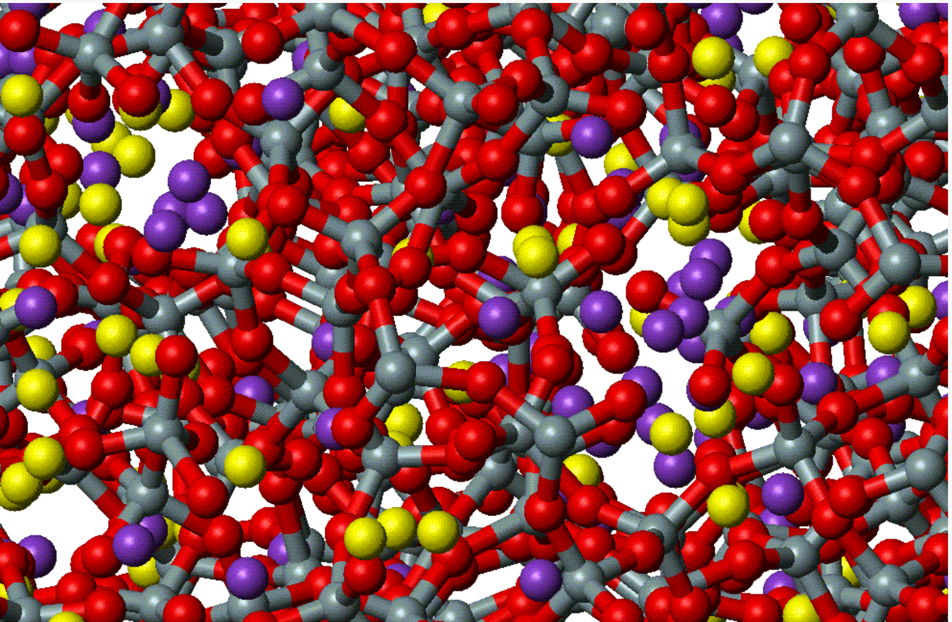
# Non-Equilibrium Thermodynamics of Glasses: The Kovacs Effect

