

Critical fluctuations and isotropic-nematic transition in polydomain elastomers

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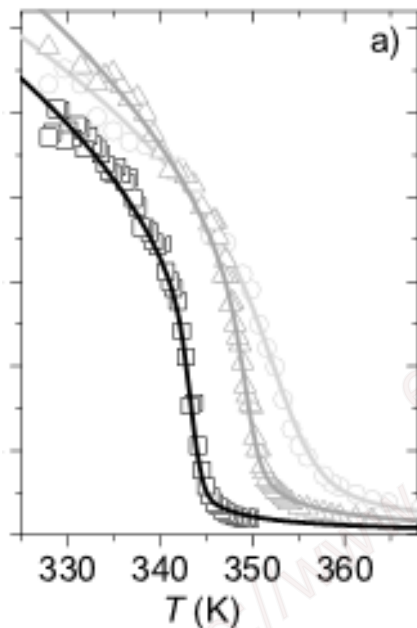
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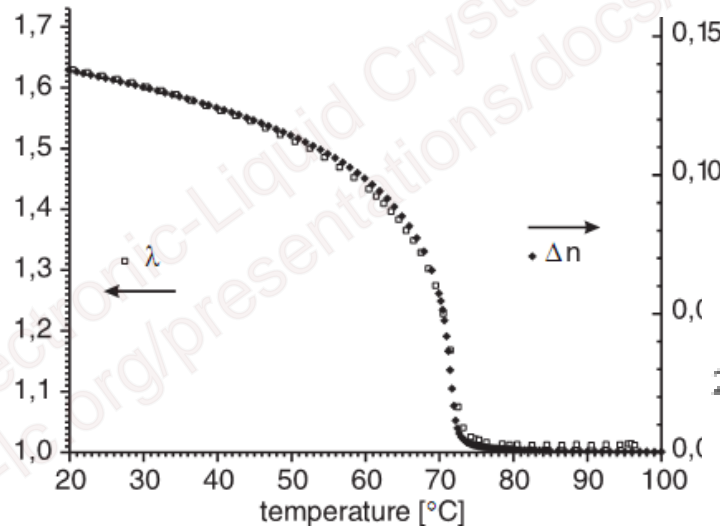
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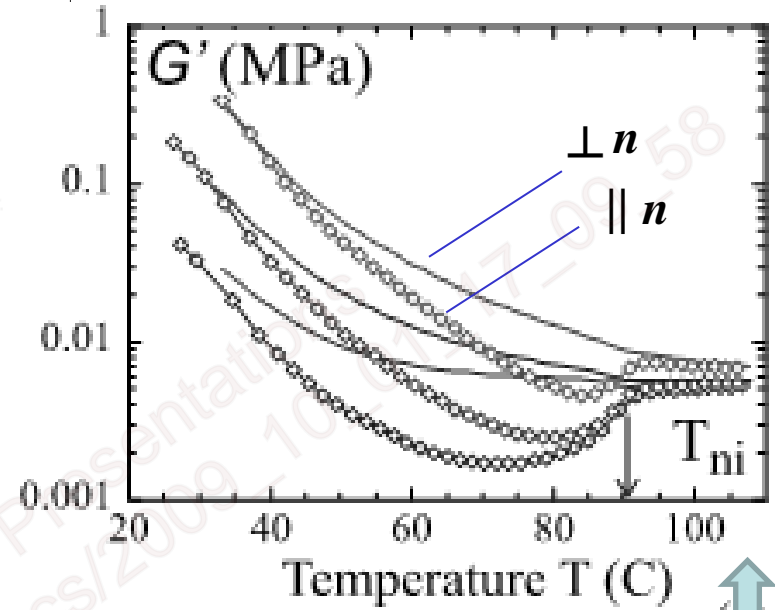
The question: is the I-N phase transition in elastomers the same or similar to that in the ordinary L.C. or polymer melts?



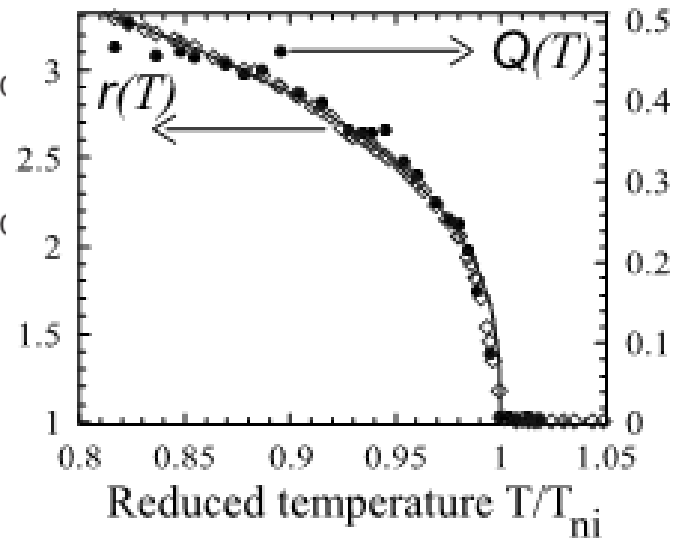
Lebar, Kutnjak, Zumer, Finkelmann, Sanchez-Ferrer, Zalar – PRL 2005



