Nonlinear Dynamics and Self-organization in the Presence of Metastable Phases

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elf-organization phenomena involving nanosiz materials (protein solutions, zeolites, etc ...)

mmon feature :

eak and short ranged attractive interactions compared to simple ato ds

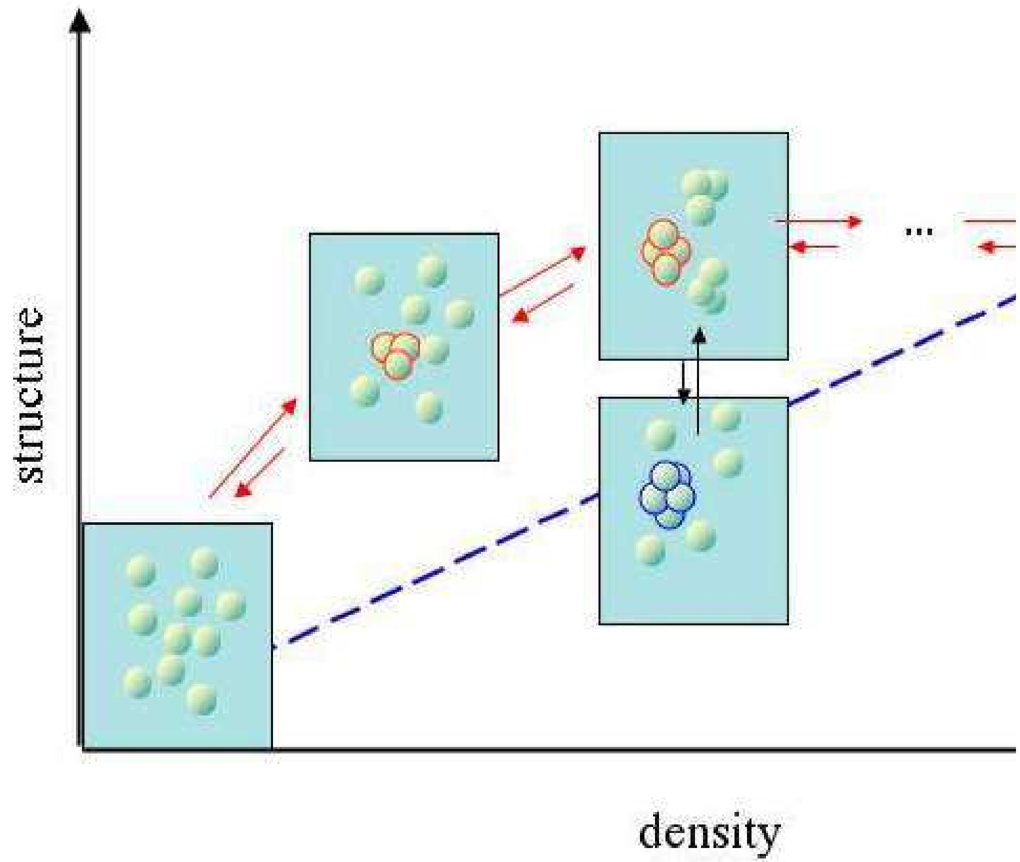
pontaneous self-assembly towards ordered phases compromized by sence of high nucleation barriers ($\approx 100 k_B T$ for the crystallization tein solutions in ordinary conditions)

easing evidence of presence, in such materials, of metastable ph igh concentration protein solutions, etc...) and of their interferen

n standard nucleation mechanisms with combi structural and density fluctuations

nportance of kinetic effects ing from the co-existence of npeting mechanisms

nhancement of nucleation rate er certain conditions via orable pathways in the two er-parameter phase diagram



bjectives :

rive the free energy landscape

lress the kinetic aspects of the
ess

ermine conditions for
nization

- Background : classical density functional theor
- Phase diagram
- The effect of metastable liquid phases on free energy landscape
- Kinetics of barrier cross : formulation
- Kinetic potential and its bifurcation set
- Transition dynamics
- Conclusions and perspectives

ackground : classical density functional theor

ing point:

ree energy is a unique functional $F[\rho]$ of the local density $\rho(r)$

Fluid

$$\rho(r) = \bar{\rho} = \text{const}$$

Solid

$$\rho(r) = \sum_i f(r - R_i)$$

$$= \bar{\rho} + \bar{\rho} \sum \exp(ik_i r) \exp\left(-\frac{k_i^2}{\cdot}\right.$$

