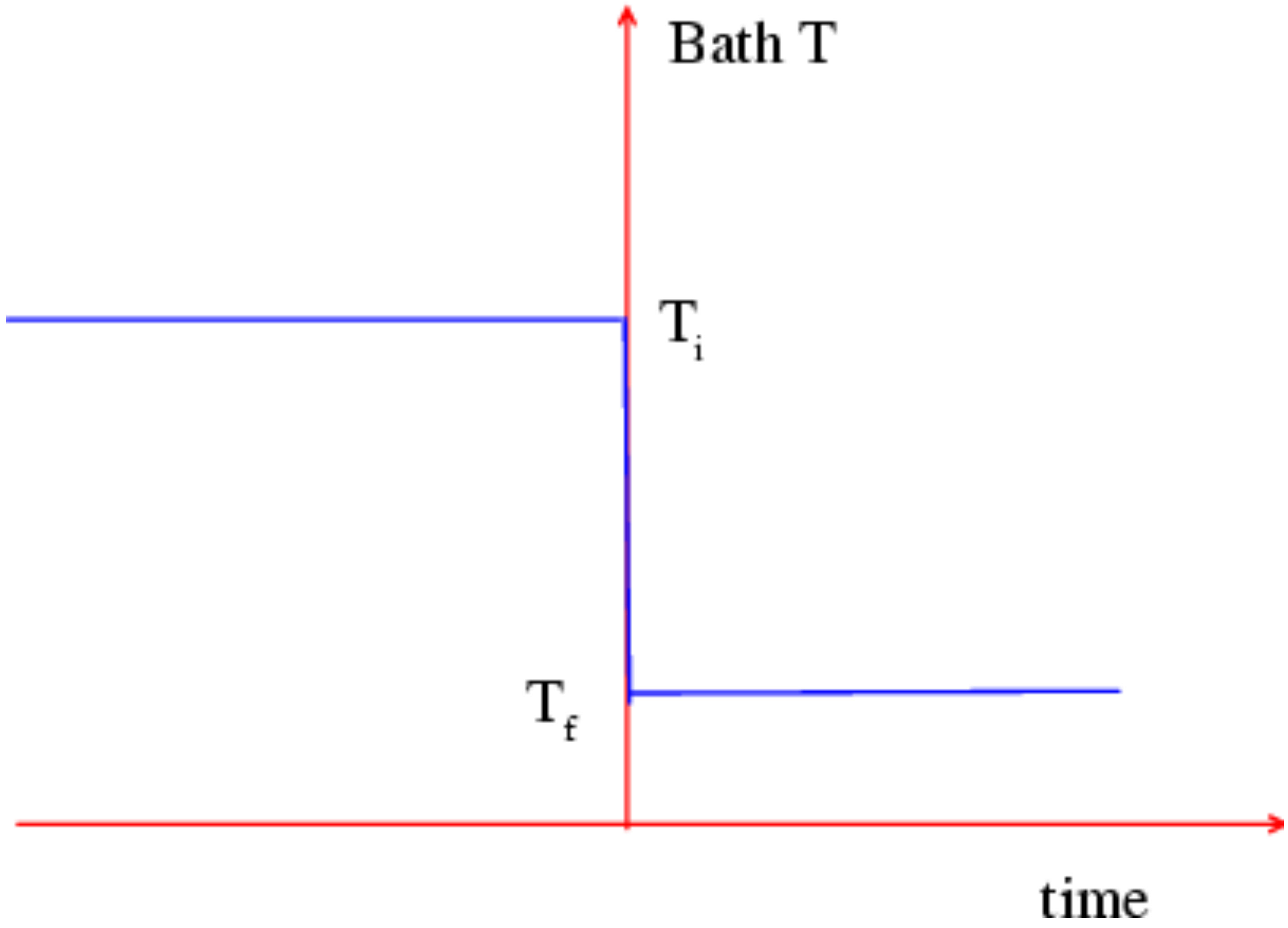
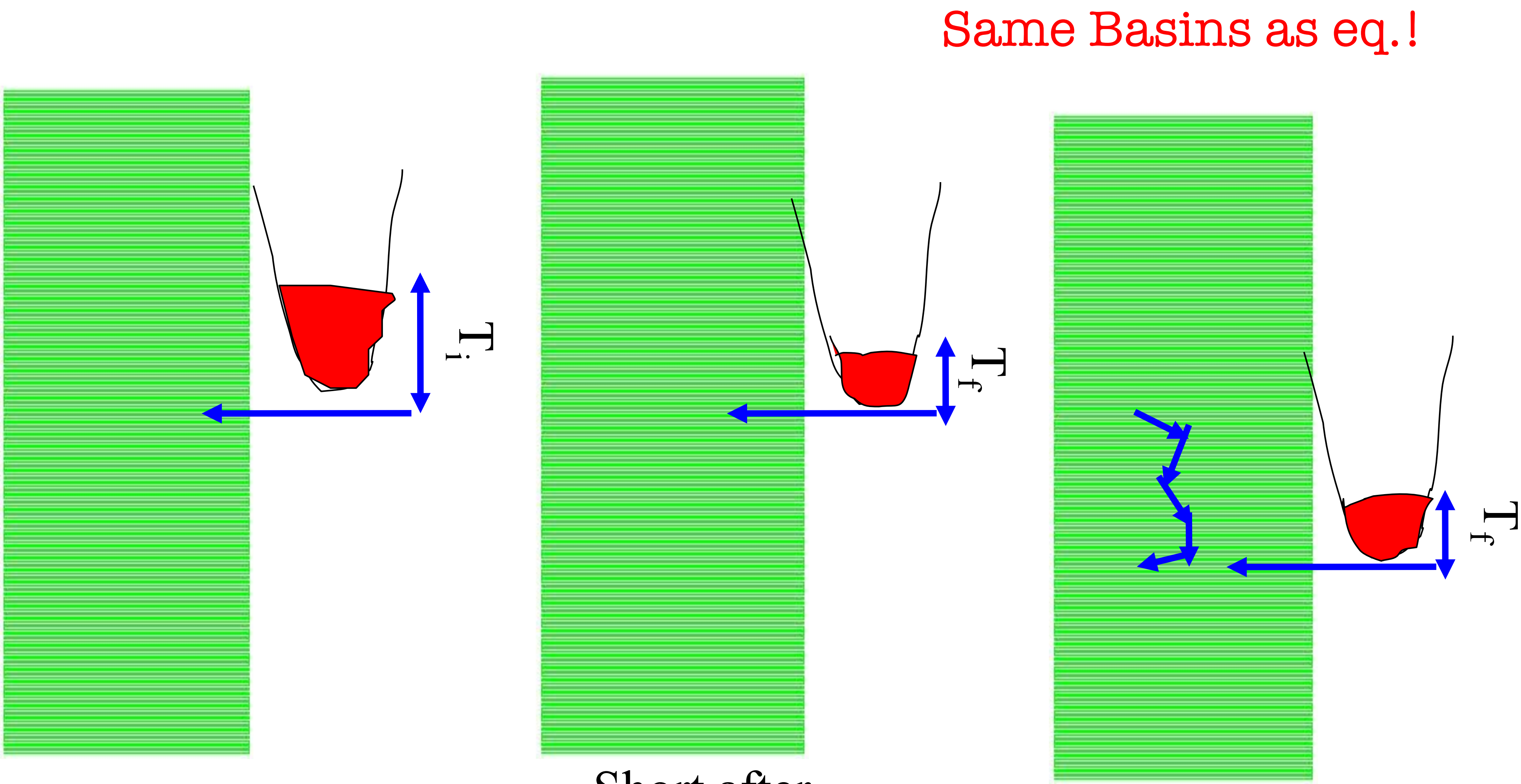
Simple (numerical) Aging Experiment