Finkelmann, Greve, Warner – EPJE 2001



Clarke, Tajbakhsh, Terentjev, Warner – PRL 2001



The question: is the I-N phase transition in elastomers the same or similar to that in the ordinary L.C. or polymer melts?

Why shouldn't it be?

Because the crosslinked polymer network retains the “memory” of local stresses that couple to the nematic order parameter Q_{ik}

In monodomain elastomers this results in an **external field** that can make the transition supercritical at sufficient crosslinking density. This is really well understood: de Gennes 1981; Kaufhold, Finkelmann, Brand 1991; Lebar, et al. 2007.

In polydomain elastomers this results in a **random field** of local orientation. Its effect is similar to random-anisotropy spin glass, with a difference that this is a quadrupolar order parameter (unlike dipolar magnetization). This is also relatively well understood: Fridrikh, Terentiev 1997; Uchida 2000; Xing, Radzihovsky 2003; Petridis, Terentjev 2006

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How to answer it?

The problem is of a 1st-order transition (dictated by quadrupolar symmetry) with quenched random impurities (essentially provided by crosslinks).

Some fundamental work exists: Imry, Wortis 1979, Cardy 1996. One of the predictions is that the discontinuous 1st-order transition changes into a continuous critical transition with no phase coexistence – in spite of the local point symmetry (this has little to do with Landau-level arguments: Petridis, Terentjev 2006).

This is extremely difficult to experimentally verify in a magnetic spin-glass system and only few papers exist: Pappas et al. 2003.

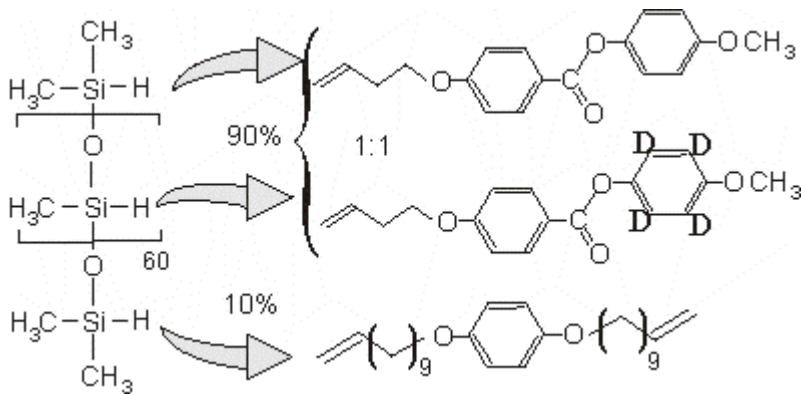
Here, in LC elastomers, we have a new opportunity to experimentally investigate this effect – and perhaps contribute to a larger body of science.

The question: is the I-N phase transition in elastomers the same or similar to that in the ordinary L.C. or polymer melts?

Experimental observations by NMR

1. Sample preparation
Genesis of polydomain nematic, choice of D-probe
2. NMR technique
Ensemble average, time average, line shape analysis
3. I-N phase transition
Apparently critical transition, divergence of fluctuations at T_{IN}

We use the “standard” Finkelmann’s side-chain nematic elastomer:



Main-chain systems are too ambiguous in dynamics of their mesogens, hairpins and entanglements

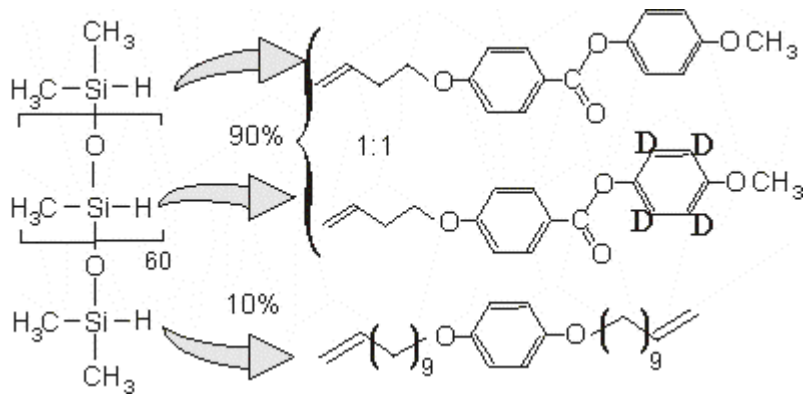
We place the D-nuclei symmetrically in the rod-unit attached to the network

Using a doped D-probe does not reflect the elastomer dynamics, homogeneity can be a question...