Crystallinity

$$m = \exp\left(-\frac{k_1^2}{4\alpha}\right)$$

$$F[\rho] = F_{HS}[\rho] + \int\int \mathrm{d}r_1 \mathrm{d}r_2 \rho(r_1)\,\rho(r_1)\,u(r_1, r_2)$$

$$= \begin{cases} \infty & r < \sigma \\ \frac{4\epsilon}{\alpha^2}\left(\frac{1}{\left(\left(\frac{r}{\sigma}\right)^2 - 1\right)^6} - \alpha\frac{1}{\left(\left(\frac{r}{\sigma}\right)^2 - 1\right)^3}\right) & r > \sigma \end{cases}$$

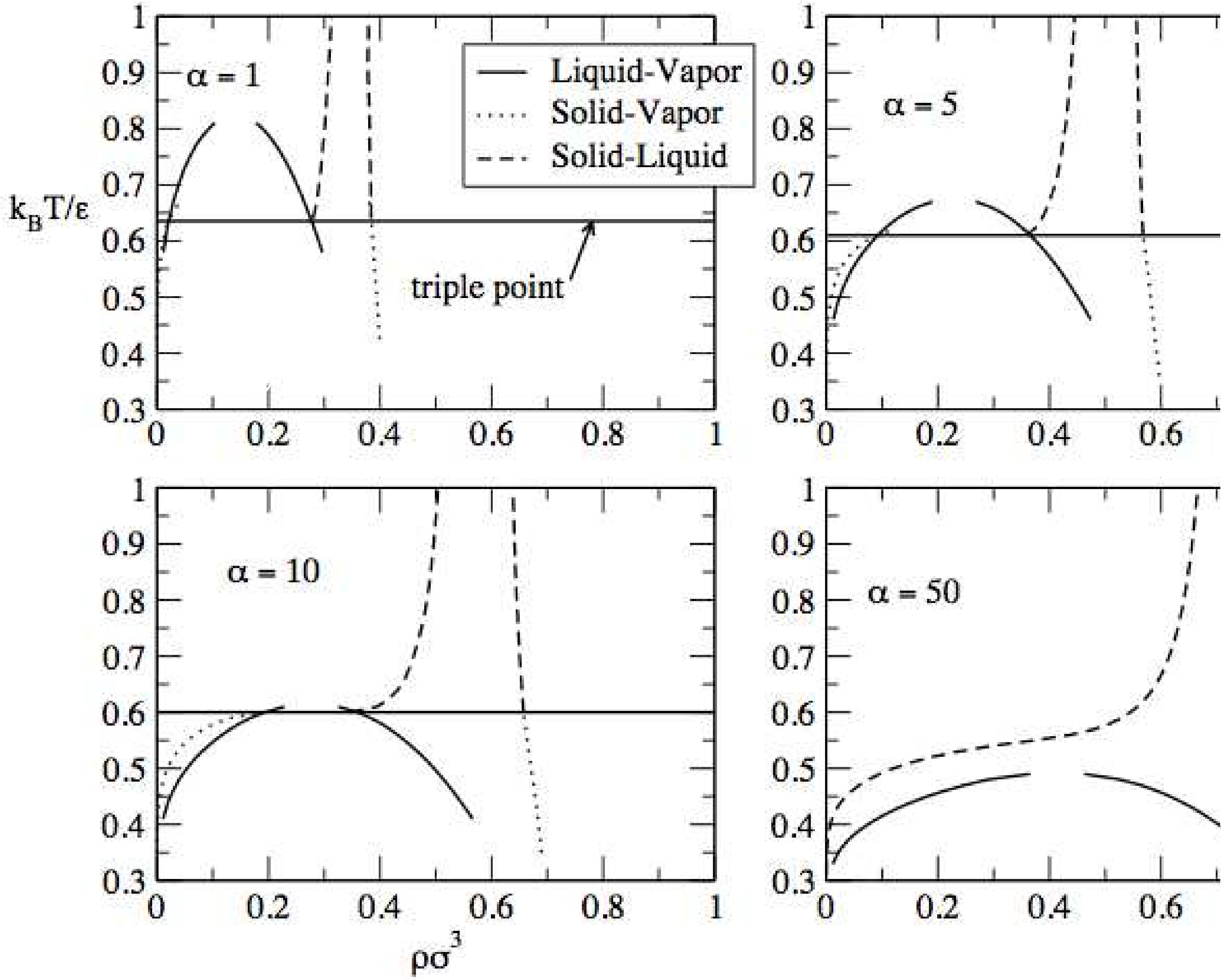
$$\frac{r_{min}}{\sigma} = \sqrt{1 + \left(\frac{2}{\alpha}\right)^{1/3}} \qquad u(r_{min}) = -\epsilon$$

$$\frac{u(2\sigma)}{u(r_{min})} = \frac{108\alpha - 4}{729\alpha^2}$$

(ten Wolde-Frenkel)