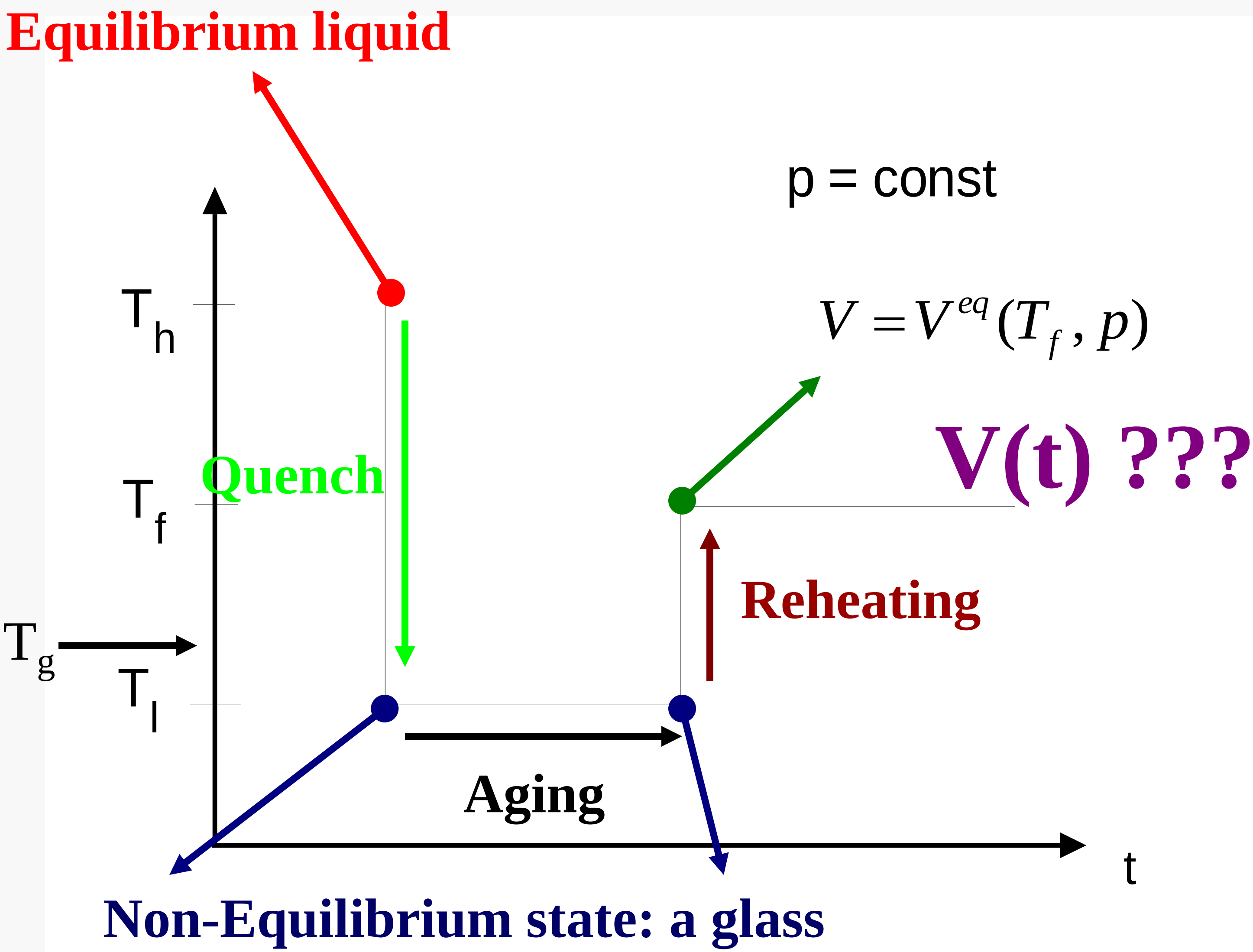
**Eran Bouchbinder**
**Weizmann Institute of Science**



