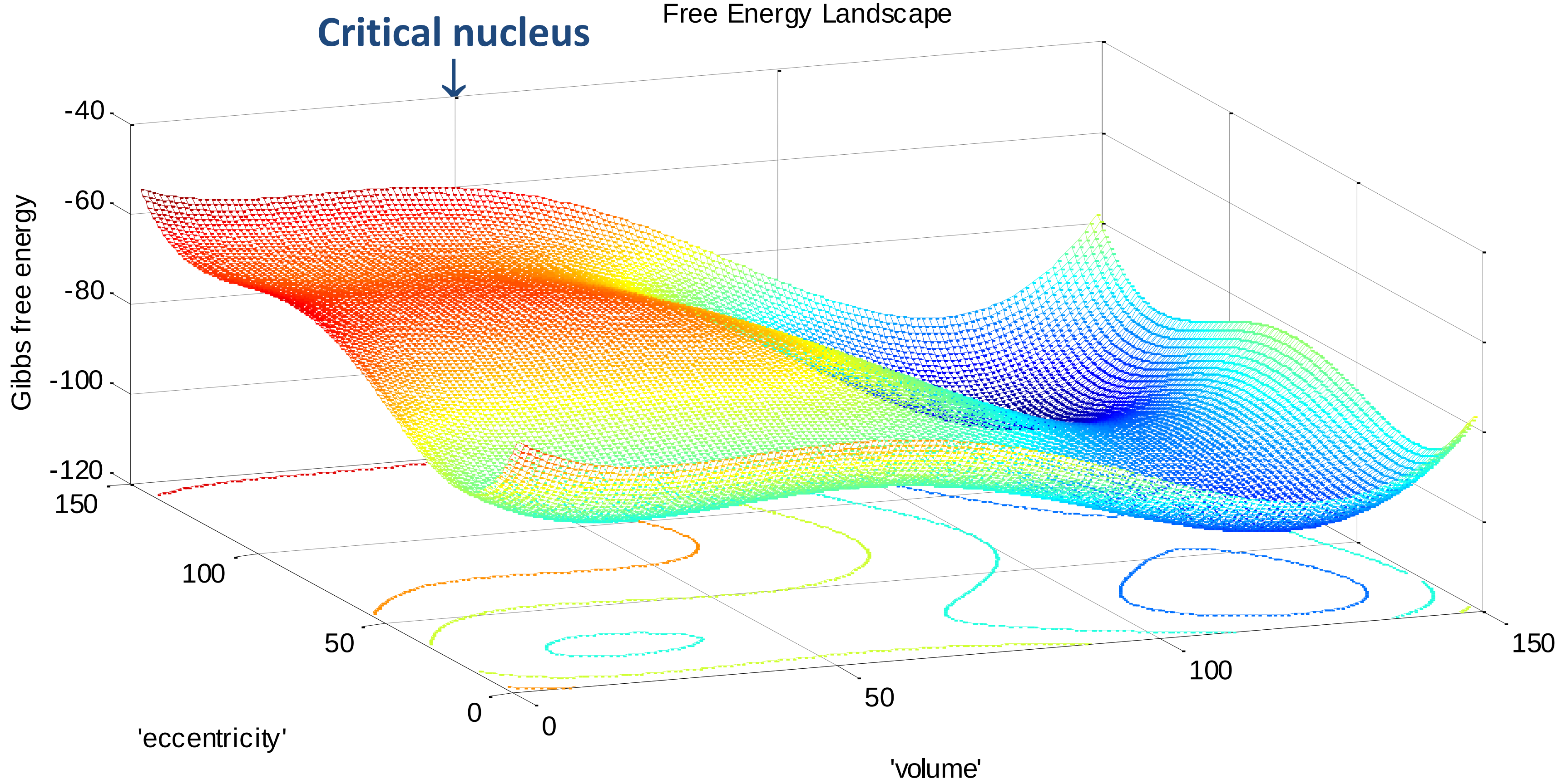
Hamiltonian

$$\frac{d\eta}{dt} = -\gamma\left(\frac{\delta\mathcal{H}}{\delta\eta}\right)_{T,P} + \zeta(x,t);\ \Gamma = 2\gamma k_B T$$

$$\langle\zeta(x,t)\zeta(x',t')\rangle = \Gamma\delta(x'-x)\,\delta(t'-t)$$

$\zeta(\mathbf{x}, t)$: Gaussian, white, additive.