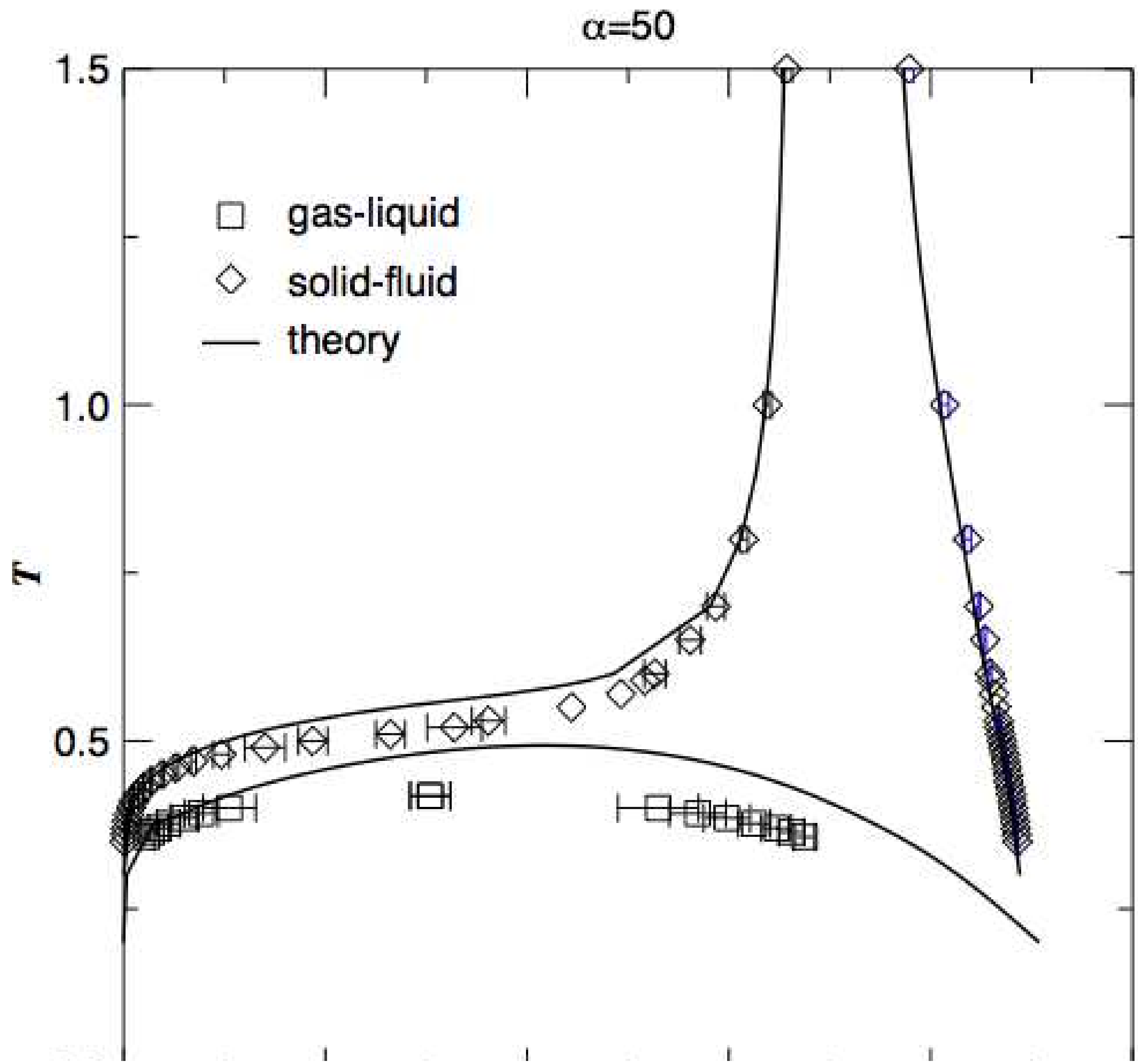
Phase diagram

ınificant and generic
ference in the phase
rams between the ten
de-Frenkel interaction
del and the standard
ıard-Jones interaction