**Work with James S. Langer**
**UC Santa Barbara**

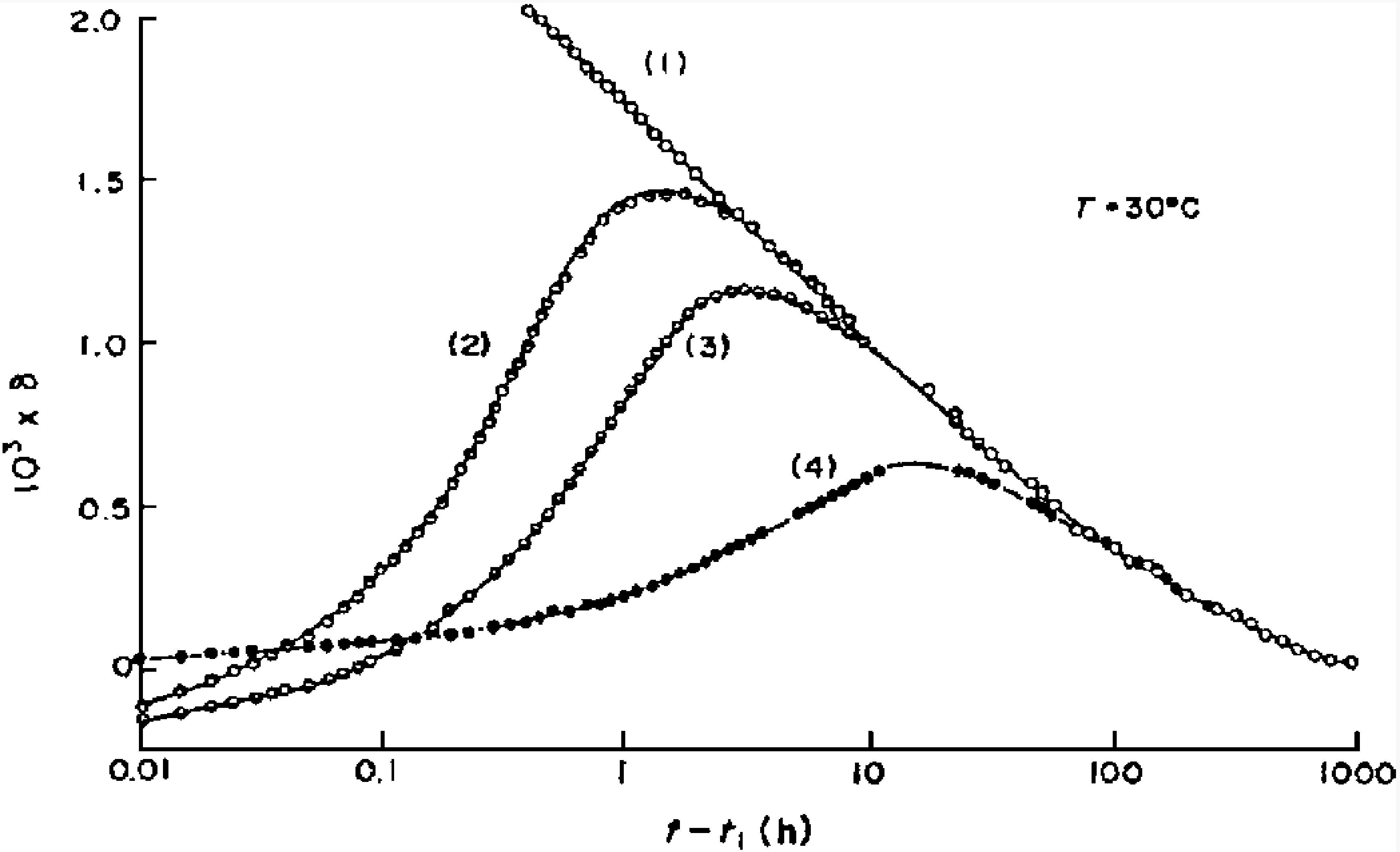
**Statistical Mechanics Day**
**Weizmann, June 2010**

# The Kovacs Effect: A glassy puzzle



# A. J. Kovacs, Adv. Polym. Sci. 3, 394 (1963)

Material: polyvinyl acetate (PVA, a glassy polymer)



- **The effect is generic and is observed in a variety of different glassy systems (e.g. colloidal glasses, ferroelectrics, gelatin gels, granular materials).**

- **Many specific models were shown to exhibit phenomena analogous to the Kovacs effect (e.g. coarsening dynamics in domain growth models, the trap model, the harmonic-oscillator–spherical-spin model).**

- **Main question:**

  **Is there a generic non-equilibrium thermodynamic theory of the Kovacs effect?**

# Non-equilibrium thermodynamics of driven amorphous materials

**Basic idea 1: Separable Configurational + Kinetic/Vibrational Subsystems**

$$\boxed{\text{Total Energy} \;\; \simeq H_C + H_K}$$

$H_C = H_C\{r_\upsilon\}$ = **configurational energy of the $\nu$'th inherent-structure**

$\{r_\upsilon\}$ = **set of molecular positions at the potential-energy minimum for the $\nu$'th inherent-structure, SLOW dof**

$H_K = H_K\{p, \delta r_\upsilon\}$ = **kinetic energy + harmonic potential energy for small excursions from configurational minima, FAST dof**

## Weak coupling between these two subsystems


**EB & JS Langer, Physical Review E 80, 031131 (2009)**
**EB & JS Langer, Physical Review E 80, 031132 (2009)**

**Basic idea 2: The non-equilibrium state of the system can be characterized by coarse-grained internal variables**

$$U_C(S_C, V_{el}, \{\Lambda_\alpha\}) \longleftrightarrow S_C(U_C, V_{el}, \{\Lambda_\alpha\})$$

**The reversible part of the deformation**

**A subextensive number of coarse-grained internal variables, represent internal degrees of freedom that are coupled to deformation**