Aging in the PEL-IS framework

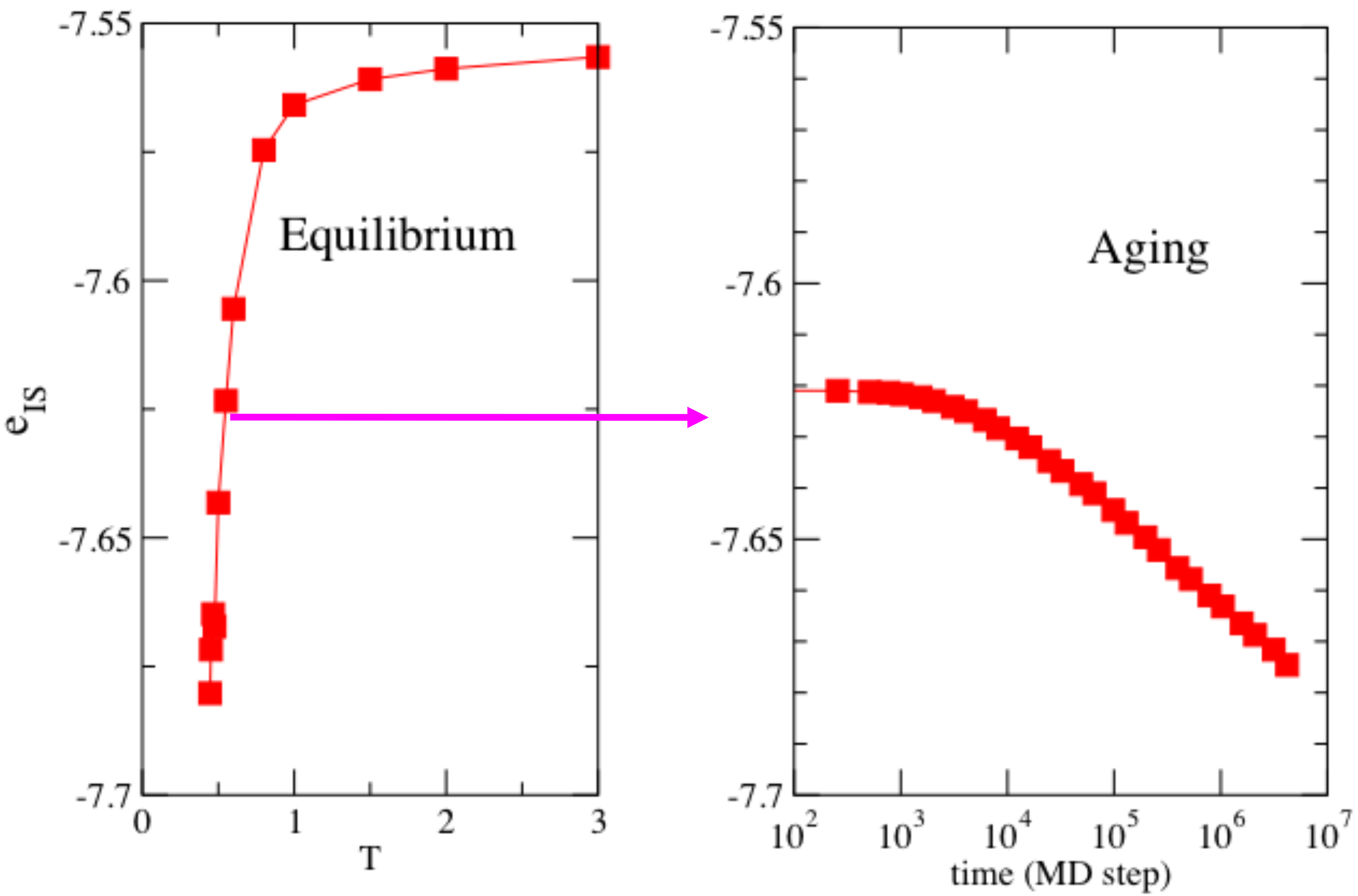


Starting Configuration (T_i)

Short after the T-change (T_i->T_f)

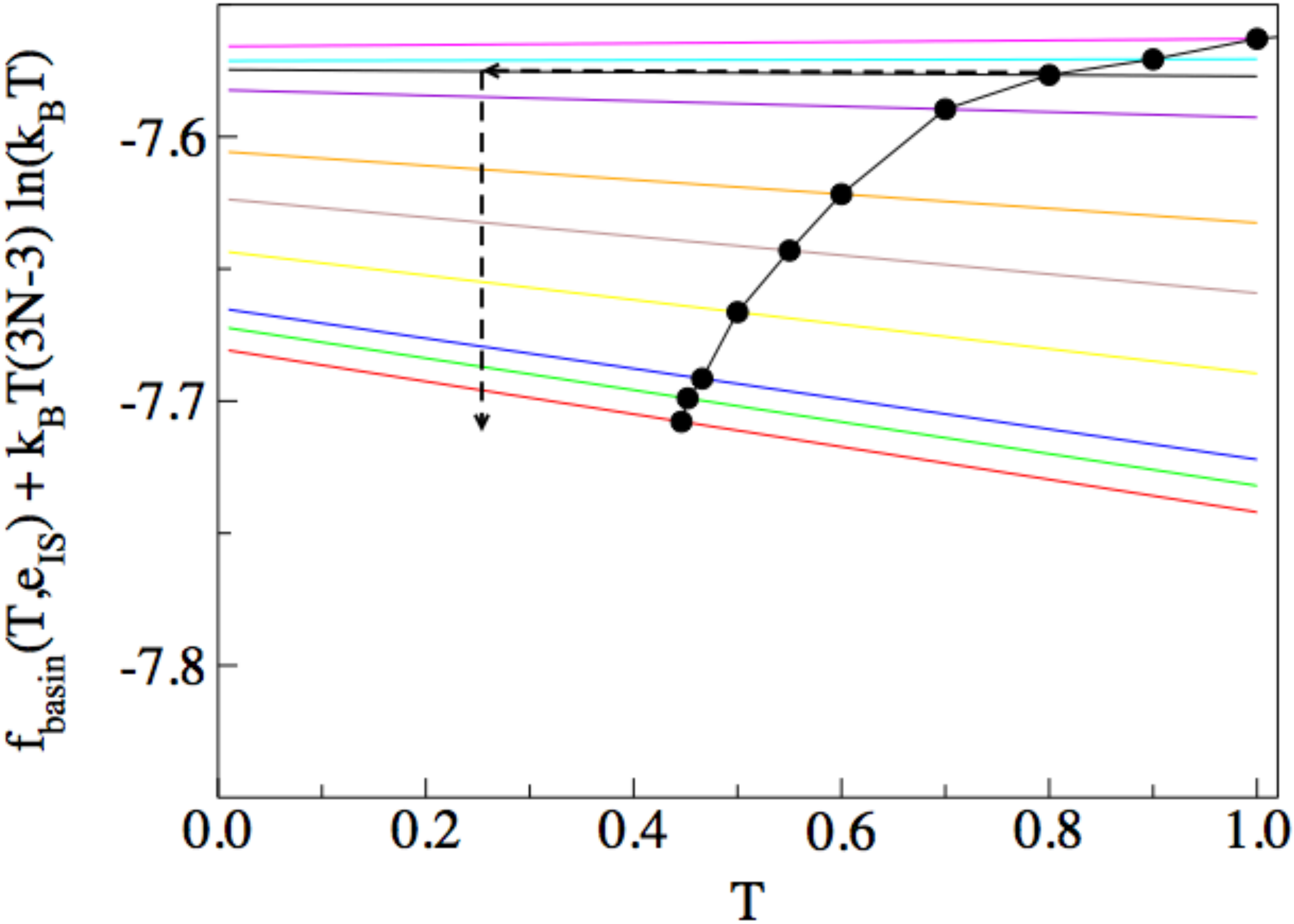
Long time

Evolution of e_{IS} in aging (BMLJ)



One can hardly do better than equilibrium !!