Free Energy Landscape



Calibration strategy: Φ{Δ, ε, V} (numerics vs theory)

Equilibrium Fluctuations: Perturbation Theory

Dimo Uzunov,
Bulgaria

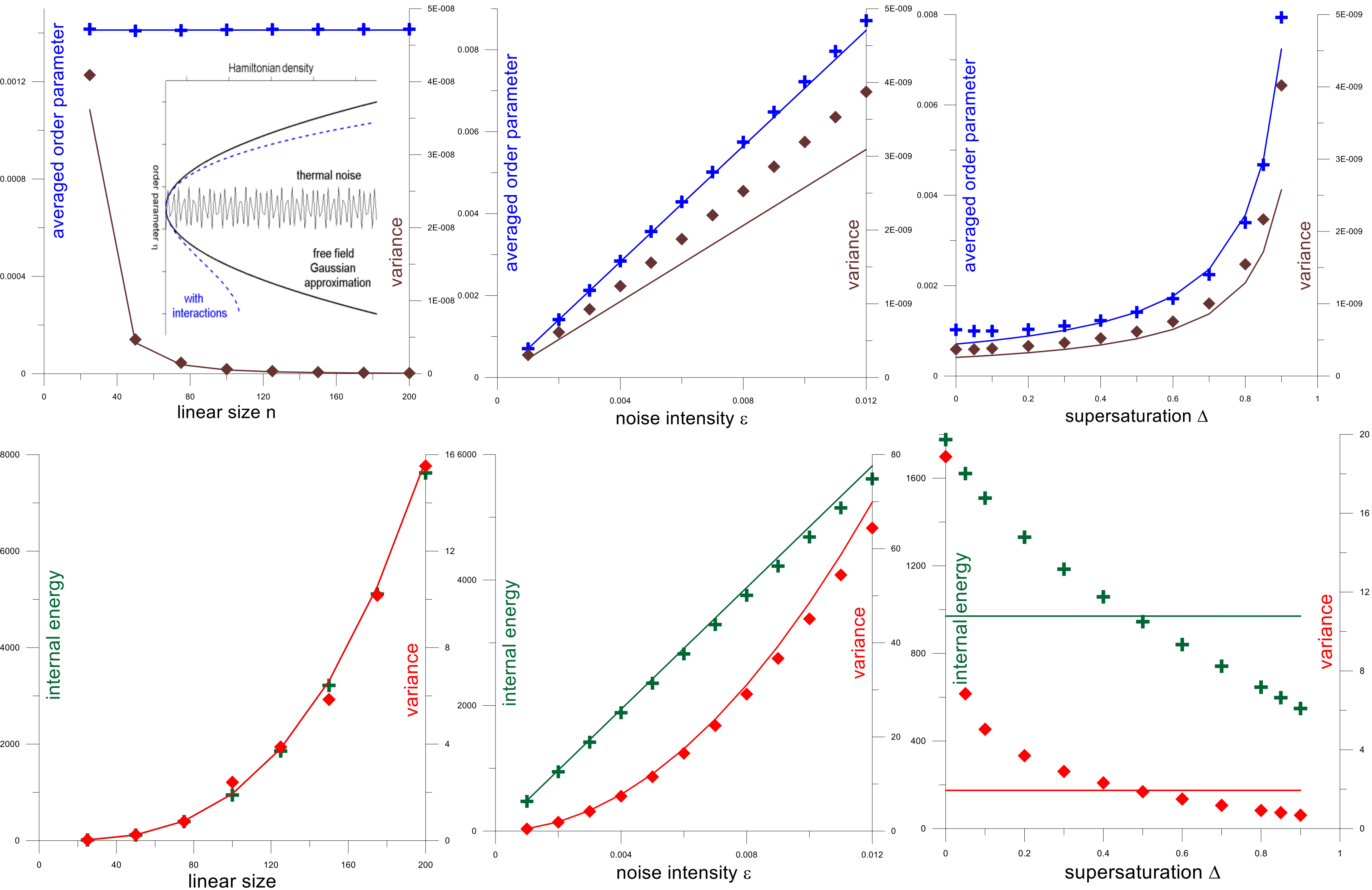
Statistical averaging → Ergodic hypothesis → Time averaging