**Non-equilibrium entropy** $S_C(U_C, V_{el}, \{\Lambda_\alpha\}) = \ln \boxed{\Omega_C(U_C, V_{el}, \{\Lambda_\alpha\})}$

**A constrained measure of the number of configurations**

**When** $\{\Lambda_\alpha\} \to \{\Lambda_\alpha^{eq}\}$ $S_C(U_C, V_{el}, \{\Lambda_\alpha\}) \to S_C^{eq}(U_C, V)$

**EB & JS Langer, Physical Review E 80, 031131 (2009)**
**EB & JS Langer, Physical Review E 80, 031132 (2009)**

**Basic idea 2 (cont.):** **The non-equilibrium state of the system can be characterized by coarse-grained internal variables**

$$U_{tot} \simeq U_C(S_C, V_{el}, \{\Lambda_\alpha\}) + U_K(S_K, V_{el}) + U_R(S_R)$$

$$S_{tot} \simeq S_C(U_C, V_{el}, \{\Lambda_\alpha\}) + S_K(U_K, V_{el}) + S_R(U_R)$$

**Temperatures**

**Vi**

$$\chi = \left(\frac{\partial U_C}{\partial S_C}\right)_{V_{el},\{\Lambda_\alpha\}}, \qquad \theta = \left(\frac{\partial U_K}{\partial S_K}\right)_{V_{el}}, \qquad \theta_R = \frac{\partial U_R}{\partial S_R}$$

**Reservoir**

**We'll assume**

$$\theta = \theta_R$$

$$S_K = 3N\left[1 + \ln\left(\frac{U_K}{3N}\right)\right] - \sum_{n=1}^{3N} \ln(\omega_n)$$

**Laws of Thermodynamics**

**1st Law:** $-p\dot{V} = \dot{U}_{tot} = \dot{U}_C + \dot{U}_K + \dot{U}_R$

**2nd Law:** $\dot{S}_{tot} = \dot{S}_C + \dot{S}_K + \dot{S}_R \geq 0$

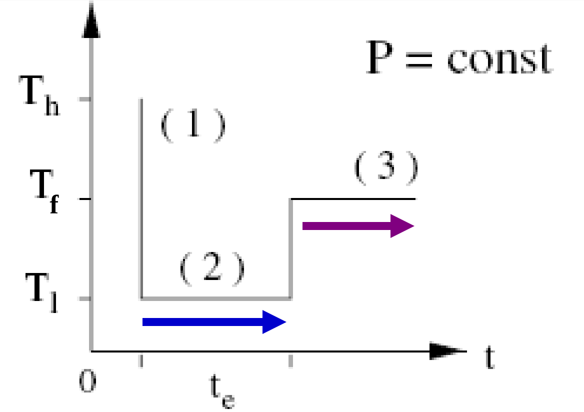
**will be used to obtain EOM for:** $\chi$ and $\{\Lambda_\alpha\}$