The “TAP” free energies……



Which T in aging ?

$$F(T, T_f) = -T_f\, S_{conf}(e_{IS}) + f_{basin}(e_{IS}, T)$$

$$-T_f \frac{\partial S_{conf}(e_{IS})}{\partial e_{IS}} + \frac{\partial f_{basin}(e_{IS}, T)}{\partial e_{IS}} = 0$$

$$T_f(e_{IS}, T) = \frac{\frac{\partial f_{basin}(T, e_{IS})}{\partial e_{IS}}}{\frac{\partial S_{conf}}{\partial e_{IS}}}$$

Equivalent form:

$$\mathbf{T_f(e_{IS}, T)} = \frac{\frac{\partial \mathbf{f_{basin}(T, e_{IS})}}{\partial \mathbf{e_{IS}}}}{\frac{\partial \mathbf{f_{basin}(T_{eq}, e_{IS})}}{\partial \mathbf{e_{IS}}}} \mathbf{T_{eq}}$$

S. Franz and M. A. Virasoro,
J. Phys. A 33 (2000) 891,

La Sapienza
Università degli Studi di Roma

INFM
Complex Dynamics in Structured Systems

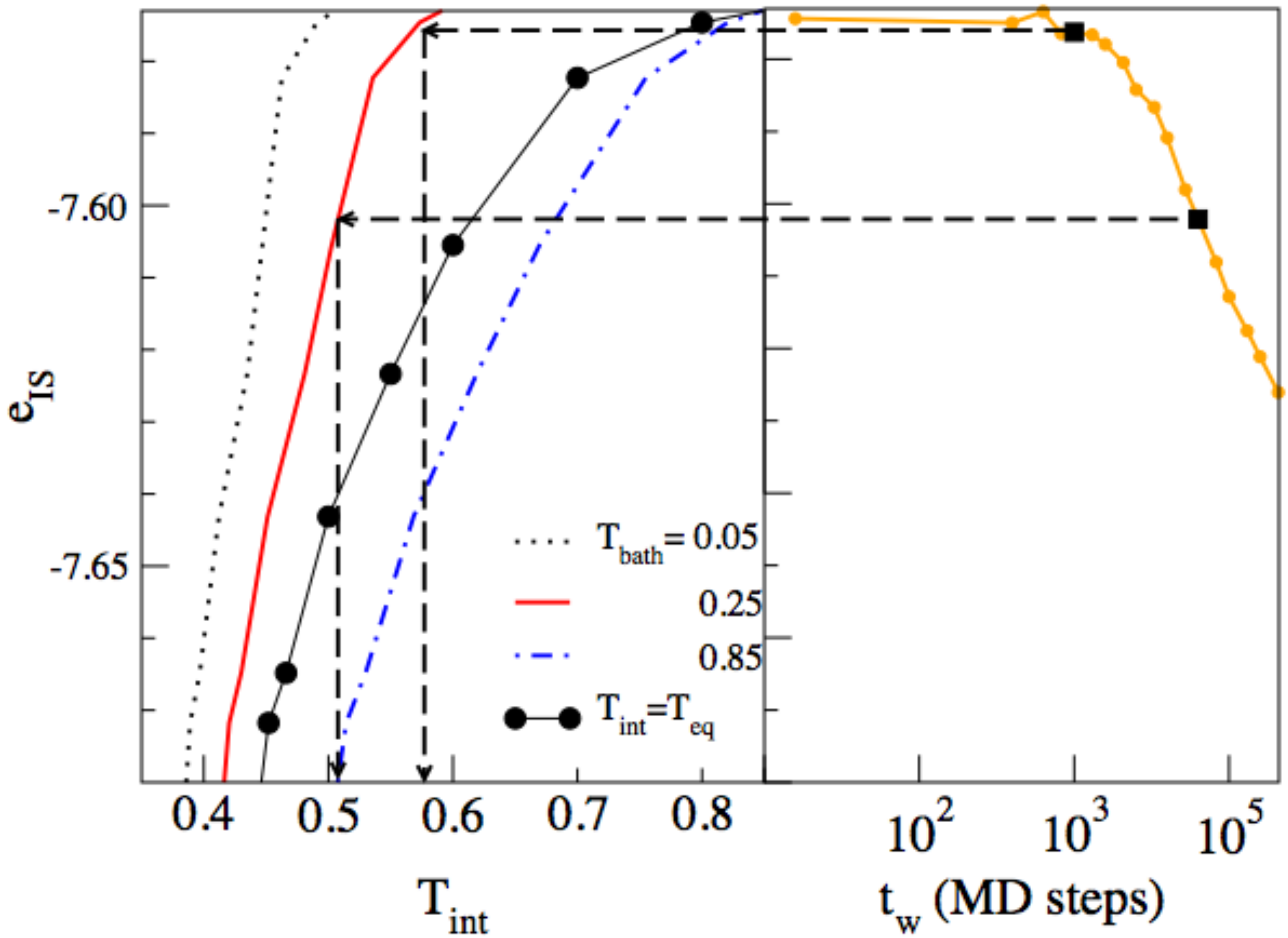
If basins have identical shape .....

$$f_{basin}(e_{IS}, T) = e_{IS} + f_{vib}(E_0, T)$$

$$\frac{\partial f_{basin}(e_{IS}, T)}{\partial e_{IS}} = 1$$

$$T_{eff} = T_{eq}$$

bmlj



-7.60
-7.65
e_{IS}
0.4
0.5
0.6
0.7
0.8
T_{int}
T_{bath}= 0.05
0.25
0.85
T_{int}=T_{eq}
10^2
10^3
10^5
t_w (MD steps)

A look to the meaning of T_{eff}

$$Z = Z_1 + Z_2 \qquad Z_i = \frac{e^{-\beta e_{IS_i}}}{\beta \hbar \omega_i}$$

$$f_{basin_i} = e_{IS_i} + kT log(\beta \hbar \omega_i)$$

$$f_{basin_2} = f_{basin_1} + \delta e_{IS}(1 + kTb) \quad b \equiv \frac{log(\frac{\omega_2}{\omega_1})}{\delta e_{IS}}$$

$$\frac{P_2}{P_1} = \frac{Z_2}{Z_1} = e^{-\beta \delta e_{IS}(1-kTb)}$$

$$\beta_{eq} \delta e_{IS}(1 - kT_{eq} b) = \beta_{eff} \delta e_{IS}(1 - kT_{bath} b)$$

$$T_{eff} = \frac{(1 - kT_{bath} b)}{(1 - kT_{eq} b)} T_{eq}$$

Heat flows.....
(case of basins of identical shape)

$$\frac{\partial f_{basin}}{\partial e_{IS}} = 1$$

$$e_{IS} \rightarrow e_{IS} - de_{IS} \qquad de_{IS} > 0$$

$$S_{conf}(e_{IS}) \rightarrow S_{conf}(e_{IS} - de_{IS})$$

$$dS_{conf} = -\frac{\partial S_{conf}}{\partial e_{IS}} de_{IS} = -\frac{de_{IS}}{T_{eff}}$$

$$dS_{reservoir} = de_{IS}/T$$

$$\Delta S = -\frac{de_{IS}}{T_{eff}} + \frac{de_{IS}}{T} > 0$$

How to ask a system its internal temperature

Linear Response Theory

The response to an external perturbation is equivalent to the response to a thermally generated fluctuation !