- Total order: $\mathrm{O} = \left\langle \int_V \eta(\mathbf{x}, t) dv \right\rangle \qquad = \overline{\int_V \eta(\mathbf{x}, t) dv}$

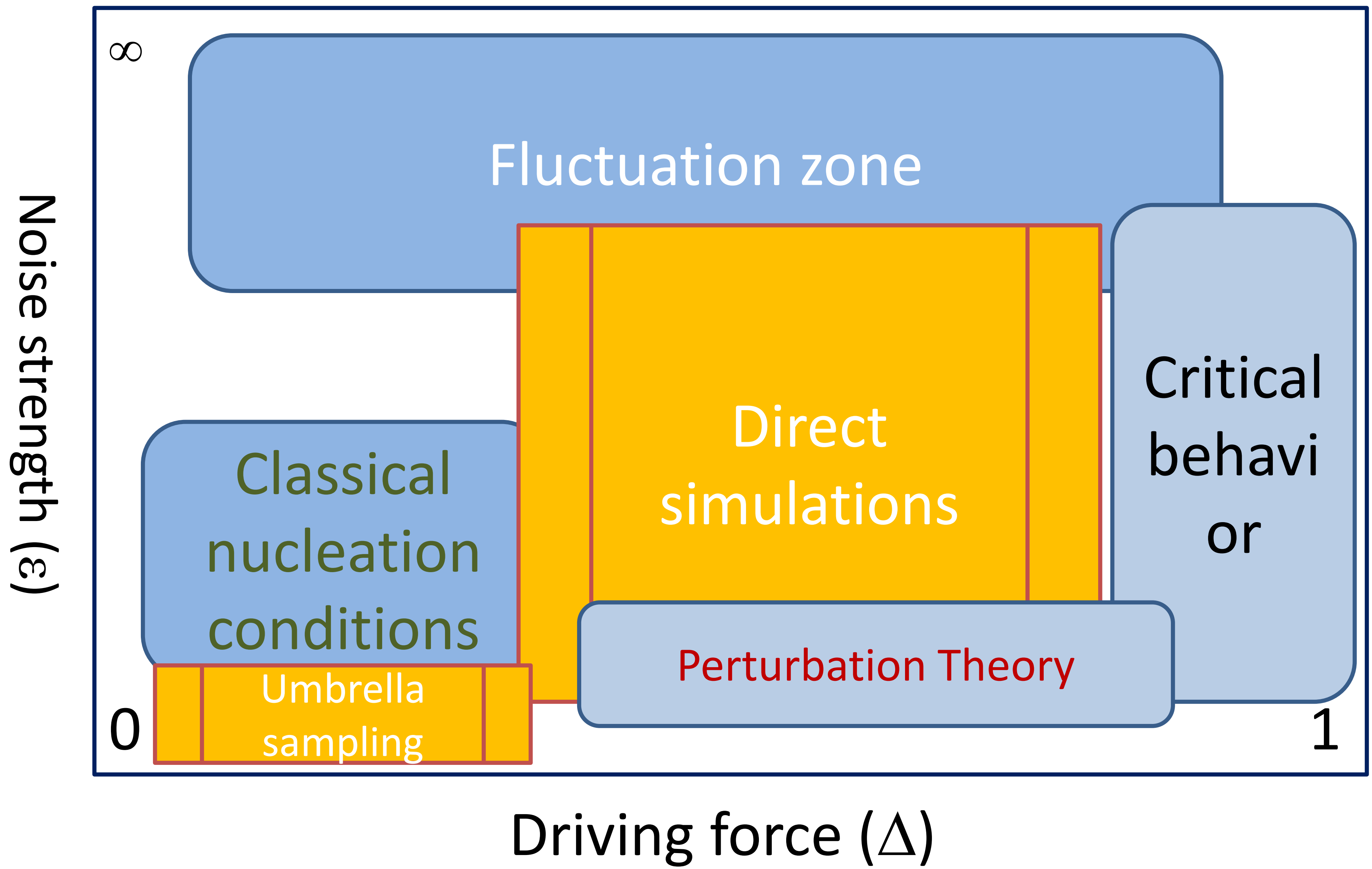
- Internal energy: $\mathcal{E} = \langle \mathcal{Hamiltonian} \rangle \quad = \overline{\mathcal{Hamiltonian}}$

- Free energy: $\mathcal{F} = -\frac{1}{\beta} \ln\{Partition\ \ function\}$ =?

