Non-Equilibrium Thermodynamics of Glasses: 
The Kovacs Effect

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Statistical Mechanics Day
Weizmann, June 2010
The Kovacs Effect: A glassy puzzle

Equilibrium liquid

Quench

Non-Equilibrium state: a glass

\[ V = V^{eq}(T_f, p) \]

\[ p = \text{const} \]

\[ V(t) \ ??? \]

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

\[ \text{Total Energy} \approx H_C + H_K \]

\[ H_C = H_C \{ r_\nu \} = \text{configurational energy of the } \nu^{th} \text{ inherent-structure} \]

\[ \{ r_\nu \} = \text{set of molecular positions at the potential-energy minimum for the } \nu^{th} \text{ inherent-structure, SLOW dof} \]

\[ H_K = H_K \{ p, \delta r_\nu \} = \text{kinetic energy + harmonic potential energy for small excursions from configurational minima, FAST dof} \]

**Weak coupling between these two subsystems**

EB & JS Langer, Physical Review E 80, 031132 (2009)
**Basic idea 2:** The non-equilibrium state of the system can be characterized by coarse-grained internal variables

\[ U_C(S_C, V_{el}, \{\Lambda_\alpha\}) \quad \text{↔} \quad S_C(U_C, V_{el}, \{\Lambda_\alpha\}) \]

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

\[ S_C(U_C, V_{el}, \{\Lambda_\alpha\}) = \ln \Omega_C(U_C, V_{el}, \{\Lambda_\alpha\}) \]

A constrained measure of the number of configurations

When

\[ \{\Lambda_\alpha\} \rightarrow \{\Lambda^{eq}_\alpha\} \]

\[ S_C(U_C, V_{el}, \{\Lambda_\alpha\}) \rightarrow S^{eq}_C(U_C, V) \]

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.

\[ U_{tot} \approx U_C(S_C, V_{el}, \{\Lambda_\alpha\}) + U_K(S_K, V_{el}) + U_R(S_R) \]

\[ S_{tot} \approx S_C(U_C, V_{el}, \{\Lambda_\alpha\}) + S_K(U_K, V_{el}) + S_R(U_R) \]

\[ \chi = \left( \frac{\partial U_C}{\partial S_C} \right)_{V_{el}, \{\Lambda_\alpha\}} \]

\[ \theta = \left( \frac{\partial U_K}{\partial S_K} \right)_{V_{el}} \]

\[ \theta_R = \frac{\partial U_R}{\partial S_R} \]

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

\[ 1^{st} \text{ Law: } - p \dot{V} = U_{tot} = U_C + U_K + U_R \]

\[ 2^{nd} \text{ Law: } \dot{S}_{tot} = \dot{S}_C + \dot{S}_K + \dot{S}_R \geq 0 \]

EB & JS Langer, Physical Review E 80, 031132 (2009)
The Kovacs effect was recently observed in MD simulations of OTP

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

$V_{tot}/N_0 \text{ [nm}^3\text{]}$

$T_l=150$ K

$T_l=T_f=280$ K

Thermal vibrations timescale:

$\tau_0 \approx 1$ ps
Major new discoveries of the MD study

Thermal vibrations timescale: $\tau_0 \approx 1\text{ps}$

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 $v_a$

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

Laurent J. Lewis*,a, Göran Wahnström

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’.

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

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A Thermodynamic Theory of the Kovacs Effect (cont.)

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

2nd law:

\[
- \left[ p v_a + \left( \frac{\partial U_K}{\partial N_a} \right)_{s_K, V_{el}} \right] \dot{N}_a \\
- \left[ p v_0 + \left( \frac{\partial U_C}{\partial N_v} \right)_{s_C, V_{el}} \right] \dot{N}_v \\
- \left[ p - p_C(\chi, V_{el}) - p_K(\theta, V_{el}) \right] \dot{V}_e - (\theta - \chi) \dot{S}_K \geq 0.
\]

1st law:

\[
\chi \dot{S}_C = - \left[ h_v - \chi \frac{\partial S_0(N_v)}{\partial N_v} \right] \dot{N}_v - \left[ h_a - \theta \frac{\partial S_0(N_a)}{\partial N_a} \right] \dot{N}_a \\
+ \frac{\gamma \tilde{\lambda}}{V_0} \left[ V_{el} - V_{el}^{eq}(\chi, \theta, p) \right]^2 + A(\chi, \theta) \left(1 - \frac{\chi}{\theta}\right).
\]

Results

\[ \frac{V_{\text{tot}}}{N_0} \text{ [nm}^3] \]

- \( \log_{10}(t-e) = 3 \) (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)