The perturbed Hamiltonian

$$H = H_0 + H_P = H_0 - V_o B(\mathbf{r}^{\mathbf{N}})\theta(t - t_w)$$

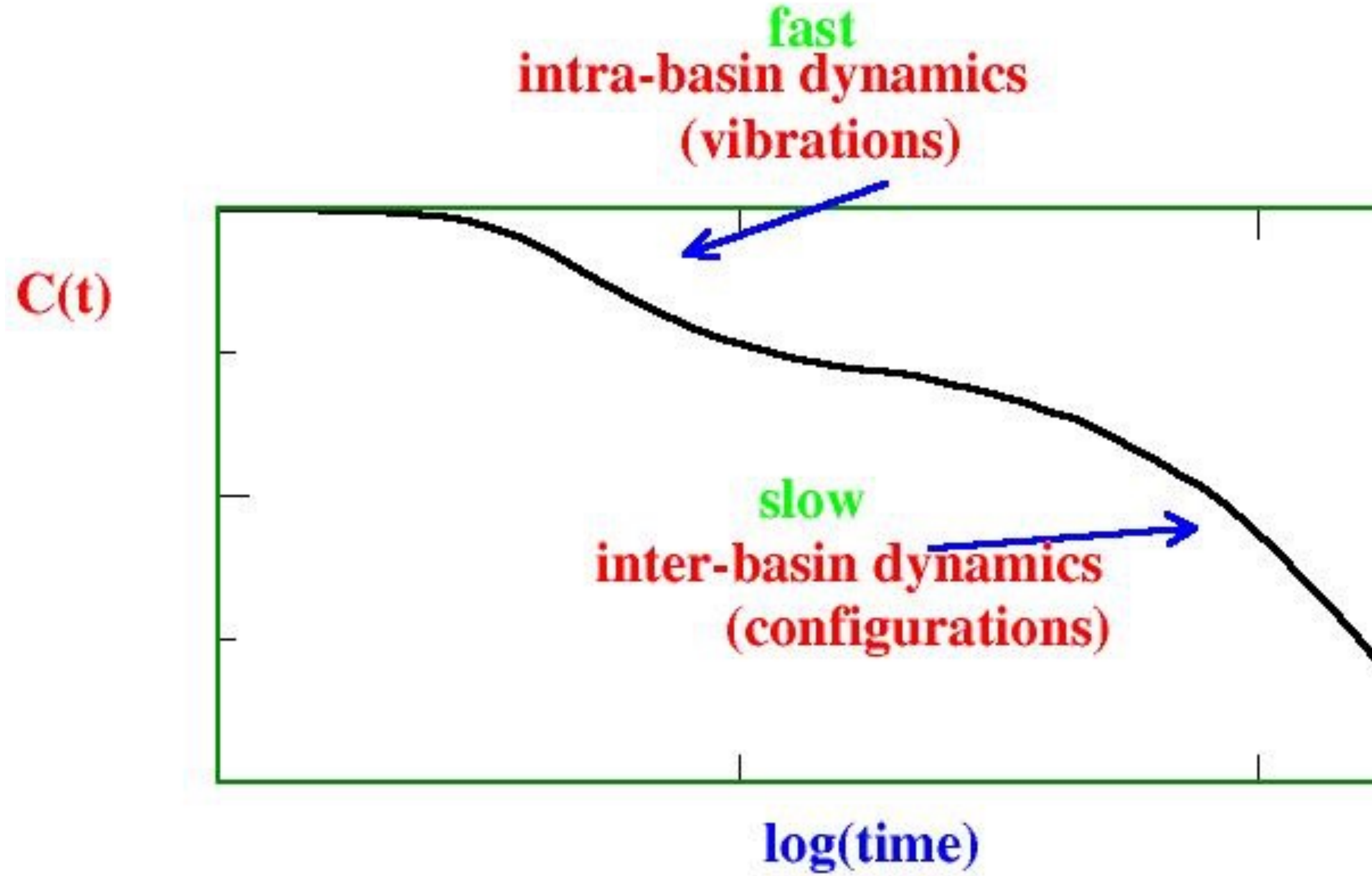
The response of the system to the perturbation

$$\langle A(\tau)\rangle = -\frac{V_o}{k_B T}[\langle A(\tau)B(0)\rangle_0 - \langle A(0)B(0)\rangle]_0]$$

We chose A and B so that the relation is

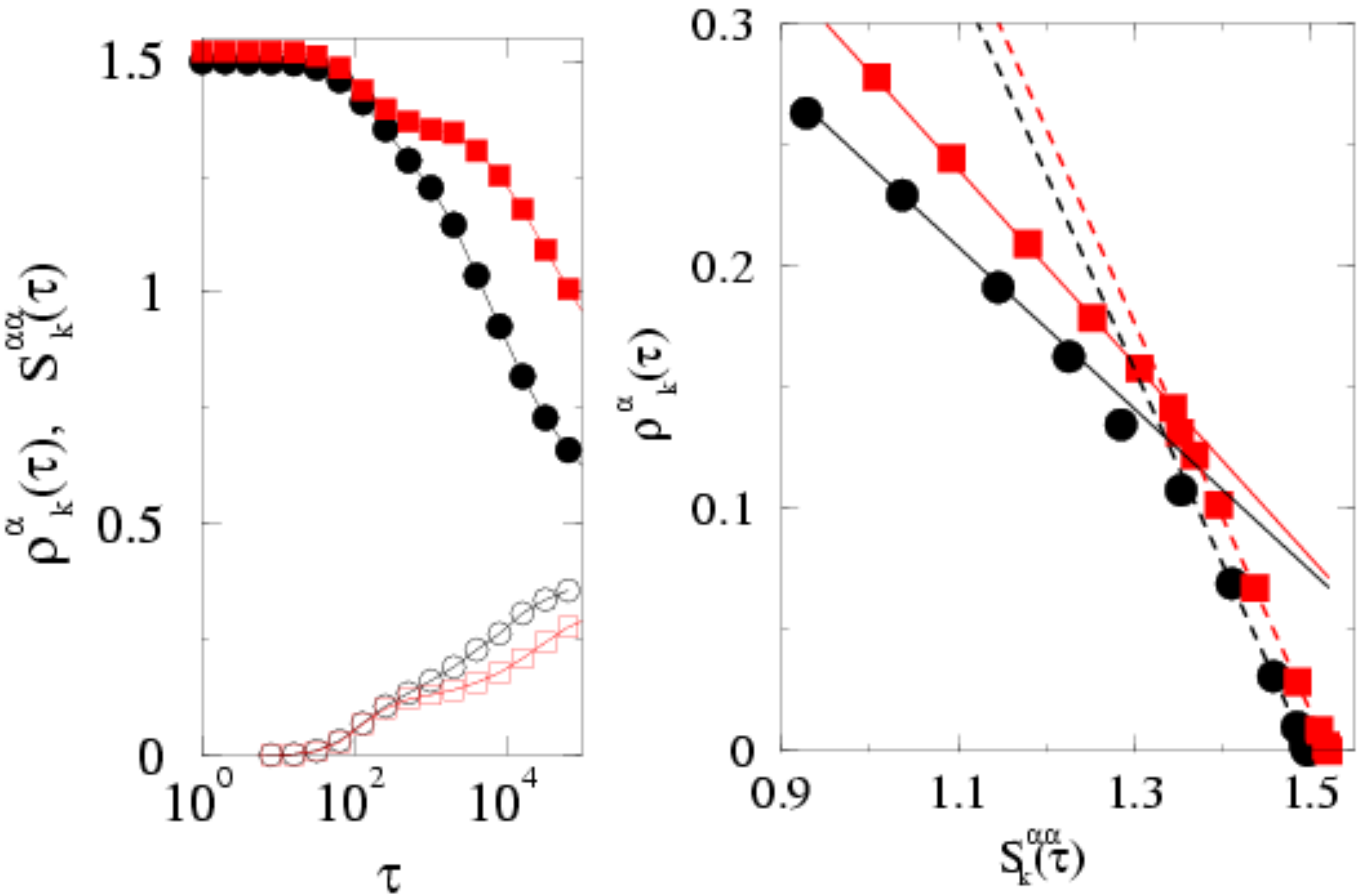
$$\langle \rho_{\mathbf{k}}^{\alpha}(\tau)\rangle = -\frac{V_o}{k_B T}[S_{\mathbf{k}}^{\alpha\alpha}(\tau) - S_{\mathbf{k}}^{\alpha\alpha}(0)]$$

with $\rho_{\mathbf{k}}^{\alpha}$ the number density and $S_{\mathbf{k}}^{\alpha\alpha}$ the dynamical structure factor


fast
intra-basin dynamics
(vibrations)
C(t)
slow
inter-basin dynamics
(configurations)
log(time)

Fluctuation Dissipation Relation

(Cugliandolo, Kurcian, Peliti, ….)