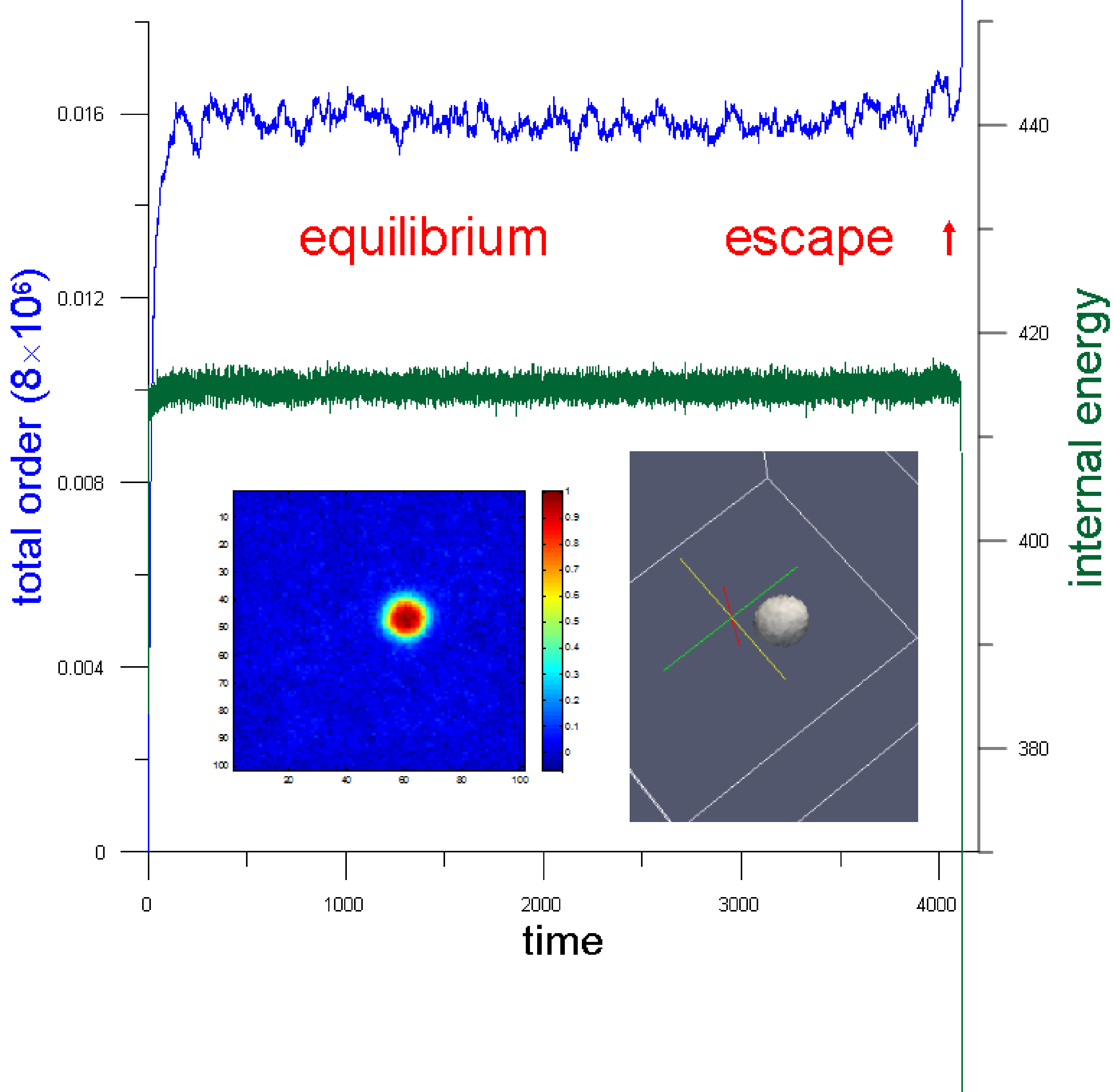
Matching Theory and Numerics



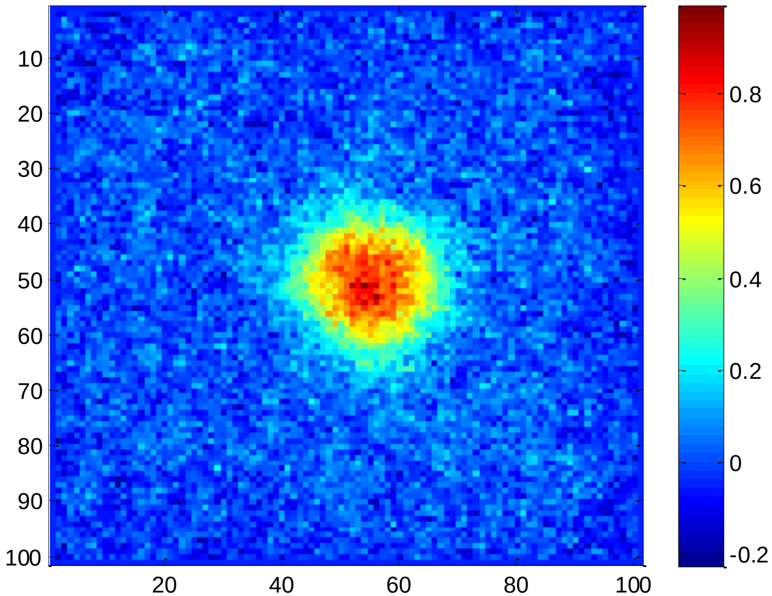
Large Driving Force



Time Evolution of the System