We fully crosslink the network in the isotropic highly swollen state and then slowly dry it while freely suspended – to avoid topological entanglements and local stress to be “recorded”

This is not the usual procedure, most of the LCE materials you hear about have a large number such internal constraints

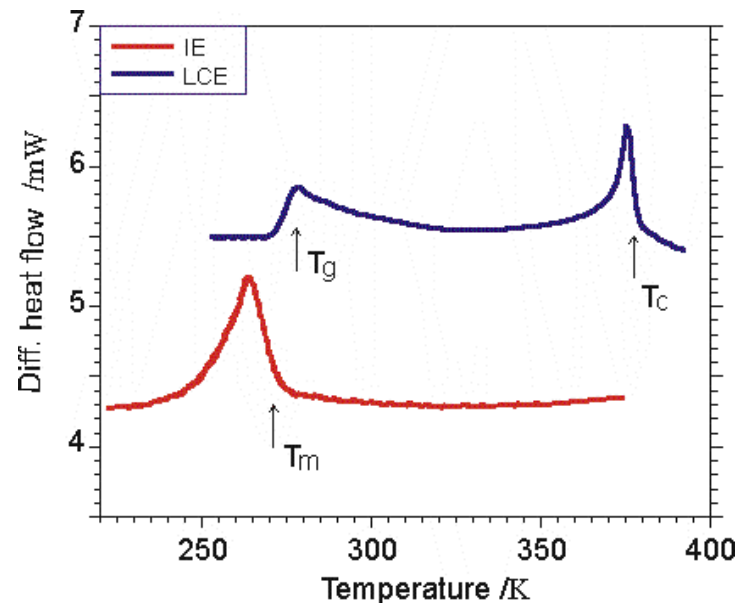
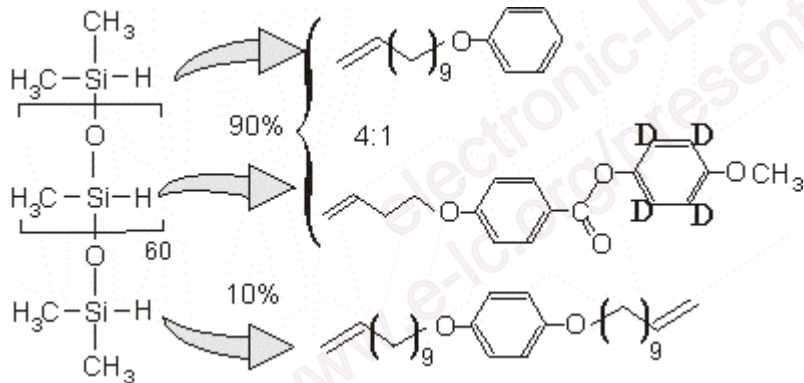
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But we will also need to compare the NMR results for nematic systems with the similar non-mesogenic system.

This is to be able to “**subtract the baseline**” – i.e. isolate the nematic ordering effects from the background polymer network.

We use the fully analogous elastomer, where rod-like units are replaced



NMR: Bruker Avance III 300 MHz spectrometer working at a resonance frequency for deuterium of 46.1 MHz

Larmor precession frequency is split: $\omega = \frac{6\pi}{2} \nu_Q \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} + \frac{1}{2} \eta \sin^2 \theta \cos 2\phi \right)$

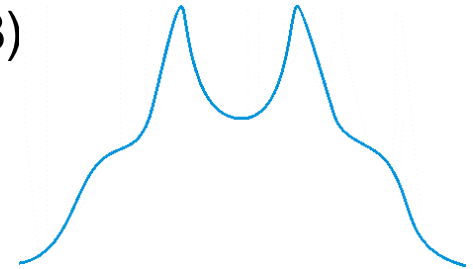
quadrupolar coupling constant:

$$\nu_Q \approx 185 \text{ kHz}$$



Polydomain system has all angles θ, ϕ present so the signal is a 3D powder average, called the **Pake pattern** (Pake 1948)

$$G(\omega) = \int \left[h\left(\omega - \frac{1}{2} \omega_Q\right) + h\left(\omega + \frac{1}{2} \omega_Q\right) \right] \sin \theta \, d\theta \, d\phi$$



The shape of individual resonance line $h(\omega)$ strongly depends on the motional averaging of the spin.