$$F(V, T, T_f) = -T_f S_{conf}(e_{IS}) + f_{basin}(e_{IS}, T)$$

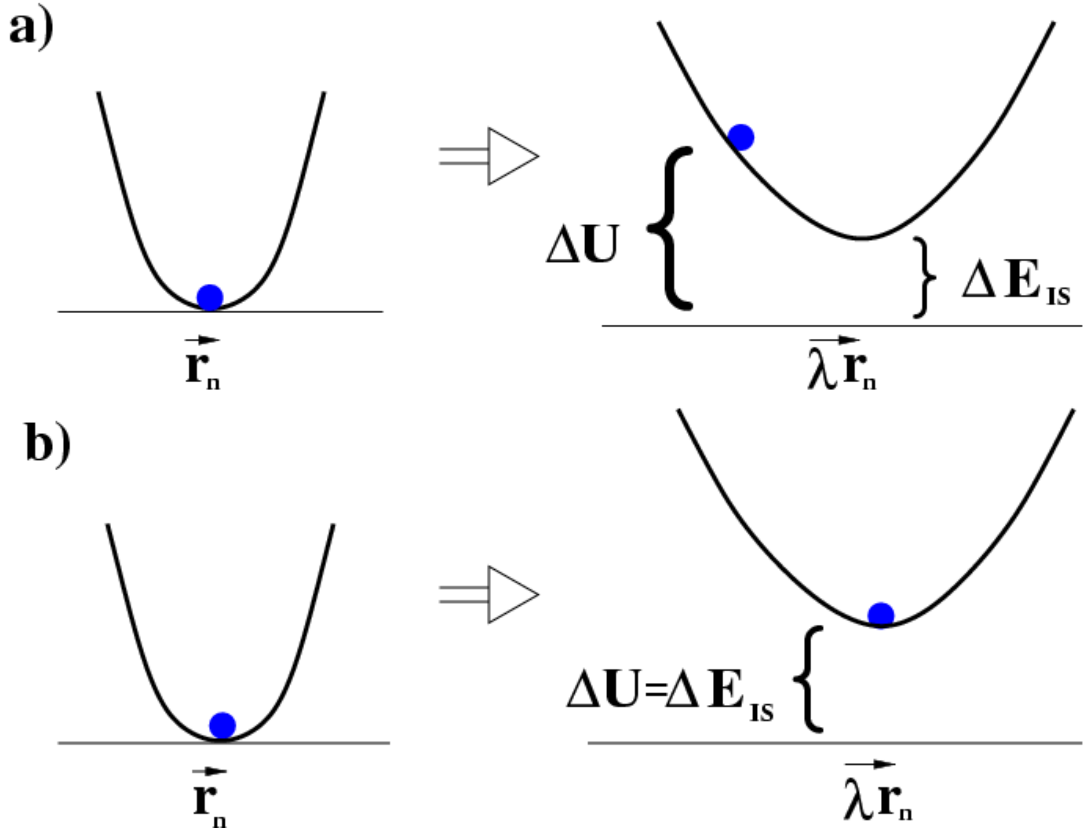
$$P(V,T,T_f) = -\left(\frac{\partial F(V,T,T_f)}{\partial V}\right)_{T,T_f}$$

$$\mathbf{P(V,0,T_f) = P_{IS}}$$

$$T_f(e_{IS},T) = \frac{\frac{\partial f_{basin}(T,e_{IS})}{\partial e_{IS}}}{\frac{\partial S_{conf}}{\partial e_{IS}}} \longrightarrow P_{IS}(V,e_{IS}) = -\left(\frac{\partial e_{IS}}{\partial V}\right)_{S_{conf}}$$

Support from the Soft Sphere Model

$$E(\lambda \mathbf{r}^N) = \lambda^{-n} E(\mathbf{r}^N)$$



La Sapienza
Università degli Studi di Roma

From Equilibrium to OOE….

If we know which *equilibrium* basin the system is exploring…

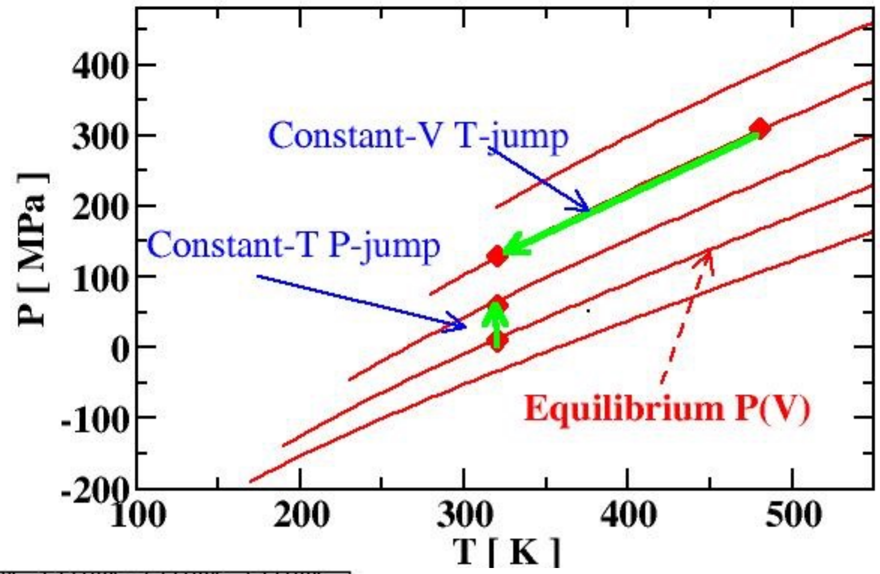
e_{IS}, V, T

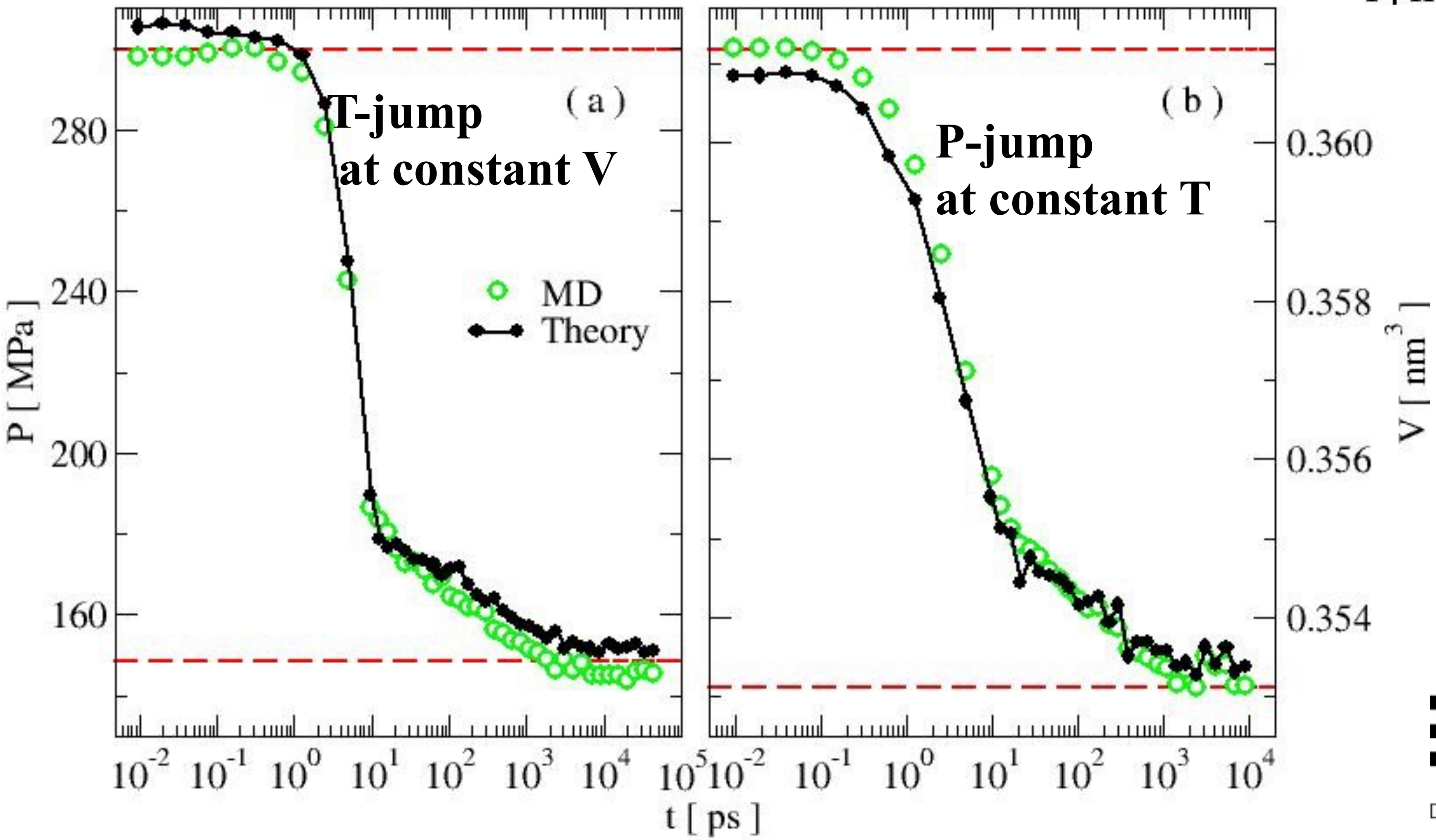
.. We can correlate the state of the aging system with an equilibrium state and predict the pressure