Metastable fluid-fluid transition for

Frenkel potential

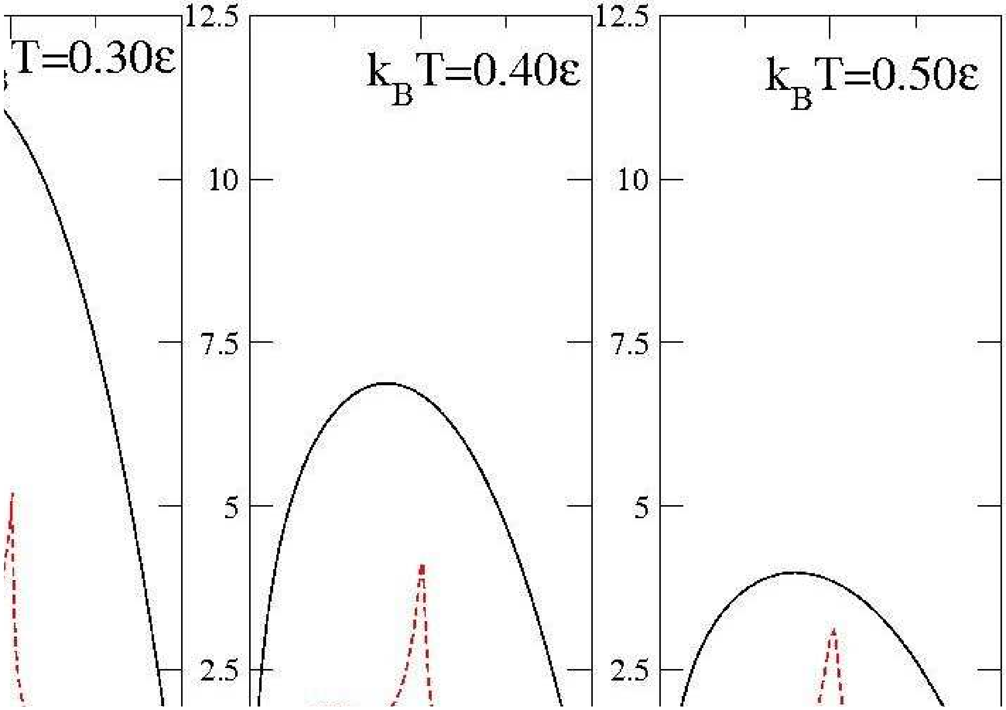


ect of metastable liquid on free energy landsca

ssical path

$$= \bar{\rho}_{\text{fluid}} + \left(\bar{\rho}_{\text{solid}} - \bar{\rho}_{\text{fluid}}\right) x$$

