Two-time correlations and coherent scattering experiments on phase-segregating materials

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Speckle intensity fluctuation spectroscopy

- Used for decades with coherent light scattering
- Commonly used to study equilibrium fluctuations
- Coherent X-rays from synchrotron sources
  - higher penetration, finer resolution than visible light
- X-ray Intensity Fluctuation Spectroscopy (XIFS) recently extended to nonequilibrium systems
- Nonequilibrium speckle fluctuations are not stationary
- Fluctuation statistics reveal spatial structure and dynamics
This work


- Numerically solved Time-Dependent Ginzburg-Landau (TDGL) equation for order-parameter field $\psi(r, \tau)$

$$
\frac{\partial \psi(r, \tau)}{\partial \tau} = \left\{-\frac{1}{2} \nabla^2 \right\}^\alpha \left[(1 + \nabla^2) \psi(r, \tau) - \psi^3(r, \tau)\right]
$$

$\alpha = 0$ for nonconserved; $\alpha = 1$ for conserved order parameter

Dynamic scaling: Characteristic length $R(\tau) \sim \tau^n$

$\Leftrightarrow$ Characteristic wave vector $k_c(\tau) \sim \tau^{-n}$

$n = \frac{1}{2}$ for nonconserved; $n = \frac{1}{3}$ for conserved order parameter

- Developed analytic scaling function for intensity correlations

- Compare with recent experiments on phase separation in borosilicate glass (Malik et al.) and Al-Li alloy (Livet et al.)
Scattering speckle

Simulated scattering intensity, conserved order parameter

Experimental scattering intensity, Sodium Borosilicate Glass

Structure factor and intensity fluctuations

Structure factor: \( S(k, \tau) = \langle I(k, \tau) \rangle \)
where \( I(k, \tau) = |\hat{\psi}(k, \tau)|^2 \) is fluctuating intensity at \((k, \tau)\)

Characteristic wave vector \( k_c \propto R(\tau)^{-1} \sim \tau^{-1/3} \)
\((n = 1/3 \text{ for conserved order parameter})\)

Simulation results (Brown et al., PRE 60, 5151 (1999))

Scaled structure factor vs \( \bar{t} \propto k^{1/n} \bar{\tau} \) Normalized speckle time series
Intensity correlations

Normalized two-time intensity correlation function

\[ \text{Corr}(k; \tau_1, \tau_2) = \text{Corr}(t_1, t_2) = \frac{\langle I(k, \tau_1)I(k, \tau_2) \rangle}{\langle I(k, \tau_1) \rangle \langle I(k, \tau_2) \rangle} - 1 ; t_i \propto k^{1/n} \tau_i \]

Natural variables: \( \delta \tau = \tau_2 - \tau_1 \) and \( \bar{\tau} = (\tau_2 + \tau_1)/2 \)

Simulated \( \text{Corr}(t_1, t_2) \)  Experimental \( \text{Corr}(\tau_1, \tau_2) \) (Malik et al.)

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Scaling function for $\text{Corr}(t_1, t_2)$

If $\langle I(k, \tau_1)I(k, \tau_2) \rangle = \langle \hat{\psi}(k, \tau_1)\hat{\psi}^*(k, \tau_1)\hat{\psi}(k, \tau_2)\hat{\psi}^*(k, \tau_2) \rangle$ breaks down into products of second moments (Gaussian Superposition Approximation), then

$$\text{Corr}(t_1, t_2) \propto \left[ \int \! dr \, e^{ik \cdot r} \langle \psi(0, \tau_1)\psi(r, \tau_2) \rangle \right]^2$$

**Scaling for SMALL $\bar{t} \propto k^{1/n} \bar{\tau}$**

In this limit, $\text{Corr}(t_1, t_2)$ is dominated by the large-scale behavior:

Scaling with $r/R(\bar{\tau})$ and $\tau_2/\tau_1$ implies

$$\langle \psi(0, \tau_1)\psi(r, \tau_2) \rangle = C(r/\bar{\tau}^n, \delta \tau/\bar{\tau})$$

To lowest order in $\bar{t}$, the Fourier transform gives

$$\text{Corr}(t_1, t_2) = \text{Corr} \left( \frac{\delta t}{\bar{t}} \right) \text{ for small } \bar{t}$$
Scaling for LARGE $\bar{t} \propto k^{1/n\bar{t}}$

Many terms in the $\bar{t}$-expansion would contribute.

