Recent developments in photopyroelectric calorimetry for phase transition studies in liquid crystals

F. Mercuri, S. Paoloni, M. Marinelli and U. Zammit
Department Of Mechanical Engineering, University of Rome “Tor Vergata”
Via del Politecnico 110, 00133 Rome (Italy)
E-mail: mercuri@uniroma2.it

Abstract. We report on calorimetric measurements carried out in an upgraded photopyroelectric setup enabling the determination of the frequency dependence of the specific heat and of the latent heat exchanged over first order transitions as well as the simultaneously determined nematic correlation length obtained from light scattering measurements. It has been applied to the study of the Nematic-Isotropic transition of 8CB liquid crystal confined in a silica nanoparticle network, where the specific heat shows a double peak structure.

1. Introduction

The photopyroelectric technique has been proved, during the last two decades, to be very useful in the study of liquid crystal (LC) phase transitions because of its high temperature resolution capability and, unlike standard ac calorimetry, due to the possibility it provides to perform simultaneous measurements of the specific heat, thermal conductivity, and thermal diffusivity. Moreover, appropriately treating the sample cell walls and/or applying an electric field enabled measurements on monodomain liquid crystal samples. More recently, it has been applied to the study of liquid crystal samples where concentration of small quartz nanoparticles have been dispersed to induce disorder and confinement effects [1]. For such applications, a technical upgrade of the experimental configuration was made, which allowed the inspection of the sample during the measurements by means of an integrated real time imaging video system. This also led to the possibility to confine the investigation on small portions of inhomogeneous samples (∼50μm) by focusing the pump beam over areas selected by the video system [2]. Lately, an improved procedure of the data analysis has been introduced, which also allows, as a function of frequency, an indirect estimate of the latent heat exchanged across the two-phase coexistence region of a first order phase transition [3]. Moreover a new configuration of the photopyroelectric (PPE) calorimeter allows the investigation of optical properties, while the thermal characterization is carried out, by means of a second laser beam passing through the sample layer [4]. That has been proved particularly useful in the study of phase transitions where structure modifications, like reorientation of anisotropic domains or the onset of two phase coexistence, take place and can be investigated also by light scattering measurements. The simultaneous characterization of the thermal and optical properties enabled an high temperature resolution correlation of the different measured quantities at the various temperatures. The sample texture inspection was simultaneously performed during the experiment providing the possibility to correlate them to the evolution of the sample morphology.
2. Experimental and results

The optical access to the sample, necessary in the PPE calorimetry configuration to introduce the laser heating beam, has been exploited to perform also reflection polarization microscopy and scattering measurements, alongside the calorimetry. The experimental setup is shown in Fig. 1. Lasers 1 and 2 provide, respectively, the heating beam for calorimetry and the transmitted beam for scattering measurements. The sample is contained in cells of thickness ranging between 10μm and 100μm. It is covered by a 300μm thick LiTO$_3$ pyroelectric transducer with ITO transparent electrodes. Half of the cell surface in contact with the sample is coated with a thin layer of Ti to ensure light absorption. Beam 2, 3mm apart from beam 1, goes through the transparent part of the cell to cross the sample for transmission detection. The two lasers are modulated at different frequencies in order to avoid any interference in the signals they give rise to. The sample cell was contained in an oven and heated typically with a rate of 1mK/min.

2.1. Latent heat detection

Fig. 2 helps illustrating the principle according to which latent heat was detected. It shows the results for the amplitude, $A$, and the phase, $\phi$, of the PPE signal, obtained for a particle concentration (mass of particles / volume of LC) of 0.02g/cm$^3$ at a frequency of 2Hz, over the first order nematic-isotropic (NI) transition region. The inset reports the $A$ and $\phi$ data obtained over the second order Smectic-A–Nematic (AN) phase transition in pure $\tilde{8}$55 where no latent heat is involved. For both transitions, only the specific heat is known to show critical behaviour, while the thermal conductivity is known to remain smooth [5]. For the second order transition, $A$ and $\phi$ show, qualitatively, very similar changes over the transition region reflecting the specific heat change affecting likewise their behaviour.
On the contrary, over the NI transition of the LC nanocolloid, $A$ and $\varphi$ show different behaviour over the transition. Such difference can only be ascribed to latent heat exchange in the present case and, in general, also to other kinds of enthalpy exchange, as previously reported [6]. So we tried to single out the relative temperature dependence, of the latent heat exchange, as well as that of the effective specific heat, over the two peaks by processing the amplitude and phase data in terms of an expression for the complex PPE signal which, in the sample thermally thick working condition we have adopted, and when the signal is normalized to that obtained when illuminating the bare pyroelectric transducer, takes the form:

$$V = \frac{e_p}{e_s} e^{-\sigma l} \left\{ 1 - \frac{1}{\sigma} \left[ \frac{2e_q}{e_s} - \left( 1 + \frac{e_q}{e_s} \right) e^{\sigma} \right] I_L e^{-j\Psi} \right\}$$

where: $e_i = (k_i \rho c_i)^{\frac{1}{2}}$ is the thermal effusivity; $i = p,s,q$ refers to, respectively, pyroelectric material, sample and quartz; $\rho$ is the density; $l$ is the sample thickness; $\sigma = (l+j)(\pi/\alpha_s)^{\frac{1}{2}}$; $j$ is the imaginary unit; $\alpha_s = k_s/\rho c_s$ is the sample thermal diffusivity; $f$ is the modulation frequency. The first and the second term in the brackets represent the relative values, respectively, of the external heating contribution for an optically opaque sample and the one associated with a PPE signal that is obtained for a sample which shows almost uniform optical absorption throughout its volume. Such a term represents an additional, volume diffused and delayed heat source, mimicking the exchange of latent heat. It is characterized by the coefficient $I_L$ and by an effective phase lag $\Psi'$ between the two terms.

Fig. 3 shows the temperature dependence of the specific heat, $c(T)$, and of the latent heat term, $I_L(T)$, obtained according to such an approach. Over the coexistence region the values of $c$ correspond to effective values. $I_L$, on the other hand does not provide absolute values of the latent heat as discussed in ref. 3. So only its relative values as a function of temperature or of the sample condition are relevant. The double peak featured is evident for both quantities. It can be observed that the peak position for $c(T)$ and $I_L(T)$ are not coincident. The temperature relative to the peak in $I_L$ correspond to the flexing point of the steep part of $c(T)$, that is where the nematic nucleation rate with respect to
temperature is largest. Moreover the presence of the low temperature peak (LTP) in $c$, indicates that a relevant fraction of nematic material has nucleated over that temperature region. In spite of this, the latent heat involved over the LTP is considerably smaller than that involved over the high temperature peak (HTP). The temperature range of non zero $I_L$ values corresponds to the NI two-phase coexistence region where the relative shape of $A(T)$ and $\phi(T)$ is different. The range where this occurs can also be considered as a marker of the coexistence region and agrees well with the one determined by the simultaneously performed polarizing microscopy observation (not shown). Fig. 4 reports the $I_L$ and $c$.

Figure 3  Effective $c$ and $I_L$ (see text) vs. temperature for the sample with 0.02g/cm$^3$ particle concentration at 2Hz calculated from data of Fig. 2.

Figure 4  Effective $c$ and $I_L$ (see text) profiles over NI coexistence region of 8CB LC nanocolloid at 2Hz with 0.02g/cm$^3$ and 0.05g/cm$^3$ particle concentration.
temperature dependence obtained for samples with particle concentrations of 0.02 g/cm$^3$ and 0.05 g/cm$^3$, at 2 Hz. The larger particle concentration leads to a decrease and an increase, respectively, of the peak values of $c$ over the HTP and LTP, indicating an increased fraction of nematic material nucleating over the LTP associated with the reduction of the mean pore size in the silica particle network [7]. The latent heat peaks show similar corresponding changes over the two regions, the one corresponding to the HTP still remaining substantially larger than the one obtained at the LTP. Concerning the lower values of $I_L$ over the LTP for both concentrations, it has been reported that, in such a system, the detected latent heat averaged over both peaks decreases over the NI transition with increasing particle concentration and, therefore, average strain in the nucleated material [7] [8]. Such an aspect has been also predicted theoretically [9] [10]. The nematic material nucleating over the LTP is affected by considerably larger strain than that at the HTP. In fact, when the sheath of material close to the particles turns nematic over the LTP, with the molecular director constrained normal to the particle surface, the large strain involved induces fragmentation of the domains and affects the nature of the transition. It is therefore not surprising to find considerable lower latent heat involved over the LTP with respect to the HTP. It is worthwhile pointing out that the application of the present method has provided the possibility and the resolution to monitor the relative latent heat involved over each of the peaks, unlike previous reports where the measured latent heat corresponded to the one integrated over both peaks [7] [8]. This capability is important also for the results shown in Fig. 5 where a comparison of what obtained at different frequencies (2 Hz and 17 Hz) for the sample with particle concentration of 0.02 g/cm$^3$ is reported. As previously mentioned, in a.c measurements the