$$m(x) = x m_{\text{solid}}$$

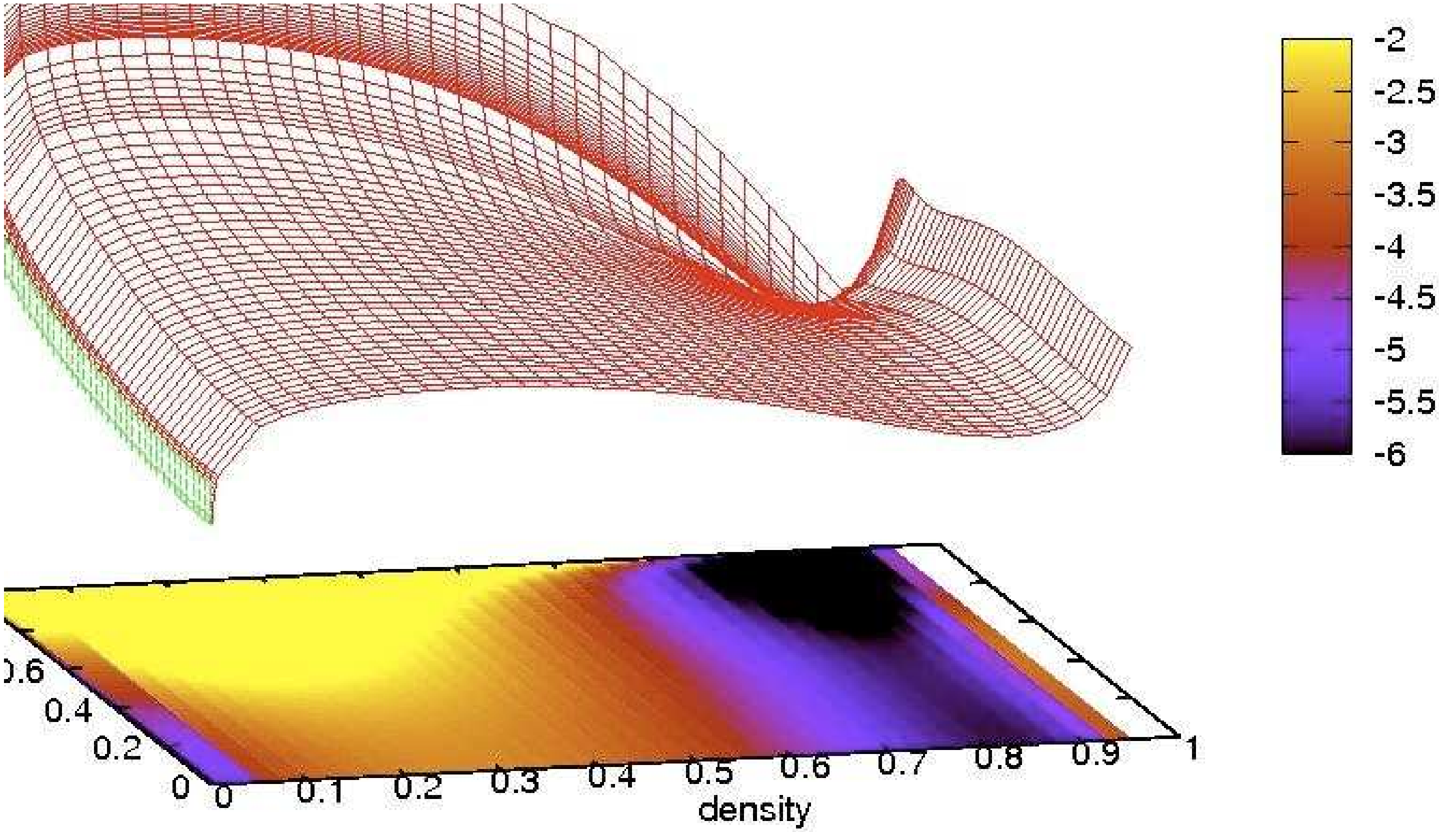


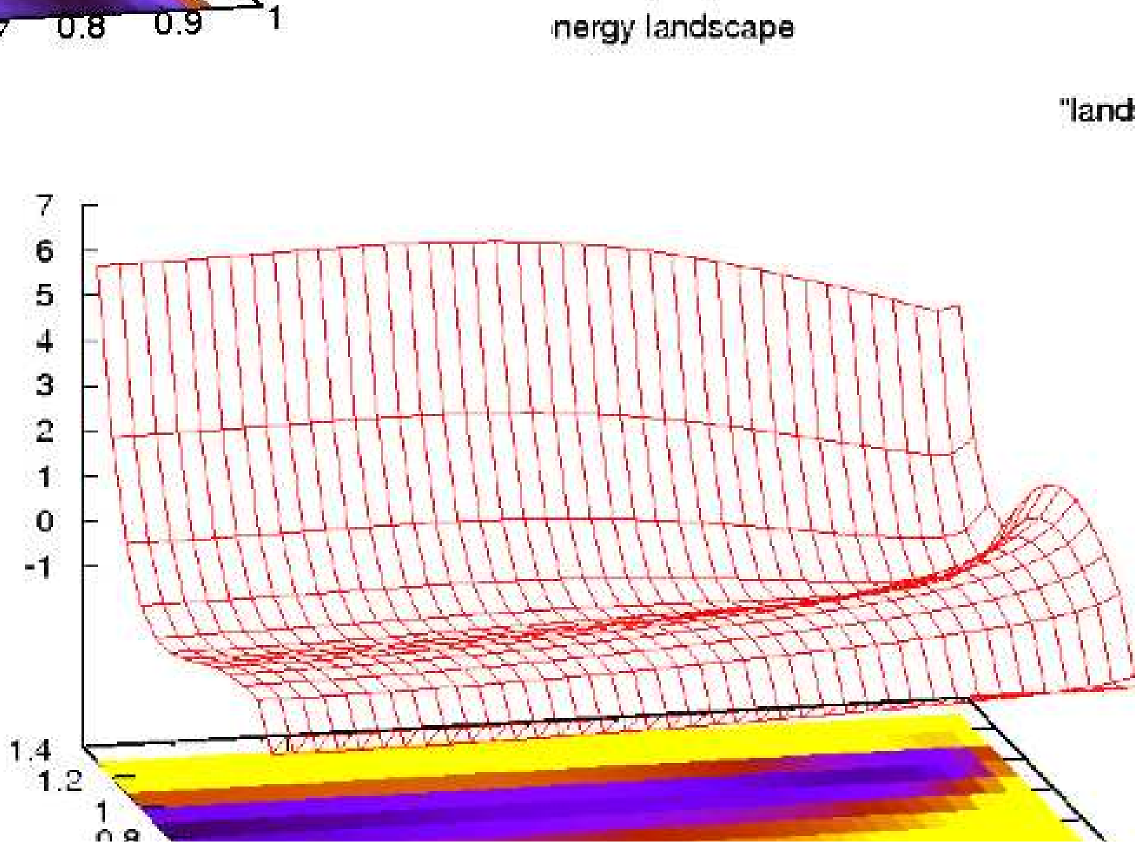
requires overcoming a higher free en
barrier compared to a *non-classical*

