Dynamically correlated regions and configurational entropy in supercooled liquids

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Outline

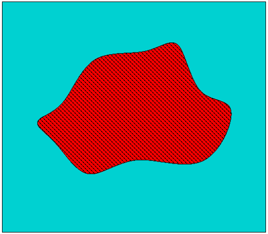
1. Motivations
   - Adam-Gibbs theory
   - Random First Order Transition theory
   - Summary
2. Methods
   - Measure of N_{corr}
   - Configurational entropy of a correlation volume
3. Results
   - Temperature dependence of σ_{CRR}
   - Correlation at T_g
   - RFOT exponents
   - Related works

Outline

Adam-Gibbs theory of supercooled liquids

$S_c(T)$: configurational entropy density per unit volume

- $\sigma_{CRR}(\xi) = \xi^d S_c(T)$
- $\tau(T) \sim e^{\xi^d \frac{A}{k_B T}}$



Relaxation is dominated by the smallest and fastest regions

Minimum size dictated by:

$\sigma_{CRR}(\xi) = \xi^d S_c(T) \geq \log n_o \quad \Rightarrow \quad (\xi^*)^d \sim \frac{\log n_o}{S_c(T)}$

$\tau(T) \sim e^{(\xi^*)^d \frac{A}{k_B T}} \sim e^{\frac{C}{T S_c}}$ *Adam-Gibbs relation*

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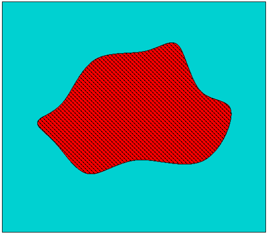

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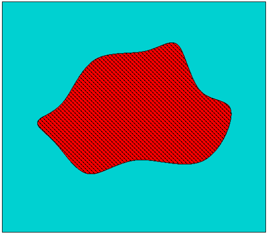
Random First Order Transition (RFOT) theory

Domain of radius r; boundary acts as "pinning field"
$\beta \Delta F_{boundary}(r) = \beta \Upsilon r^{\theta}$

If the state of the bubble can change: "entropy gain"
$\beta \Delta F_{bulk}(r) = -S_c(T) r^d$



Typical size ξ of the domains given by $\beta \Delta F(\xi) = 0 \Rightarrow \xi = \left(\frac{\beta \Upsilon}{S_c}\right)^{\frac{1}{d-\theta}}$
"Mosaic state" made of domains of typical radius ξ, each one relaxing almost independently.

Thermodynamic free energy barrier for nucleation inside a domain:
$\beta \Delta F(r^\star) = \max_r \beta \Delta F(r) \propto \xi^d S_c(T) \equiv \sigma_{CRR}(T)$, $\quad r^\star \propto \xi$,

Relaxation time $\tau \sim e^{A \xi^{\theta \psi}} \sim e^{C S_c^{-\frac{\theta \psi}{d-\theta}}} \sim e^{\sigma_{CRR}^{\psi}}$

Note: Adam-Gibbs $\frac{\theta \psi}{d-\theta} = 1$

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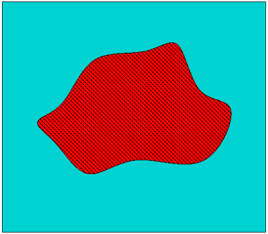

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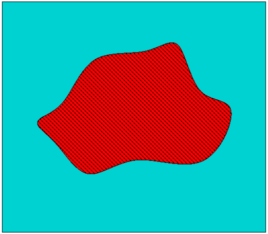

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Summary

$\sigma_{CRR} = \xi^d S_c$ is a central quantity in both theories

Recent advance:

ξ can now be accessed experimentally!