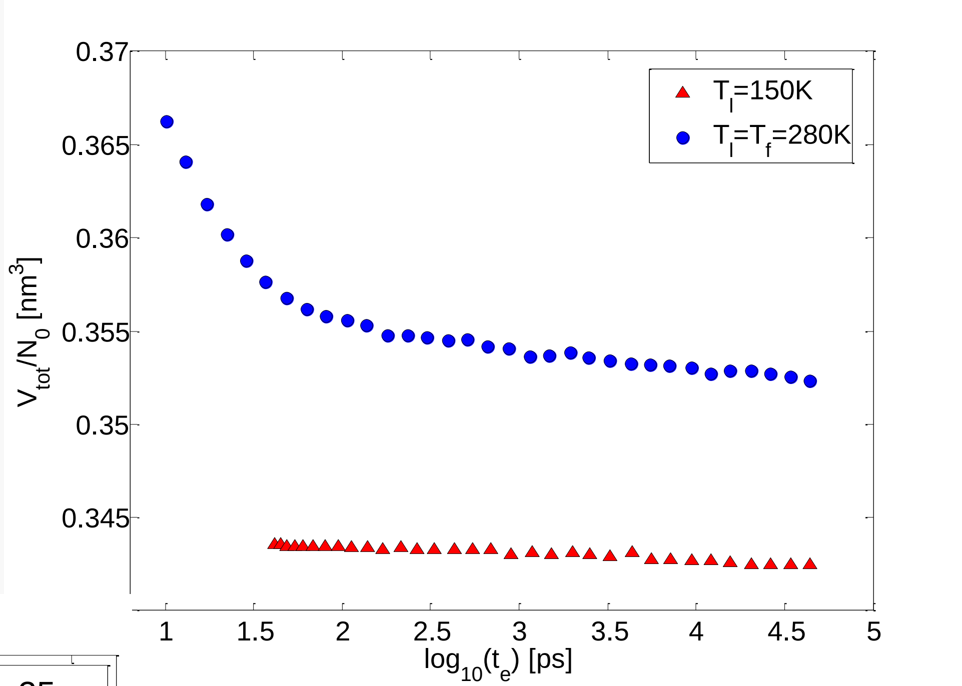

EB & JS Langer, Physical Review E 80, 031131 (2009)
EB & JS Langer, Physical Review E 80, 031132 (2009)

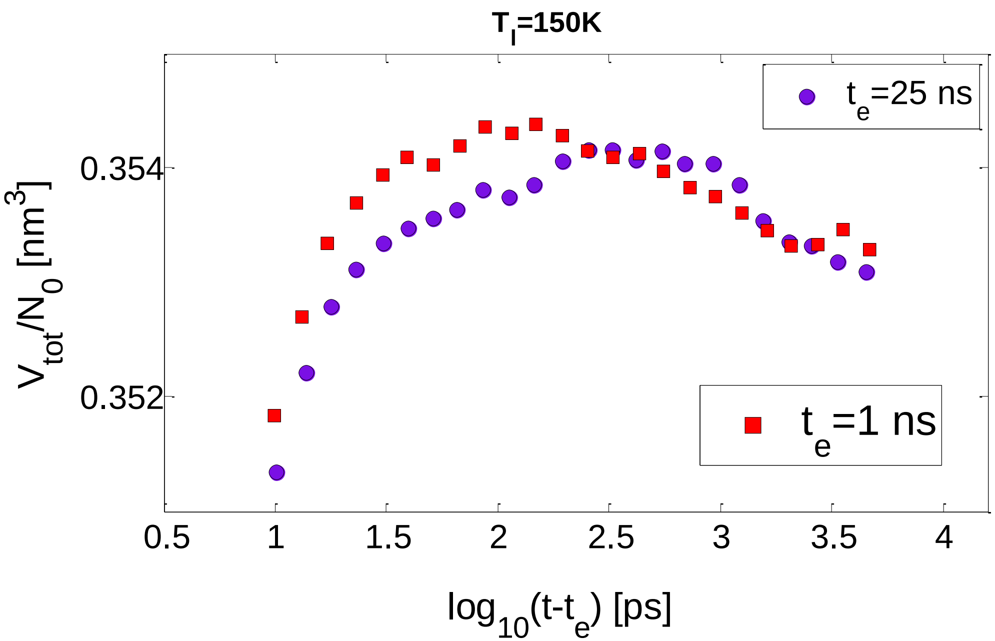
# The Kovacs effect was recently observed in MD simulations of OTP