$$\bar{\rho}(x) = \left(\bar{\rho}_{\text{fluid}} + 2x\left(\bar{\rho}_{\text{solid}} - \bar{\rho}_{\text{f}}\right.\right.$$

$$\theta\left(\frac{1}{2} - x\right) + \bar{\rho}_{\text{solid}}\theta\left(x\right.$$

$$m(x) = \theta\left(x - \frac{1}{2}\right)(2x - 1)\, m$$


-2
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
density


nergy landscape
"land
7
6
5
4
3
2
1
0
-1
1.4
1.2
1

Kinetics of barrier crossing : formulation

m order parameters

$\mu, \cdots$ control parameters

Landau type free energy

trix of Onsager coefficients

Transitions between states governe
by

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\rho \\ m\end{pmatrix} = -\mathbf{L}\cdot\nabla F(\rho,\ m) + \begin{pmatrix} R_\rho (\\ R_m (\end{pmatrix}$$

where R_ρ, R_m are Gaussian wh
noises whose covariance ma
must satisfy fluctuation-dissipat
type relationships

er-Planck equation integrating the above condition

$$\ldots = \mathrm{div}\left(Ł\left(\nabla F\ P + \epsilon\nabla P\right)\right)$$

where ϵ is small

$\ldots k_B T$ or 1/(system size))

Original dynamics does not derive fr… potential. Mapping to a dynamics in t… of new order parameters *x*, *y* deriving… a *kinetic* potential, *U* by means … congruent transformation,

$$\Lambda = \tilde{\phi}Ł\phi$$

diagonalizing $Ł$:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\partial U}{\partial x}P + \epsilon\frac{\partial P}{\partial x}\right) + \frac{\partial}{\partial y}\left(\frac{\partial U}{\partial y}P + \epsilon\frac{\partial P}{\partial y}\right)$$

Kinetic potential and its bifurcation set

quirements : Switch as the control
ameters are varied, from

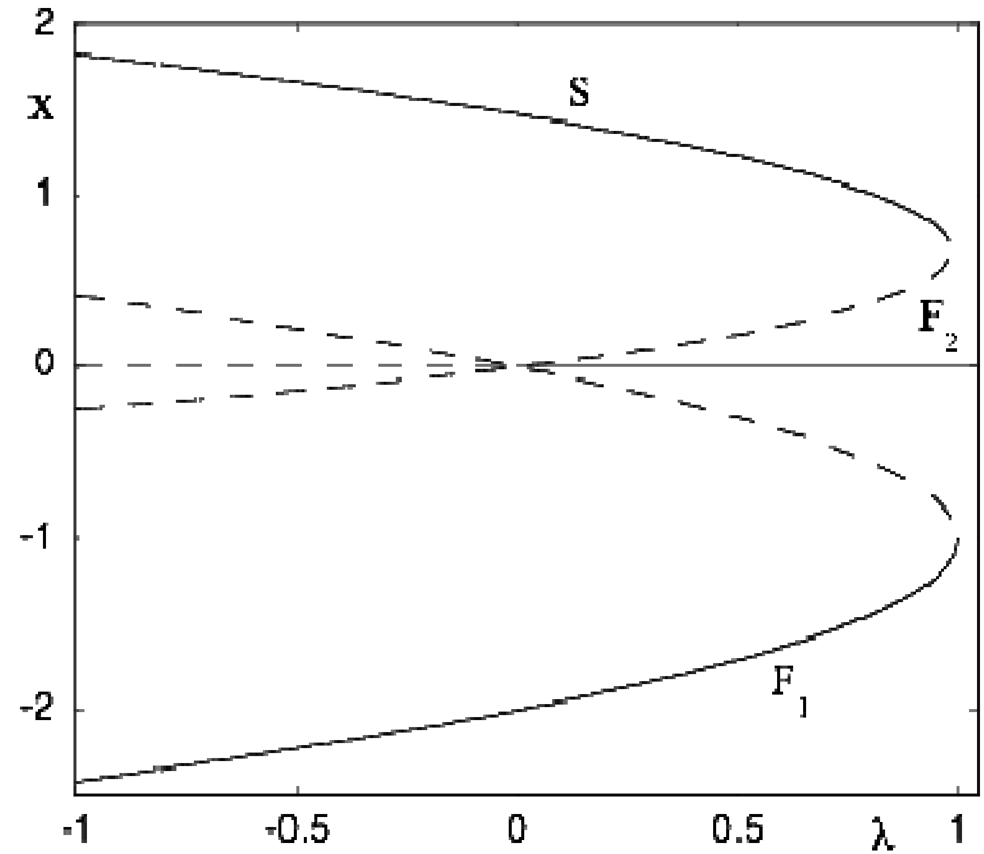
$$F_1 \rightarrow S\,(2 \;-\text{well } U)$$