Usually (**really, almost always!**) the characteristic rate of dipole rotation is much higher than ν_Q and the fully averaged LORENTZIAN shape results:

$$h(\omega) = \frac{T_2}{1 + (T_2 \omega)^2}$$

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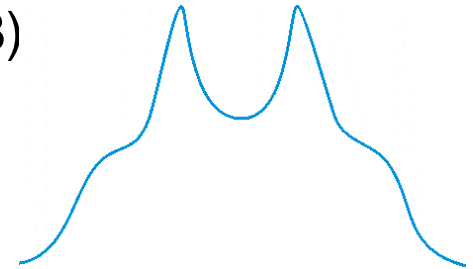
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However, in the slow-motion limit, when the rotational rate of the moiety is lower than ν_Q the analysis suggests that the line shape is instead a GAUSSIAN:

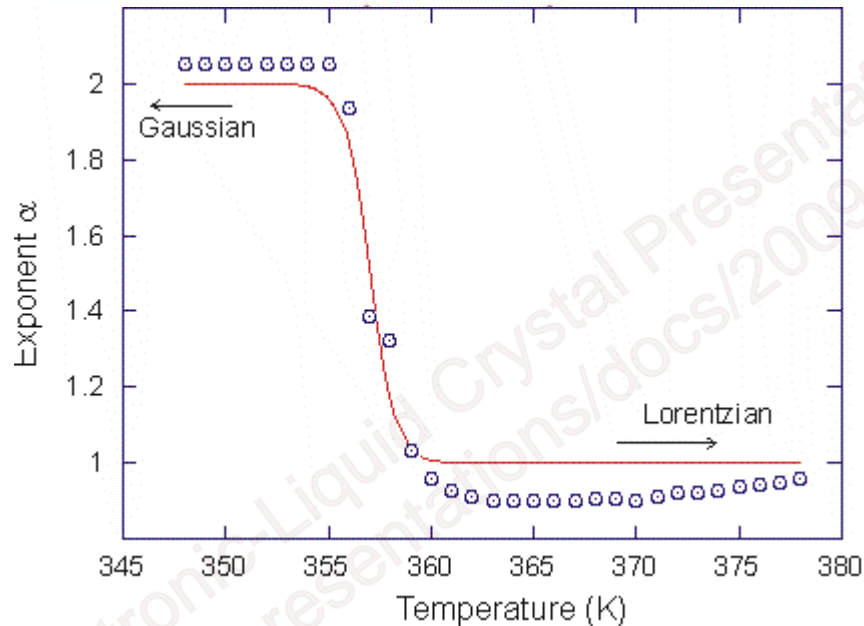
$$h(\omega) = t_G e^{-\frac{1}{4} \omega^2 t_G^2}$$

Can this ever be the case?

http://www.electronic-liquids.com/presentations/2009_10_01_17_03_58

In our fitting procedure we first allow the line shape to have a “free” choice between the Lorentzian and the Gaussian limits, using the $h(\omega)$ as Fourier-transform of $h(t) = e^{-(t/T)^\alpha} \Rightarrow h(\omega, \alpha)$