(OOE-EOS)

e_{IS} acts as a fictive T !

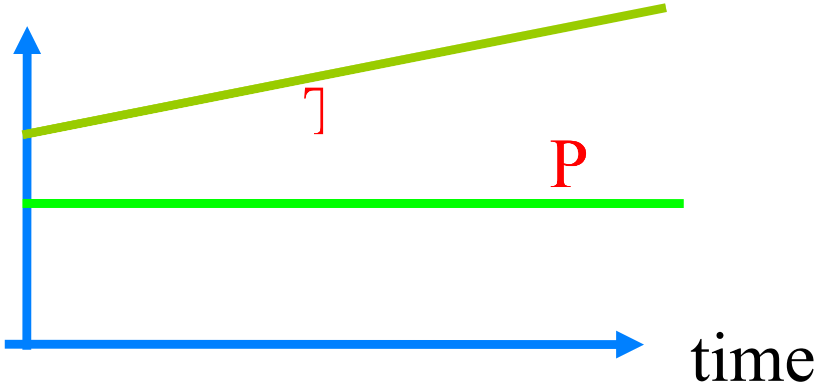
Numerical Tests
Liquid-to-Liquid

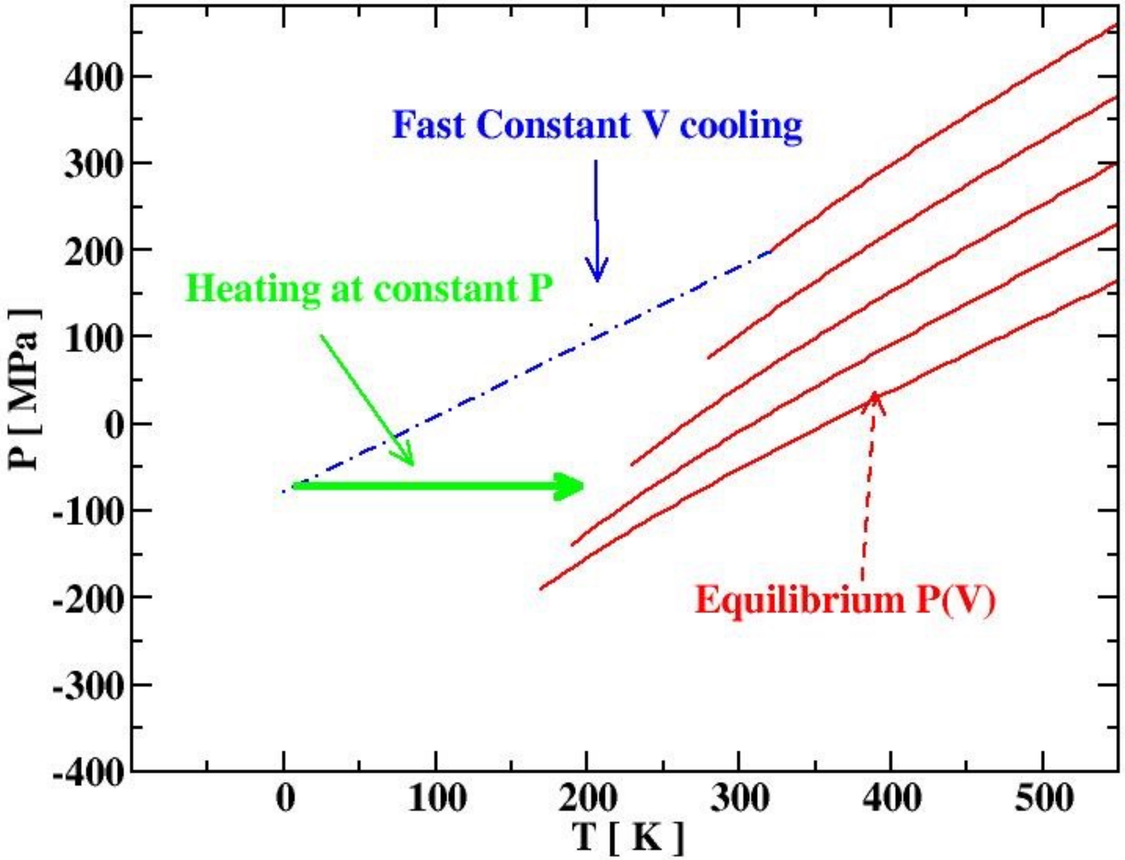


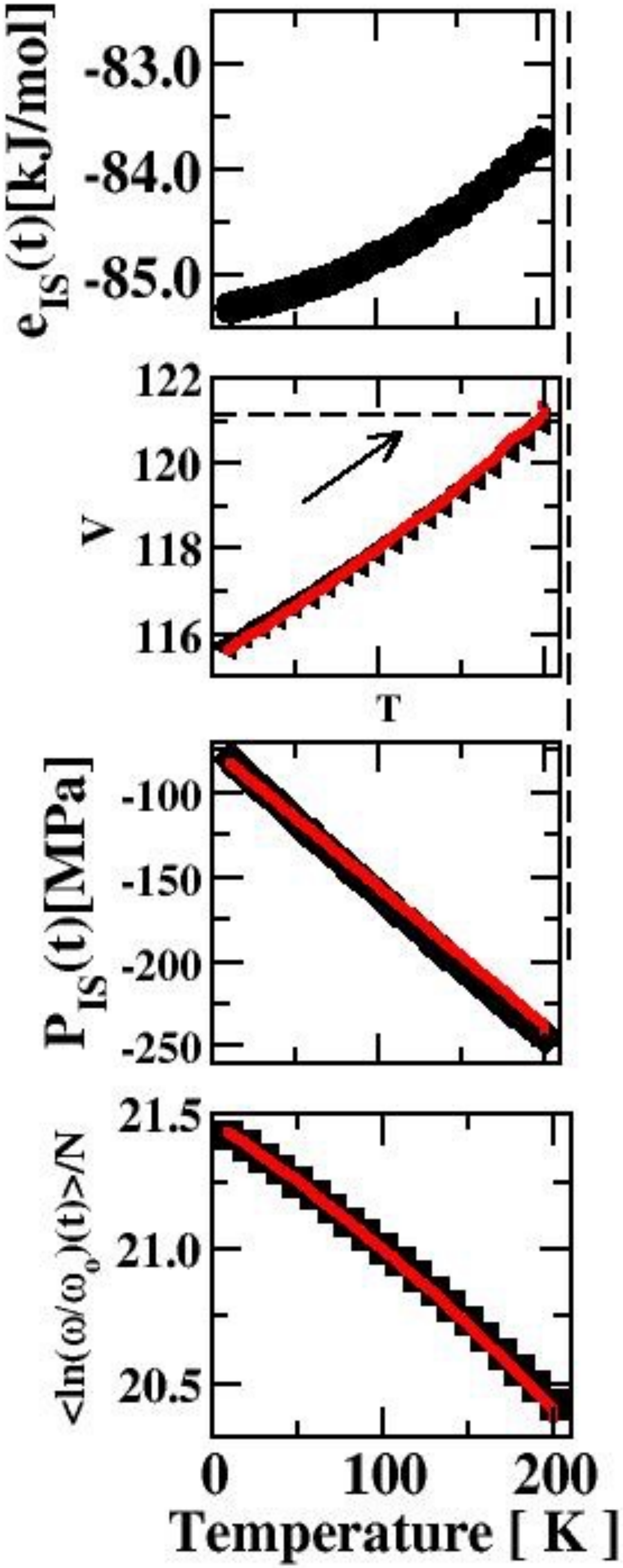


Dynamics in Structured Systems