![Graph](image_url)

**Fig. 5** $I_L$ (see text) and effective $c$ (inset) curves over NI coexistence region of 8CB LC nanocolloid with 0.02 g/cm$^3$ particle concentration at 2 Hz and 17 Hz.

detected values of both $I_L$ and $c$ may be frequency dependent over a first order transition because of the characteristic time involved in the phase inter-conversion [7]. A substantial decrease with frequency occurs for both such quantities over the HTP while negligible effects are observed over the LTP in the present frequency range. So while the inter-conversion dynamical effect clearly affects the HTP feature, no effect is detectable over the LTP. This can imply that either the phase inter-conversion characteristic time has substantially been changed by the considerable strain over the LTP


or that the heat exchange giving rise to $I_L$ over such a peak could be caused also by a mechanism different from latent heat, such as, for example, enthalpy exchange associated with relaxing strain as observed over the Hexatic-B–Smectic-A transition in pure 65OBC [6]. These results agree with the previously reported ones indicating different dynamics of the processes occurring over the two peaks [11].

2.2 Scattering measurements

Fig. 6 shows the simultaneously measured specific heat, latent heat term and nematic correlation length $\xi$, obtained from the light scattering data, when cooling the sample over the N-I transition. In particular, the temperature dependence of $\xi$ has been derived, according to the model presented in Ref. [12], from the optical turbidity $\tau$. This was determined by the analysis of the transmitted beam intensity: $I_T=I_0\exp(-\tau d)$ where $I_0$ is the intensity of the incident beam and $d$ the sample thickness. Details of the model adopted for the evaluation of $\xi$ are reported in ref. [4] and [12]. A double step feature is evident in all the quantities. Outside the coexistence region, the obtained saturation value, $\xi$~25 $\mu$m in the nematic phase is very close to the one reported for 6CB LC with very similar concentration of aerosil particles [12].

![Figure 6](image)

Figure 6 Effective $c$ and $I_L$ (see text) and nematic correlation length $\xi$ vs. temperature for the sample 0.02g/cm³ particle concentration at 31Hz.

If the curves of the various quantities reported in Fig. 6 are compared, the following scenario occurring over NI transition can be proposed. When cooling from the isotropic phase, the system enters the two phase coexistence region where the bulk-like nematic domains nucleate and expand while their number rapidly increases giving rise to the fast increase of both $I_L$ and $\tau$ (not shown), the latter reaching a maximum value where the expanding single domains tend to saturate the available volume for their free growth. Correspondingly, $c$ is also found to grow rapidly with the steep part of
its shape corresponding to the maximum of $I_L$ where the release of latent heat is largest. Upon further cooling, the nucleated nematic domains start to coalesce thus leading to a local maximum of $\xi$ due to the increased optical homogeneity of the sample. At lower temperature, also the LC close to the particle surface, which has a lower transition temperature because of its disorder, starts nucleating in strained nematic domains, as confirmed by the renewed increase of $I_L$ and $c$. The domains then break into smaller ones relieving the strain and giving rise to the observed fine-grained texture [3]. Over such a temperature range, $I_L$ and $c$ approach the low temperature maximum value while $\xi$ reaches the local minimum. Such feature is associated with the nematic domains fractioning due to the transition of the LC strongly interacting with the particles. At still lower temperatures the nematic correlation length tends towards the saturation value in the N phase, compatible with the given concentration of aerosil particles. It is also interesting to point out that the low temperature peaks of $I_L$ and $c$ are broader towards the lower temperature region with respect to $\xi$. In our opinion, as the temperature is lowered beyond the LTP, the average nematic domain size nucleating in the vicinity of the particle surface cannot substantially change, since it is strongly limited by the LC molecules pinning on the particle surface. The turbidity is therefore not significantly affected by the nucleation of the new nematic volumes, a process which, on the contrary, still affects both $c$ and $I_L$.

3. Conclusions
In conclusion, thanks to an upgraded version of our PPE calorimeter, we have presented the simultaneous, high temperature resolution characterization of the optical turbidity, specific heat and latent heat of a LC nanocolloid sample. The detection of the frequency dependence of the specific heat and of the latent heat have shown a substantially different dynamics of the nematic material which nucleates at each peak. The obtained scattering results allowed to correlate the two-step nematic nucleation process, previously observed in the specific heat over the NI coexistence region, to the one we have also observed in the nematic correlation length.

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