To be tested (around T_g):

1. Adam-Gibbs: σ_{CRR} is constant in temperature
2. RFOT: $\sigma_{CRR}(T) \sim \xi(T)^\theta$ increases in temperature
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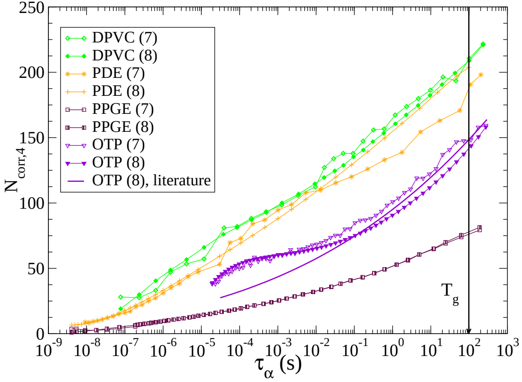
Outline

Measure of N_{corr}

$$N_{corr,4}(T) = max_t \frac{k_B}{\Delta C_p}[T\frac{d\langle C(t)\rangle}{dT}]^2 = \frac{k_B}{\Delta C_p(T)}\frac{\beta(T)^2}{e^2}\left(\frac{d\log\tau_\alpha}{d\log T}\right)^2$$

Berthier et al., Science (2005)



We tested the method following Dalle-Ferrier et al., Phys.Rev.E (2007)

Configurational entropy of a correlation volume

Definition

$$\sigma_{CRR}(T) = \frac{S_c(T)}{k_B} N_{corr,4}(T) = \frac{S_c(T)}{\Delta C_p(T)} \frac{\beta(T)^2}{e^2} \left(\frac{d \log \tau_\alpha}{d \log T} \right)^2 = \log \mathcal{N}(T)$$

$\mathcal{N}(T)$ = number of states in the correlation volume

Advantages

1. Independent of normalizations (beads, etc.)
2. We want to test if $\sigma_{CRR}(T_g)$ = cost. for different materials
3. According to RFOT $\sigma_{CRR}(T)$ is the thermodynamic barrier; relation with $\tau_\alpha(T)$?

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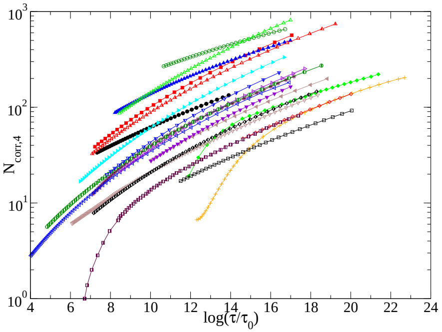
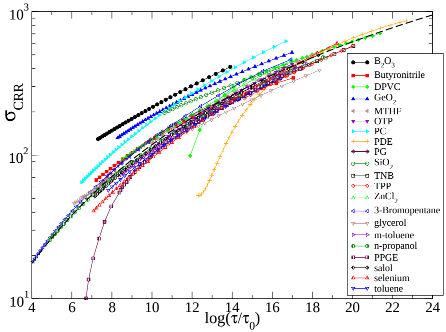
Temperature dependence of σ_{CRR}





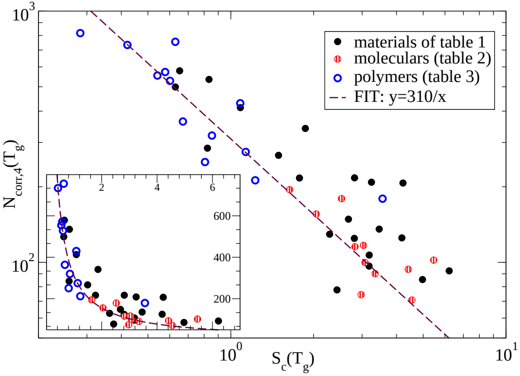
$$\log(\tau_\alpha/\tau_0) = (\sigma/\sigma_o)^{\psi} + z\ln(\sigma/\sigma_o) + \ln A$$

$A = 0.65$, $\sigma_o = 2.86$, $z = 1.075$, and $\psi = 0.5$ (but $\psi = 0.3 \div 1.5$ is ok)

Inconsistent with Adam-Gibbs theory, $\sigma_{CRR}(T) = const.$

Correlation at T_g

$$\log(\tau_\alpha(T)/\tau_0) = f[\sigma_{CRR}(T)]$$
$$\Downarrow$$
$$\sigma_{CRR}(T_g) = \text{const.}$$
$$\Downarrow$$
$$S_c(T_g) \propto 1/N_{corr,4}(T_g)$$