**[S. Mossa and F. Sciortino, Phys. Rev. Lett. 92, 045504 (2004)]**

**P=16MPa, $T_h$=400K, $T_f$=280K, $T_{MCT}$=260K, $T_m$=330K**



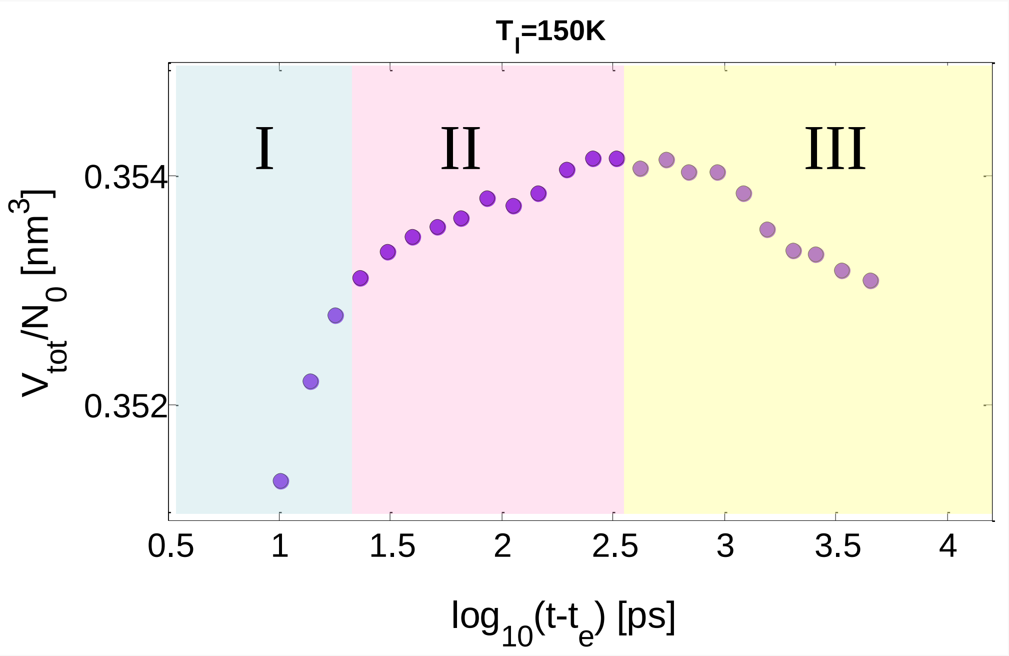




## Thermal vibrations timescale:

$$\tau_0 \approx 1ps$$

# Major new discoveries of the MD study

**[S. Mossa and F. Sciortino, Phys. Rev. Lett. 92, 045504 (2004)]**




**Thermal vibrations timescale:** $\tau_0 \approx 1ps$

## Three stages:

**I: Short timescales quenching effects**

**II: Intermediate timescales pre-peak dynamics**

**III: Long timescales post-peak aging**

## Major observation:

**The dynamics in stage III follow a sequence of quasi-equilibrium states fully characterized by an effective temperature, while stage II cannot be described by an effective temperature alone.**

**A hierarchy of different non-equilibrium behaviors!**

# A Thermodynamic Theory of the Kovacs Effect

## Two steps:

**Step 1** – Identify internal state variables and associate with them energy and entropy

$N_v$ - vacancy-like “defects” | $N_a$ - “misalignment defects”

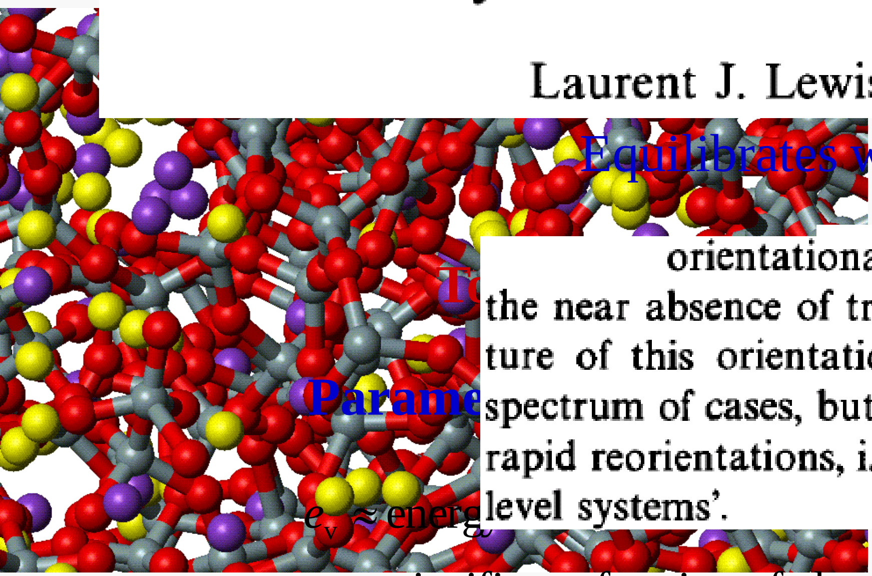
**Step 2** – Derive equations of motion based on the laws of thermodynamics