In this limit, $\text{Corr}(t_1, t_2)$ is dominated by the small-scale behavior:

$$\frac{\langle \psi(0, \tau_1) \psi(r, \tau_2) \rangle}{\langle \psi^2 \rangle} = 1 - \frac{\delta\tau}{\bar{t}} G \left( \text{const.} \frac{r}{\Delta R} \right)$$

\[ G(x) \sim \begin{cases} 
1 & \text{for } x \ll 1 \\
x & \text{for } x \gg 1 
\end{cases} \quad \text{and} \quad \Delta R = \delta\tau \left. \frac{dR(\tau)}{d\tau} \right|_{\tau = \bar{t}} \propto \frac{\delta\tau}{\bar{t}(1-n)} \]

is the “new” relevant length scale

Fourier transforming we obtain:

$$\text{Corr}(t_1, t_2) = \text{Corr} \left( \frac{\delta t}{\bar{t}(1-n)} \right) \text{ for large } \bar{t}$$
Characteristic time difference (correlation time), $\delta t_c$

Define $\delta t_c(t)$ by $\text{Corr}(\delta t_c, \bar{t}) = 1/2$

Simulated $\delta t_c$ vs $\bar{t}$
(Brown et al., PRE 60, 5151 (1999))

Experimental $\delta t_c$ vs $\bar{t}$
$Al_{0.91}Li_{0.09}$
(Livet et al., unpublished)

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Speckle-intensity correlation scaling function for large $\bar{t}$

Analytical result

$$C_d(z) = \left[ \frac{2}{\Gamma\left[\frac{d+1}{2}\right]} \left(\frac{A\bar{z}}{2}\right)^{\frac{d+1}{2}} K_{\frac{d+1}{2}} (A\bar{z}) \right]^2$$

$$\sim \begin{cases} 
1 - O((A\bar{z})^2) & \text{for } A\bar{z} \ll 1 \text{ (persistence)} \\
(A\bar{z})^d \exp[-2A\bar{z}] & \text{for } A\bar{z} \gg 1
\end{cases}$$

where $z = \delta t / \bar{t}^{(1-n)}$

$K_\nu$ is a modified Bessel function, $d$ is the spatial dimension, and $A$ is a numerical constant

Valid for conserved and nonconserved order parameter and in 2 and 3 dimensions!
Speckle-intensity correlation scaling function for large $\bar{t}$

Comparison with numerical and experimental results

$z = \delta t / t^{2/3}$

$\Phi_2(0.62z)/2\pi$

Simulated $\text{Corr}(\delta t, \bar{t})$ vs $z = \delta t / t^{(1-n)}$

(Brown et al., PRE 60, 5151 (1999))

Al$_{0.91}$Li$_{0.09}$ (Livet et al.)

$\tau_1 = 2163$ s, 7920 s, 16320 s

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Conclusions

- Speckle-intensity fluctuations in phase-segregating nonequilibrium systems
  - Give nonstationary, persistent time series
  - At early times reflect large-scale dynamics and structure
    Speckle correlation time $\delta t_c \sim \bar{t}$
  - At late times reflect local interface dynamics and structure
    Speckle correlation time $\delta t_c \sim \bar{t}^{(1-n)}$
  - Are observable in XIFS experiments

- Analytic large-$\bar{t}$ scaling function involving modified Bessel function valid for systems with both conserved and nonconserved order parameter, and in 2 and 3 dimensions

- Good agreement between analytic results, simulations, and XIFS experiments on Sodium Borosilicate Glass and Al-Li alloy