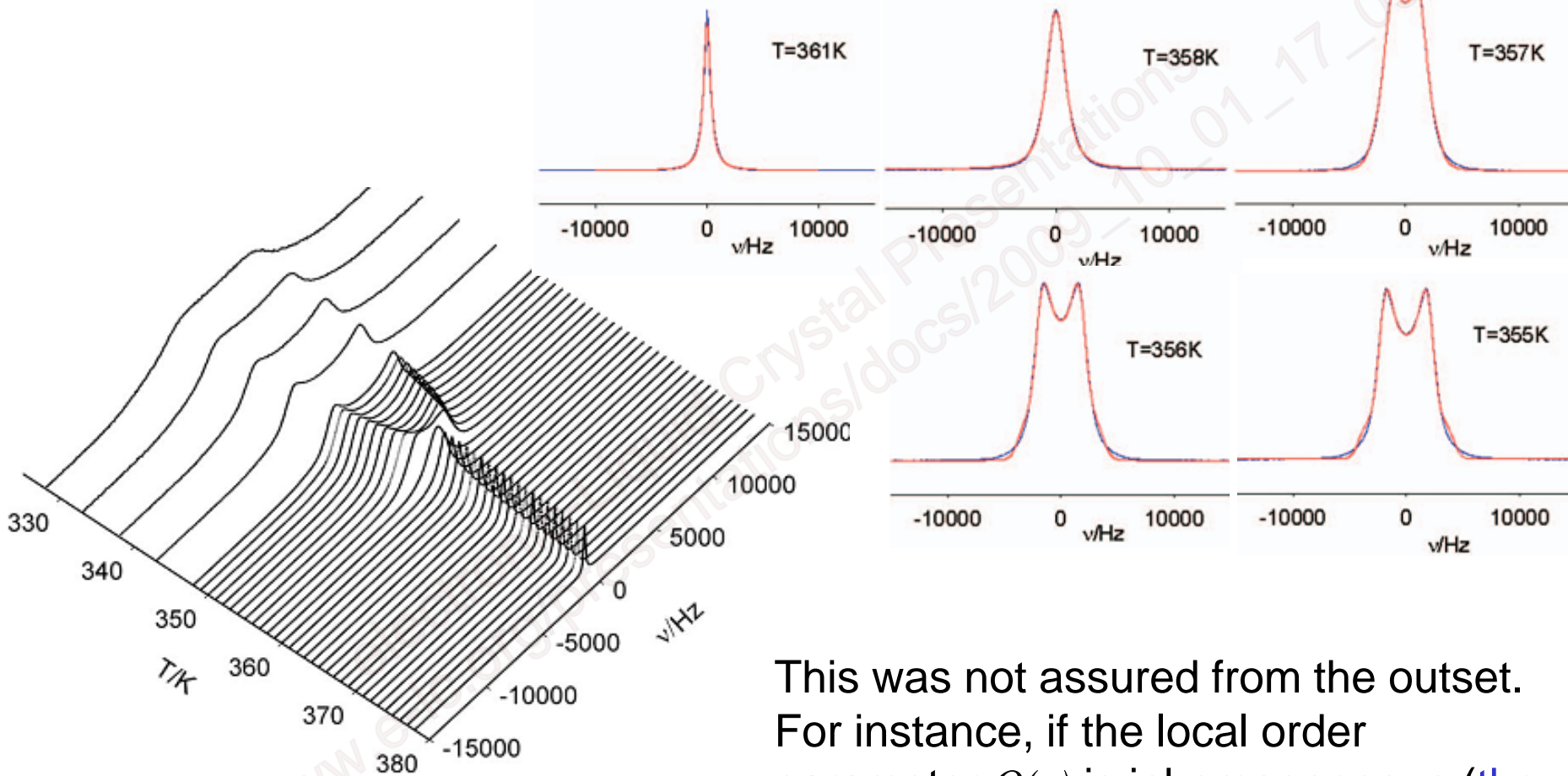
The fitting gives:



However, since we know that in both fast- and slow-limits we have the real Lorentzian and Gaussian, there is no point keeping this parameter free. So we interpolate:

$$\alpha(T) = \frac{3}{2} - \frac{1}{2} \tanh \left[\frac{T - T^*}{m} \right]$$

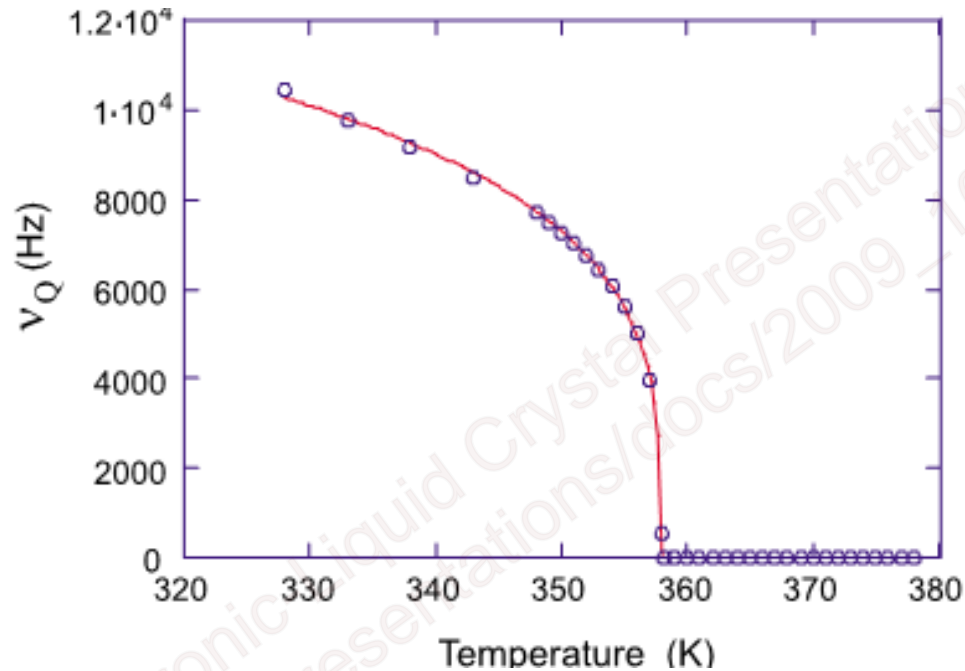
In this way all our NMR spectra have only 2 free parameters to fit: the average quadrupolar splitting $\bar{\nu}_Q$ (which is the nematic order parameter) and the line width $\Delta\nu$ (related to the orientational relaxation time)