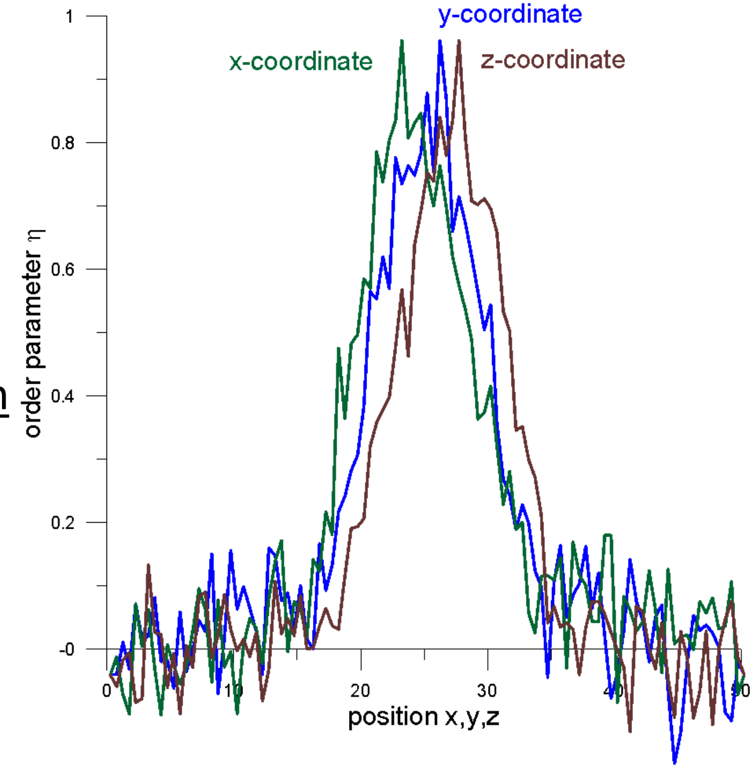


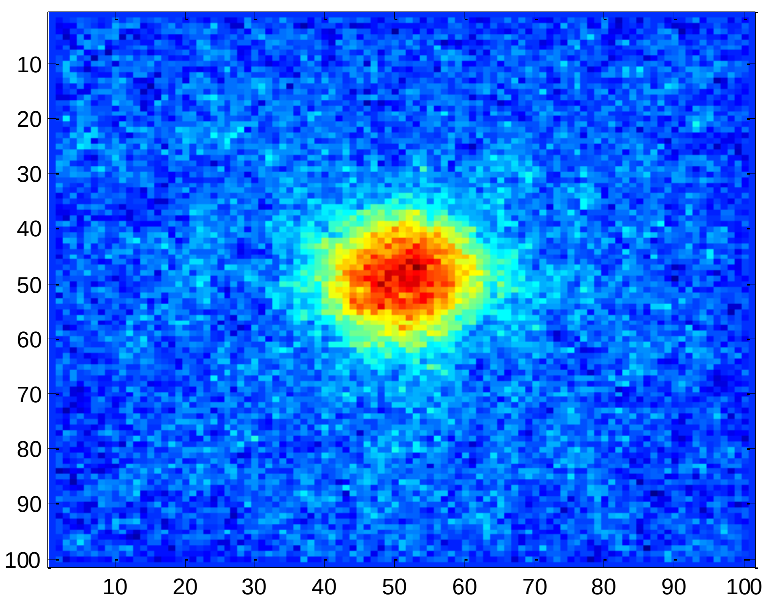
Supercritical nucleus

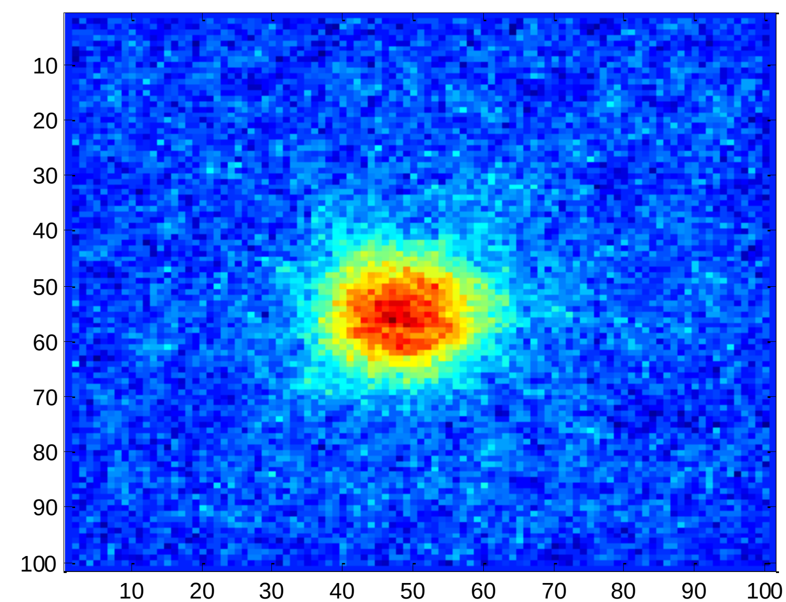