Energy and excess volume $e_v$ and $v_v$ | Energy and excess volume $e_a$ and $v_a$

Journal of Non-Crystalline Solids 172–174 (1994) 69–76

Rotational dynamics in *ortho*-terphenyl: a microscopic view

Laurent J. Lewis*[,a], Göran Wahnström[b]



Equilibrates with $\chi$ | Equilibrates with $\theta$

orientational motion takes place despite the near absence of translational motion. The nature of this orientational motion covers a large spectrum of cases, but we find a preponderance of rapid reorientations, i.e., jumps or ‘two- (or more-) level systems’.

$N_a \, v_a$

To

Parame

$e_v \approx$ energ

$v_v \approx$ significant fraction of the volume per molecule $\rightarrow 0.07\text{nm}^3$, $\quad v_a = 0.1 v_v$

**EB & JS Langer, to appear in Soft Matter (2010)**

# A Thermodynamic Theory of the Kovacs Effect (cont.)

**Step 2** – Derive equations of motion based on the laws of thermodynamics

**2nd law:**

$$\boxed{-\left[p\,v_a+\left(\frac{\partial U_K}{\partial N_a}\right)_{S_K,V_{el}}\right]\dot N_a}$$
$$\boxed{-\left[p\,v_0+\left(\frac{\partial U_C}{\partial N_v}\right)_{S_C,V_{el}}\right]\dot N_v}$$
$$\boxed{-\left[p-p_C(\chi,V_{el})-p_K(\theta,V_{el})\right]\dot V_{el}}\;\boxed{-\,(\theta-\chi)\,\dot S_K}\geq 0.$$