This was not assured from the outset. For instance, if the local order parameter $Q(\mathbf{r})$ is inhomogeneous (the director $\mathbf{n}(\mathbf{r})$ certainly is!), we would not have a successful fitting

The key results

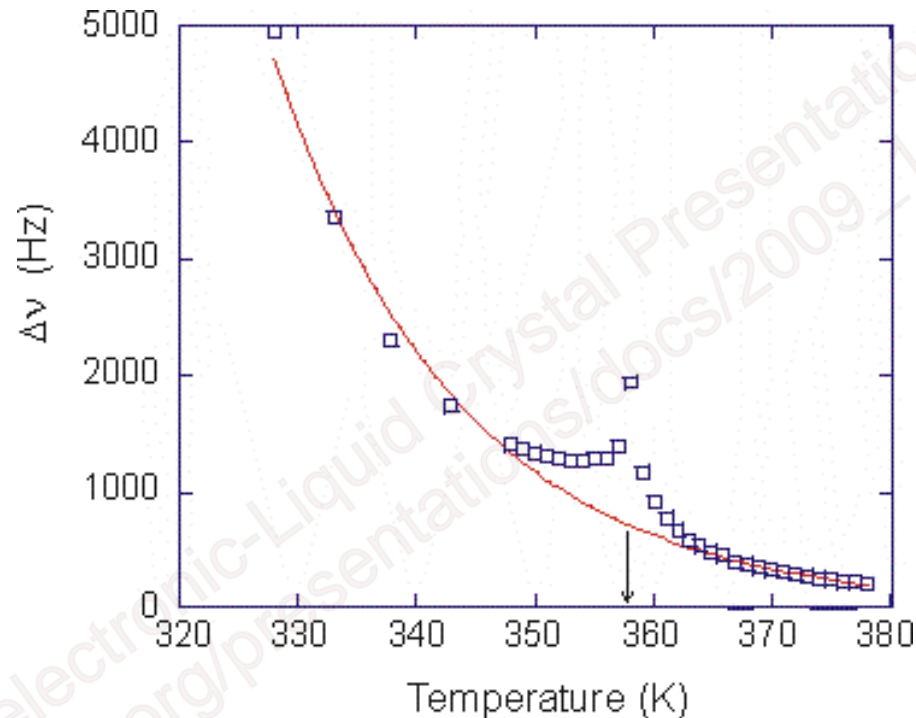
The average quadrupolar splitting is a function of temperature on cooling:



We deliberately moved in steps of 0.5° with a very long equilibration at each T-value, so that we could cleanly distinguish a possible step: a “1st order jump” in the order parameter, and also any pre-transitional “paranematic” signature. **Neither is found.**

The key results

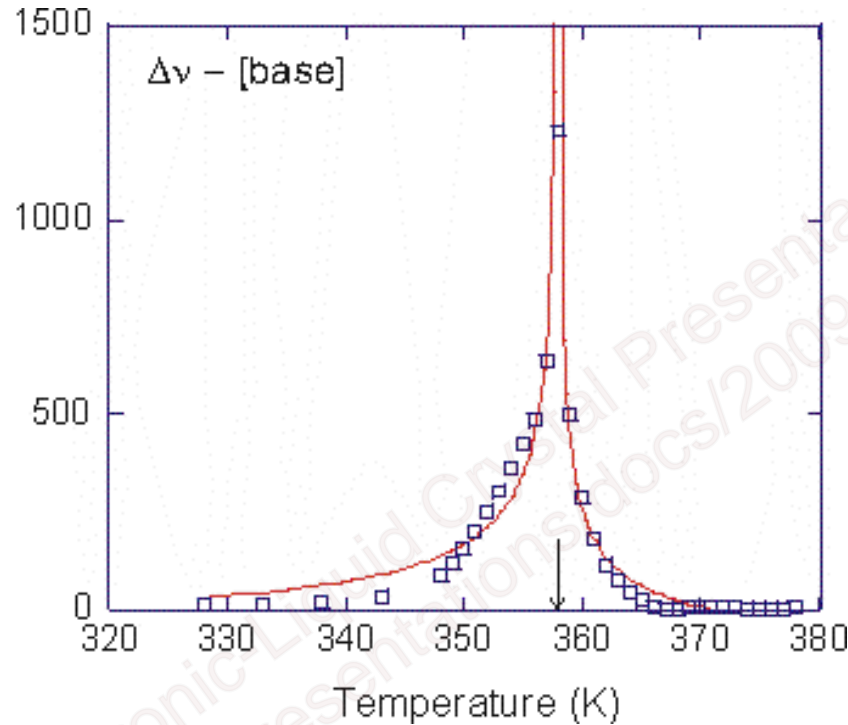
The width of the NMR line, which is the inverse correlation time of average spin fluctuations, has an unusual behavior on cooling:



There are clearly two processes at play here: the “**baseline**” reflecting the monotonic increase of relaxation time of segments in the polymer network, and the “**peak**” at the nematic transition.

The key results

The transition peak (with the baseline subtracted) has critical T-dependence

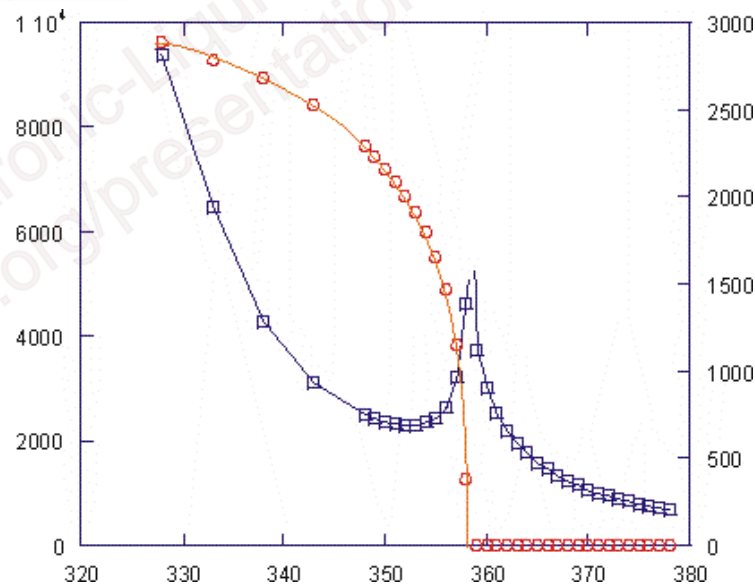
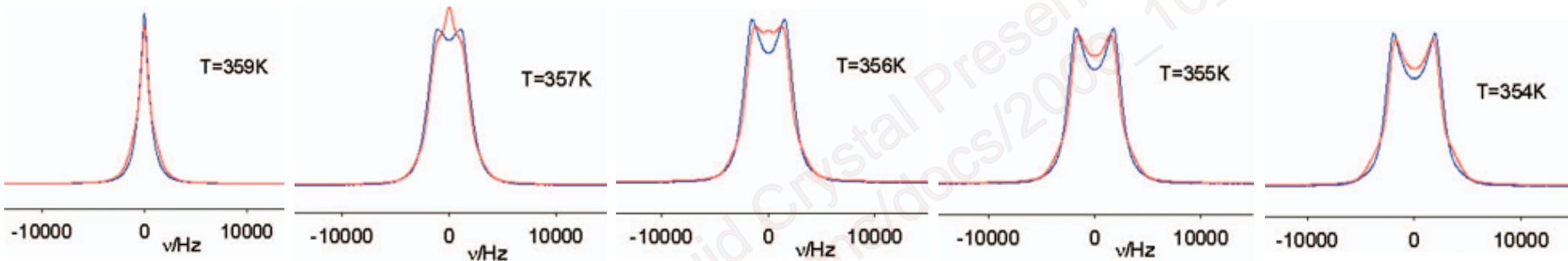


Remarkably, fitting is $|T - T_{NI}|^{-1/2}$ on both sides of the transition. It is tempting to relate this to a Landau mean-field value of correlation length – but no, it is just a coincidence...