<u>Shape characterization</u>

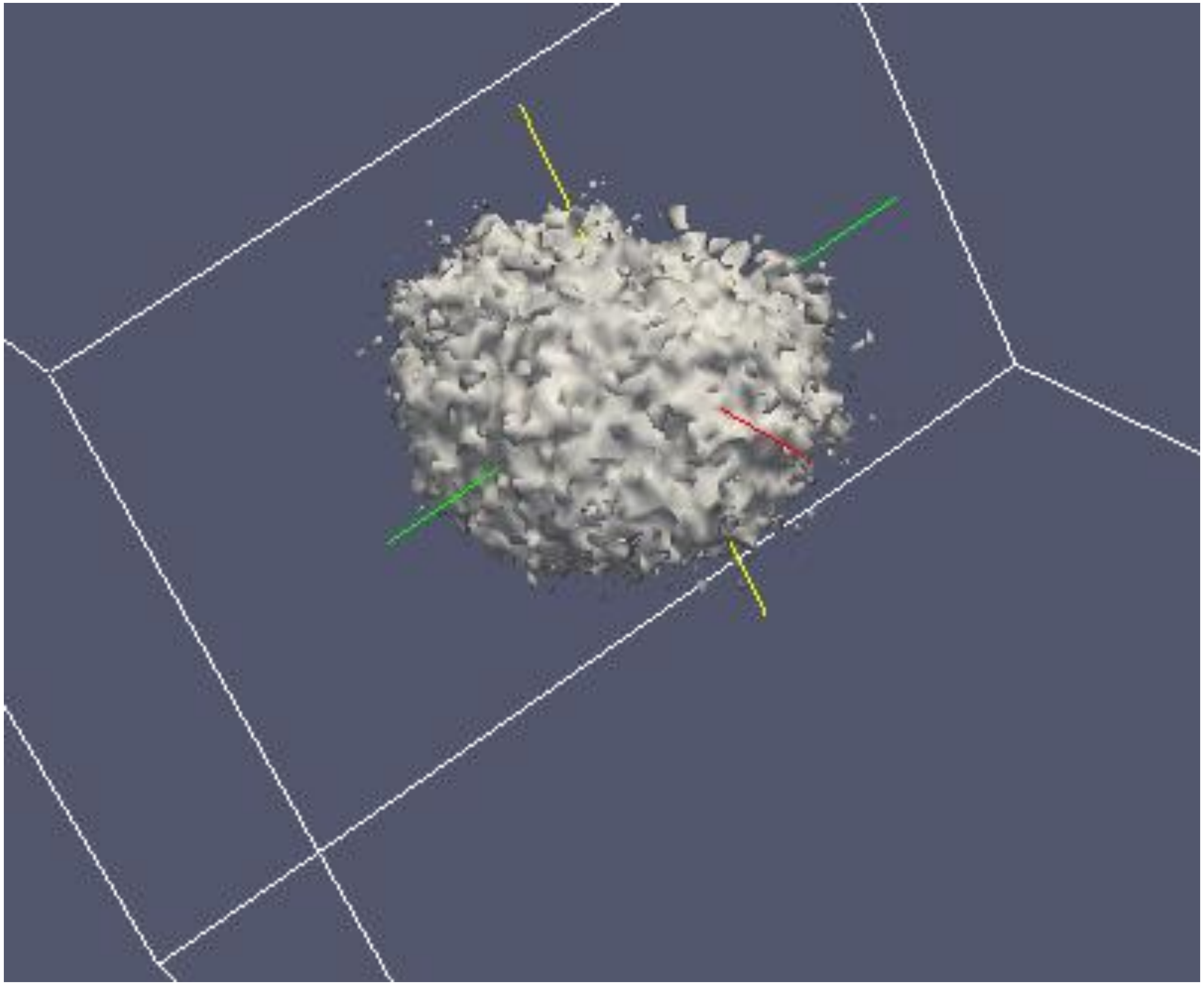
1. Volumetric content
2. Eccentricity
3. Roughness
4. Probability distribution