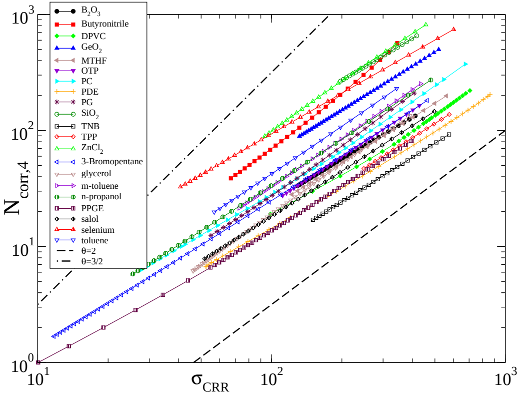


$$\sigma_{CRR}(T) = \frac{S_c(T)}{\Delta C_p(T)} \frac{\beta(T)^2}{e^2} \left(\frac{d \log \tau_\alpha}{d \log T}\right)^2$$

Consistency check: Using $m \sim \Delta C_p(T_g)/S_c(T_g) \;\Rightarrow\; \beta^2 m = \text{const.}$

RFOT exponents

RFOT predicts $\sigma_{CRR} \propto N_{corr,4}^{\theta/d} \quad \Rightarrow \quad \theta = 2 \div 2.2$



Together with $\psi \sim 0.5 \quad \Rightarrow \quad \frac{\theta\psi}{d-\theta} \sim 1$ Adam-Gibbs relation!

Related works

Karmakar, Dasgupta, Sastry - arXiv:0805.3104

Numerical determination of exponent θ, consistent results

Biroli et al. - Nature Physics 4, 771 (2008)

Fluctuating surface tension with exponent $\theta = 2$; can give a pre-asymptotic effective exponent $\theta_{eff} \gtrsim 2$

Bhattacharyya et al. - PNAS 105, 10677 (2008)

Schematic MCT + RFOT gives $\sigma_{CRR}^{\psi} \sim \log \tau$ with similar values of ψ

Conclusions

Main assumptions

1. Dynamical correlation length $\Leftrightarrow$ Adam-Gibbs CRR
2. $N_{corr,4} \propto$ "number of correlated molecules"
3. S_c estimated by the difference between liquid and crystal entropies

Main results

1. σ_{CRR} increases on lowering T, inconsistent with AG theory
2. Data seem to indicate that $\log[\tau_\alpha(T)/\tau_0] = f[\sigma_{CRR}(T)]$
3. This implies $\sigma_{CRR}(T_g) =$ const. which is checked
4. Consistent with $m \sim \Delta C_p(T_g)/S_c(T_g)$ and $\beta^2 m =$ const.
5. RFOT exponent $\theta \sim 2 \div 2.2$ (smooth interface)
6. $\psi \sim 0.5$ best fit, consistent with Adam-Gibbs relation

`See the paper for details...`

Puzzle

What is the physical interpretation of $\psi < 1$?

How to measure ξ (sketchy)

1. $\chi_4(t) \equiv \rho \int d^3\mathbf{r} \, \langle c(\mathbf{0};t) c(\mathbf{r};t) \rangle$ with $\langle c(\mathbf{0};t) c(\mathbf{r};t) \rangle \propto e^{-\frac{r}{\xi(t)}}$
   $\Rightarrow \quad \chi_4(t) \propto \xi(t)^d$ (Assumption!)

2. $\chi_4(t) \geq \frac{k_B}{\Delta C_p} [T \frac{d\langle C(t) \rangle}{dT}]^2$; Berthier et al., Science (2005)

3. Assume $\langle C(t) \rangle = \exp \left[- \left(\frac{t}{\tau_\alpha(T)} \right)^{\beta(T)} \right]$
   $\Rightarrow N_{corr,4}(T) = max_t \chi_4(t) = \frac{k_B}{\Delta C_p(T)} \frac{\beta(T)^2}{e^2} \left(\frac{d \log \tau_\alpha}{d \log T} \right)^2 \propto \xi(T)^d$
   (+ two negligible corrections: $\beta'(T)$ and shift of the peak)