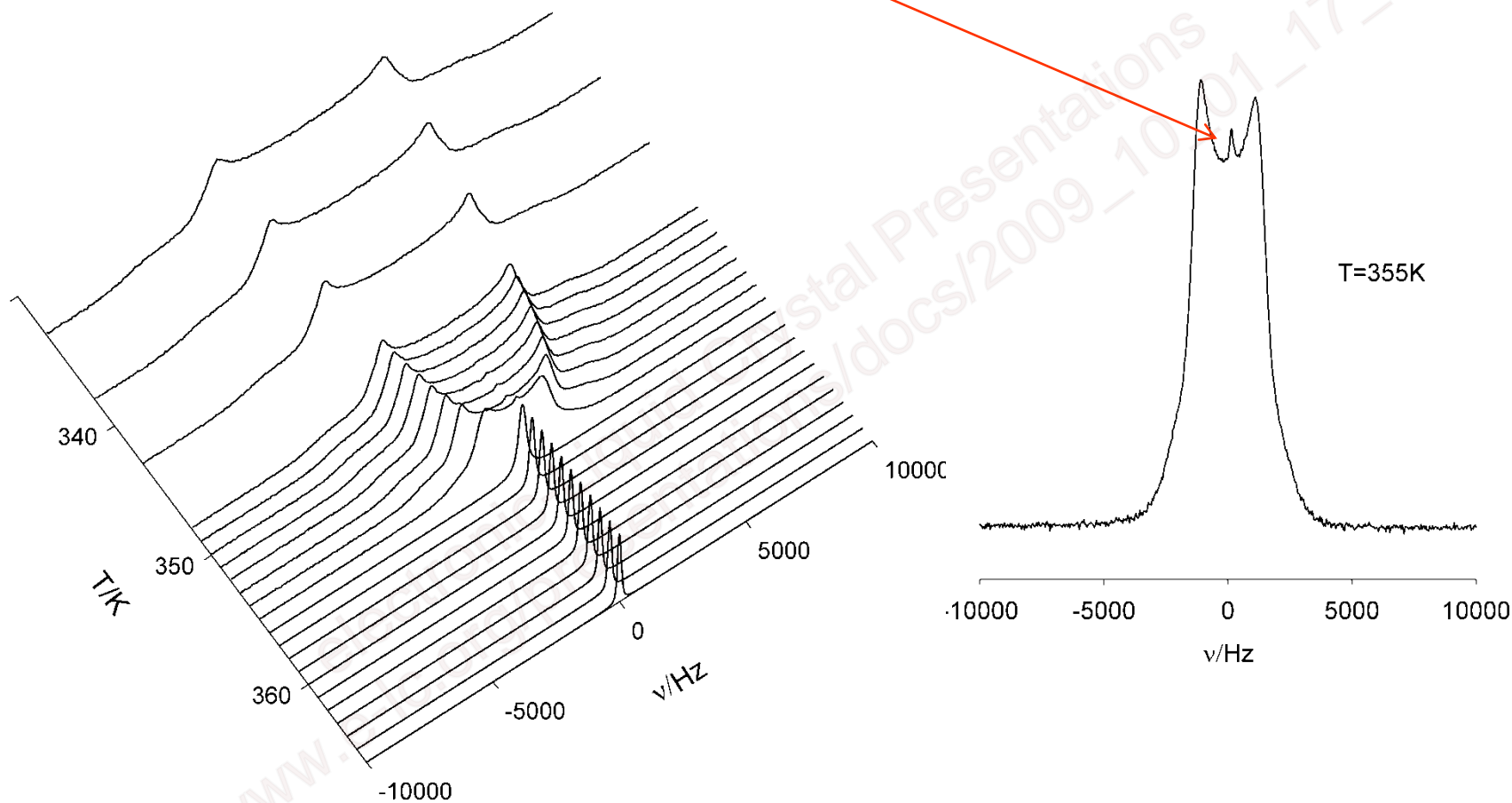
However, the apparent critical behavior of relaxation rate isn't a coincidence: growth of critical fluctuation size at T_{NI} should be related to the average time of spin (local director) re-orientation, which is what Δv represents.

Consider alternatives:

1. The “heterogeneity model” (Selinger, Ratna 2002-04, Lebar et al. 2005)
2. Using the Lorentzian below T_{NI}
3. Using D-probe in a flexible moiety or as a swelling dopant



If we use the **doped D-probe**: the nematic monomer not attached to the network, the results immediately show the phase coexistence, which we believe is due to the inhomogeneous distribution of the probe.



Conclusions

1. NMR study of ordering in polydomain (macroscopically misaligned) systems requires delicate analysis and very careful sample preparation.
2. There is a strong suggestion that the rotational dynamics of mesogens (attached to the network) slows down dramatically in the nematic phase. We suggest an interpolation method that bridges between the fast- and slow- NMR regimes that seems to work well.
3. Within our accuracy (which is not small) we find the I-N transition in a locally unconstrained nematic with weak quenched disorder to become a continuous critical phase transformation.

Need to do

1. Verify these results by an independent group
2. Have a high-precision measurement near T_{NI} to analyze criticality

Thanks Any questions?