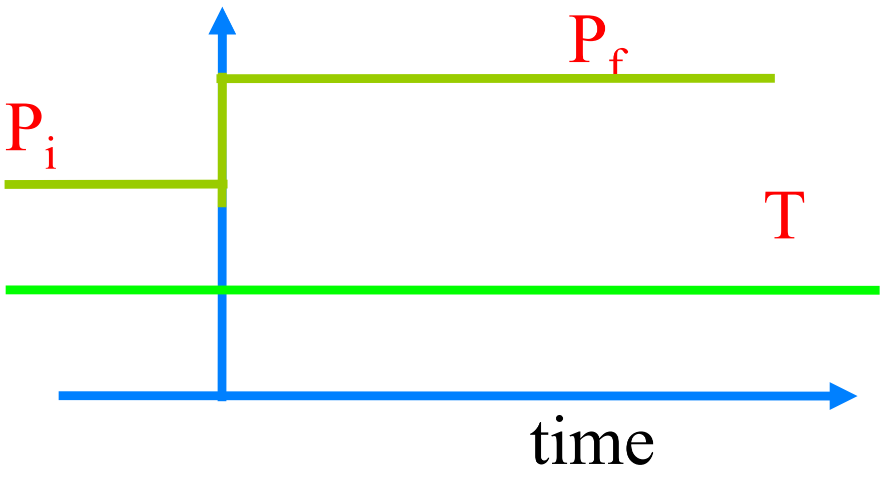
Numerical Tests
Heating a glass at constant P

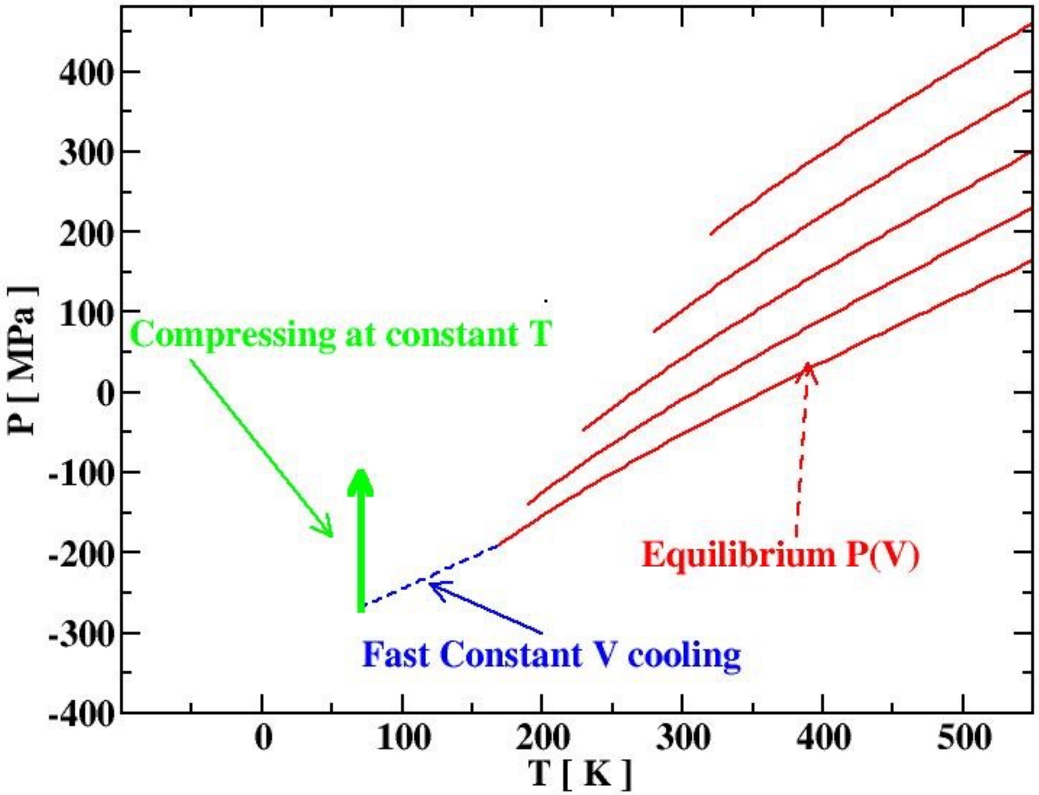


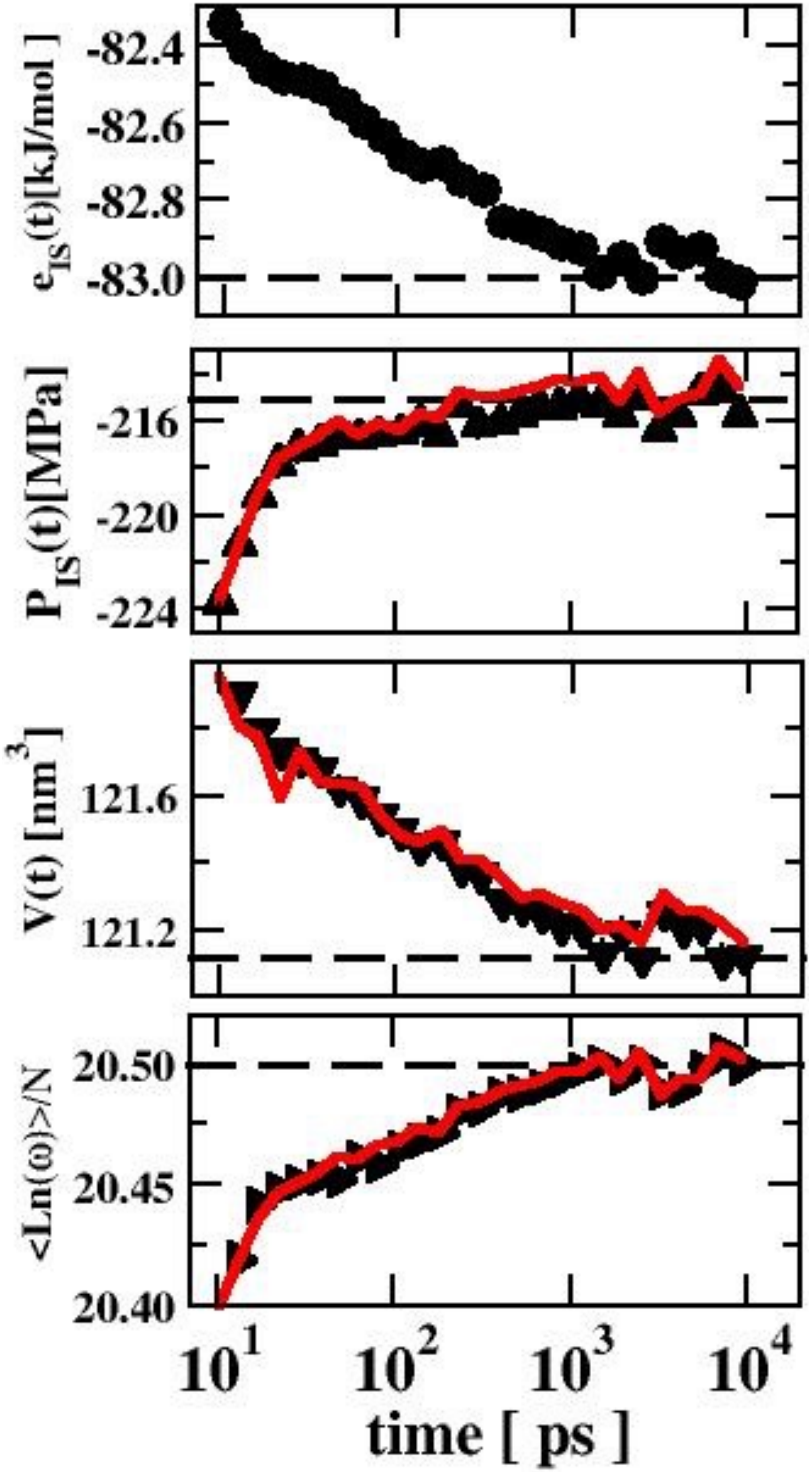




Numerical Tests
Compressing at constant T







Breakdowns !