$$F_1 \underset{\longrightarrow}{\overset{\longleftarrow}{}} F_2 \rightarrow S\;\;(3 \;-\text{well } U)$$

Parabolic umbilic catastr
scenario. Full unfolding by
control parameters

bsence of external fields and other sources of asymmetry

$$, y) = \frac{\lambda}{2}\left(x^2 + y^2\right) + \frac{\mu}{3}x^3 - \gamma x y^2 + \frac{1}{4}\left(x^4 + y^4\right)$$



Transition dynamics

$\lambda < 0, \ \mu$ fixed :

ect $F_1 \rightarrow S$ transition

$$\frac{dp_1}{dt} = -k_1 p_1$$

$\lambda > 0, \ \mu$ fixed :

transition via F_2

$$\frac{dp_1}{dt} = -k_1 p_1 + k_1' p_2$$
$$\frac{dp_2}{dt} = k_1 p_1 - (k_1' + k_2)$$

where the $k's$ are related to mean first passage times statistics associated to the Fokker-Planck equation

$$\frac{1}{2\pi}\left(\frac{\sigma_u^+}{|\sigma_u^-|}\right)^{1/2}(\sigma_{s_1}\sigma_{s_2})^{1/2}$$

$$\exp\left(\frac{U(unst)-U(st)}{\epsilon}\right)$$

$(F_1 \to S)$: *lowest eigenvalue*

- for $\lambda < 0$

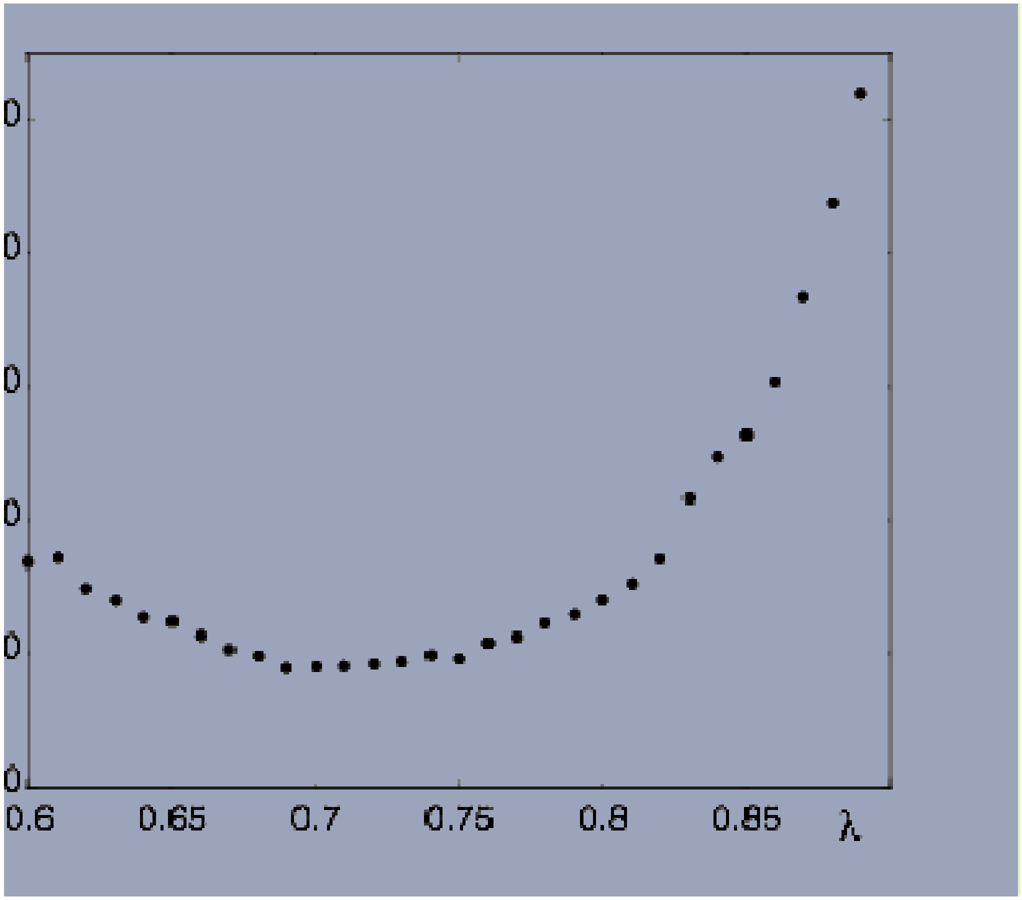
$$k_1$$

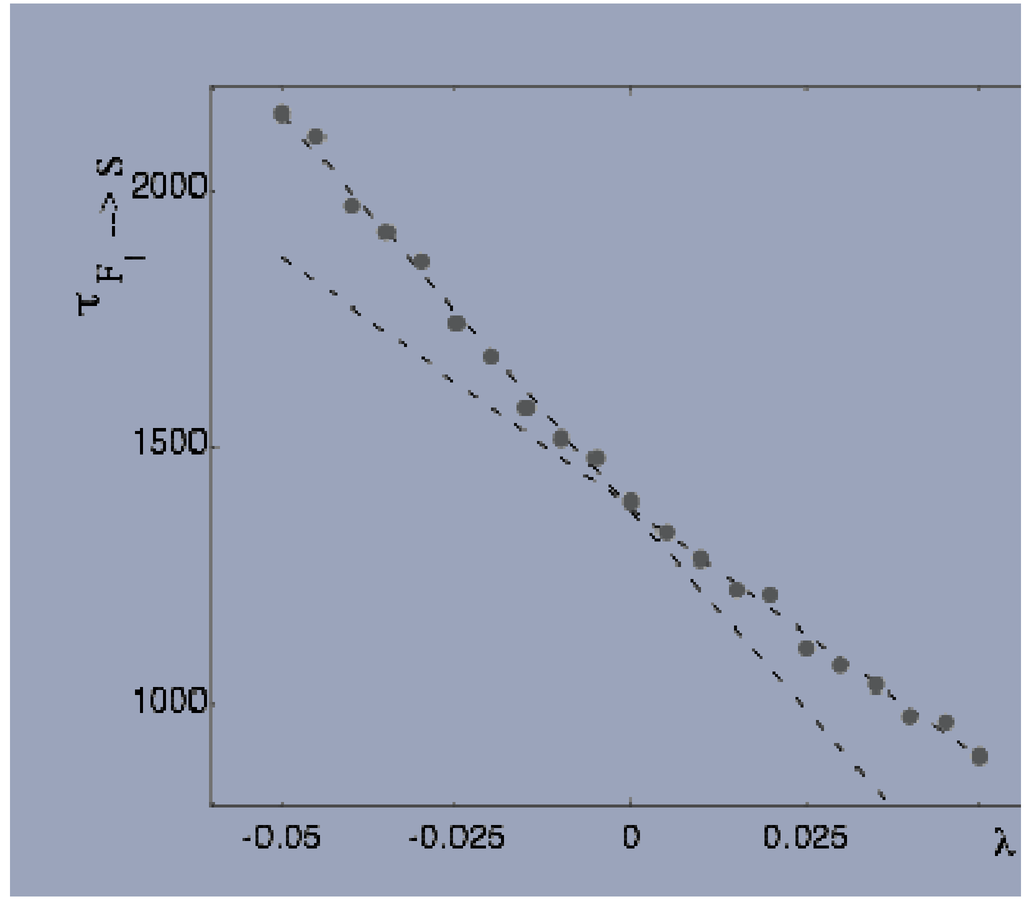
- for $\lambda > 0$

$$\frac{1}{2}\,|-(k_1+k_2+k$$

$$\sqrt{(k_1-k_2)^2+k_1'^2+2k_1'(k_1+}$$

$$(\to k_2 \text{ for } k_1' << k_1)$$





ptimization near the F_1 - F_2 coexistence

on -trivial cross-over at $\lambda = 0$

Conclusions and perspectives

Enhancement of nucleation by the presence of F_2 is a generic possibility

Universality

Thermodynamic (Landau) versus kinetic potential

- Connection to experiment a suggestions for further experiments
- Further unfolding scenarios
- Spatial degrees of freedom, asymmetric interactions