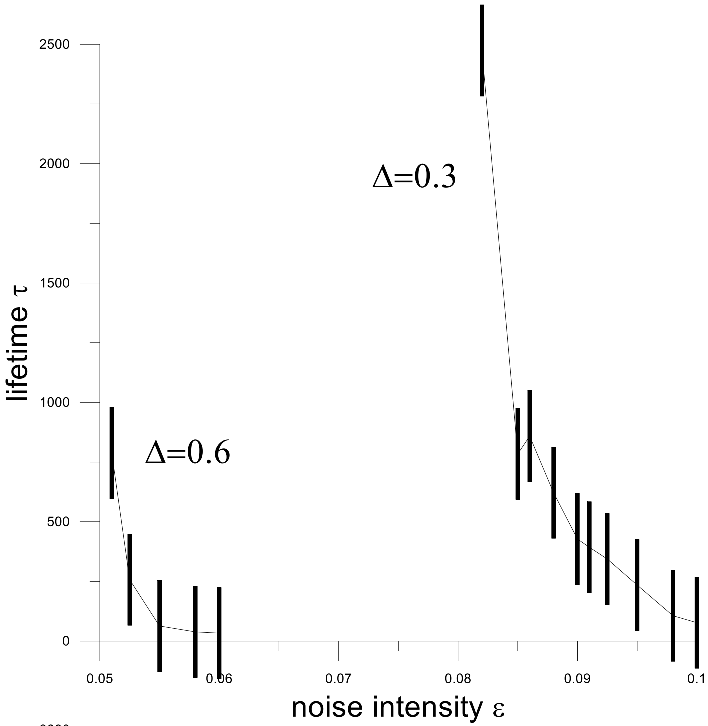


3D as opposed to 2D



http://www.paraview.org/

Preliminary Results



Level line of $\tau(\varepsilon, \Delta, V=8x10^6R_0)$