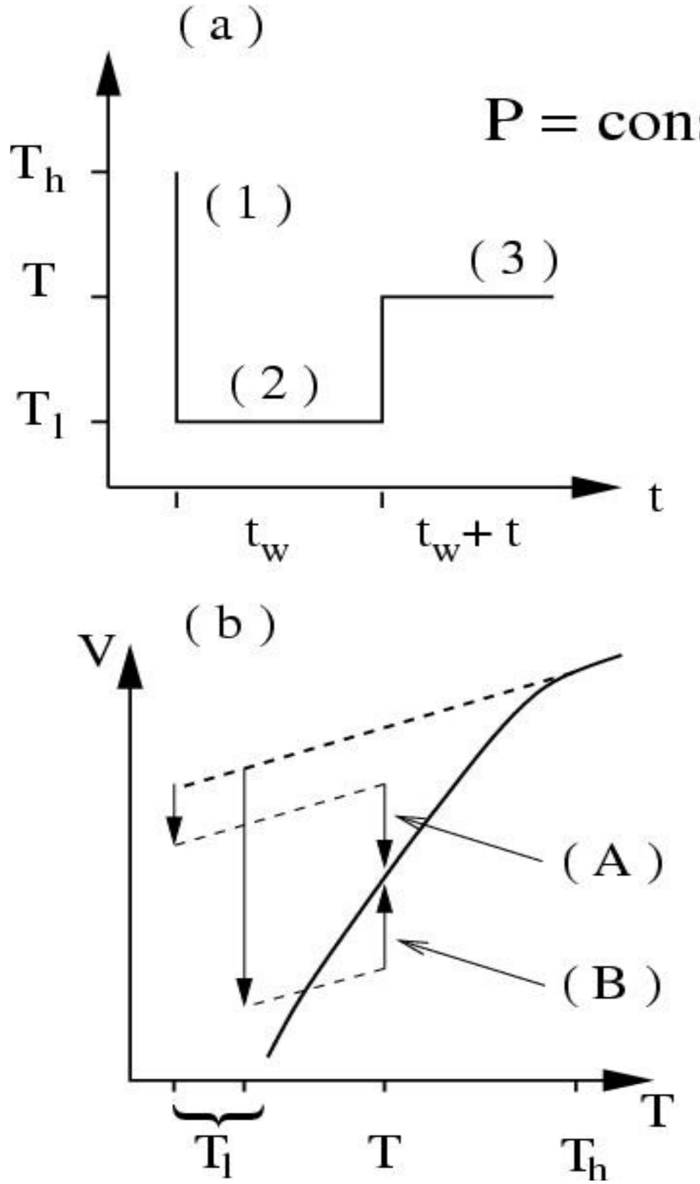
(things to be understood)

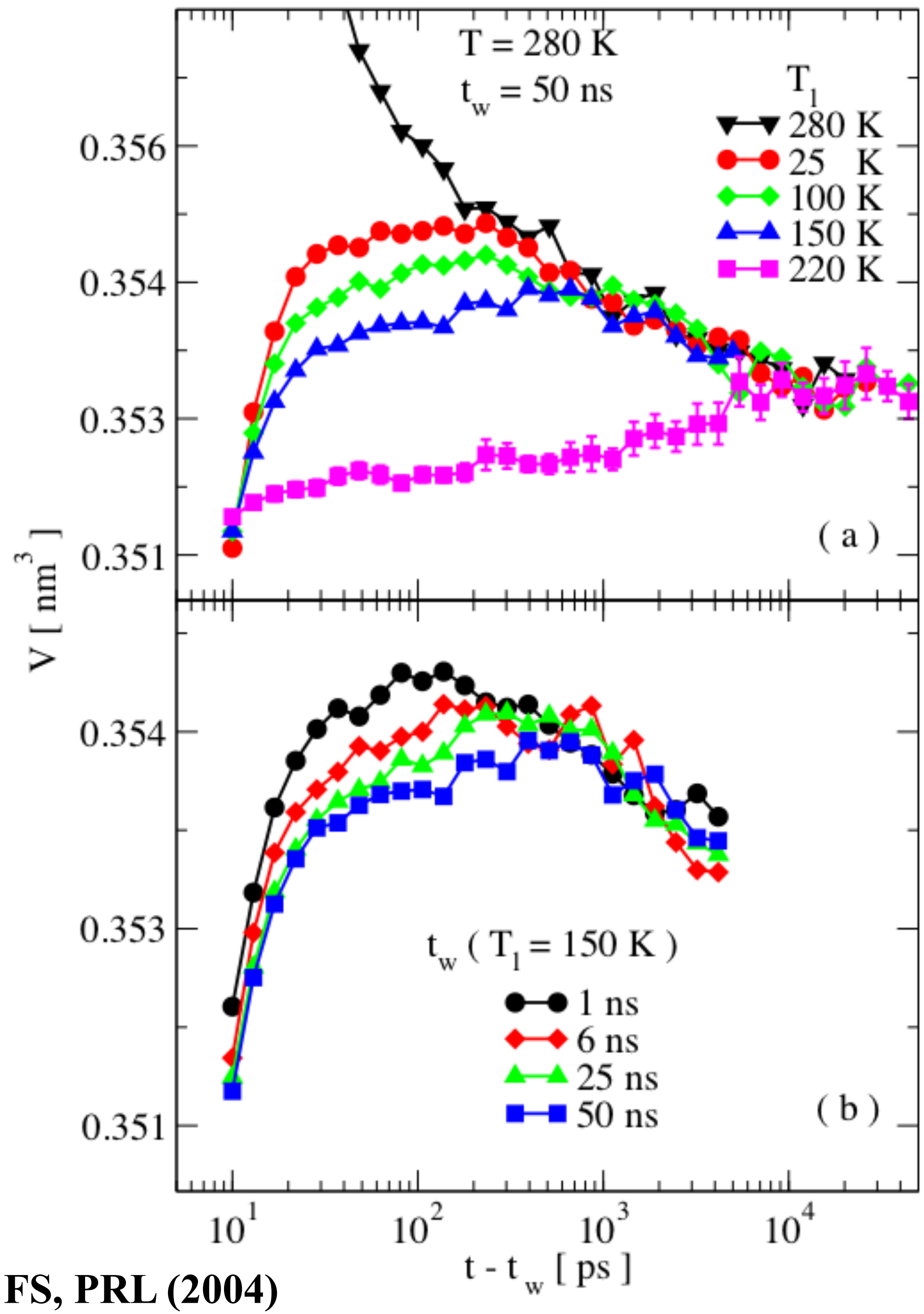
La Sapienza
Università degli Studi di Roma

Complex Dynamics in Structured Systems

Breaking of the out-of-equilibrium theory….

Kovacs (cross-over) effect





La Sapienza
Università degli Studi di Roma

S. Mossa and FS, PRL (2004)