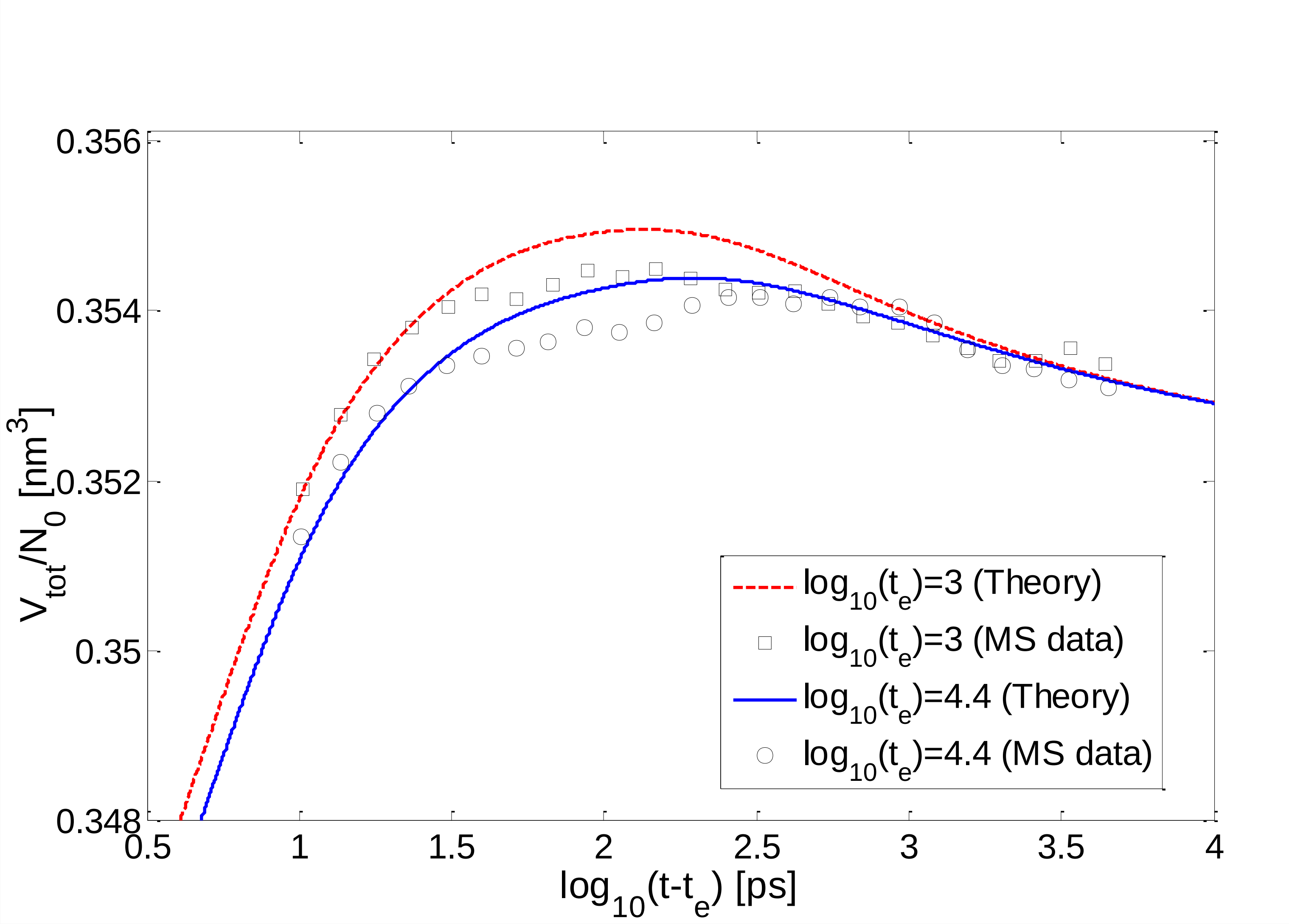
→ **4 independent inequalities**

**1st law:**

$$\chi\,\dot S_C=-\left[h_v-\chi\,\frac{\partial S_0(N_v)}{\partial N_v}\right]\dot N_v-\left[h_a-\theta\,\frac{\partial S_0(N_a)}{\partial N_a}\right]\dot N_a$$
$$+\frac{\gamma\,\bar\lambda}{V_0}\left[V_{el}-V_{el}^{eq}(\chi,\theta,p)\right]^2+A(\chi,\theta)\left(1-\frac{\chi}{\theta}\right).$$

**EB & JS Langer, Soft Matter (2010)**

# Results



0.356
0.354
0.352
0.35
0.348
0.5
1
1.5
2
2.5
3
3.5
4
$V_{tot}/N_0$ [$nm^3$]
$\log_{10}(t-t_e)$ [ps]
$\log_{10}(t_e)$=3 (Theory)
$\log_{10}(t_e)$=3 (MS data)
$\log_{10}(t_e)$=4.4 (Theory)
$\log_{10}(t_e)$=4.4 (MS data)

# Conclusions

**The Kovacs effect can be described within a non-equilibrium thermodynamics framework**

**A hierarchy of non-equilibrium processes are at play:**

1) **A short time visco-elastic response (unique to extreme quenching rates)**

2) **Intermediate timescales processes:**

   **An internal variable ($n_a$) that goes in and out of equilibrium directly with the heat bath**

   **An internal variable ($n_v$) that goes in and out of equilibrium with the effective disorder temperature**

3) **Long timescales structural relaxation in which the effective temperature equilibrates with the heat bath (quasi-equilibrium)**