Thermodynamic vs. Structural Changes during the Pre- and Main Transition in DPPC

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Phase transitions in lipid systems are found to be first order phase transitions. Since a first order phase transition is related to latent heat, it is common believe that changes in thermodynamics drive the structural phase transition. However, the functional relationship between thermodynamic and structural changes is far from being understood.

In our experiment we are targeting the processes occurring during the phase transitions. We have performed time-resolved small angle x-ray measurements at the slow scan rate of 0.1K/min, i.e. in the quasi static limit, on a 10w/w%-suspension of multilamellar dipalmitoylphosphatidylcholine (DPPC) vesicles. The temperature protocol used consisted of a first heating from 25°C to 50°C, a cooling back to 25°C and a second heating up to 45°C. We therefore cover the pre and the main transition of this lipid. Fig.1 shows the change of the lamellar lattice parameter d:

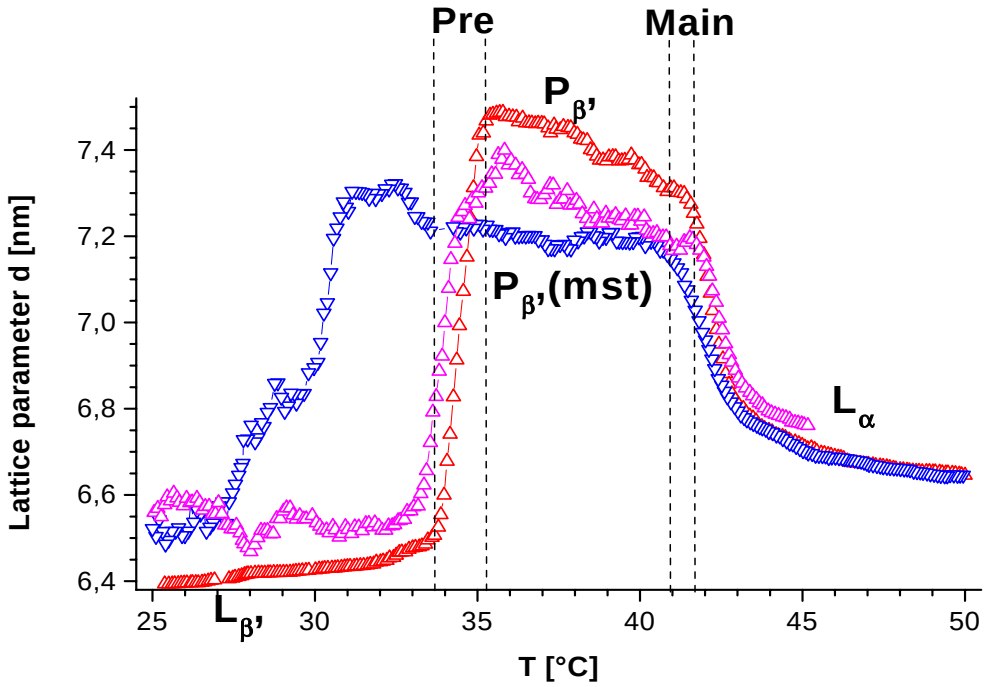

Figure 1: Up-triangles refer to data taken on heating, down-triangles on cooling. The indication of the pre and main transition refer to the first heating. The determination of the d-spacing below the main transition and after the first heating is inaccurate due to overlap of ripple reflections.

A major change in the lattice parameter indicates a phase transition. We begin in the $L_{\beta'}$-phase, pass the pretransition to the ripple phase $P_{\beta'}$ and finally reach the L_{α}. On cooling the L_{α} converts into the

metastable ripple phase $P_{\beta'}$(mst) [1]. This phase apparently undergoes a further structural change upon further cooling. Fig.1 indicates that the two transitions are to varying degree hysteretic. Whereas the main transition has a hysteresis of less than 1K, the pretransition shows a temperature hysteresis of at least 5K. The reproducibility of the transition temperature on the second heating is for the main transition exact within experimental resolution. On second heating the pretransition, or more accurate, the major increase in the lattice parameter is seen a short Kelvin below the pretransition in the first heating.

We have applied the maximum entropy principle to calculate the thermodynamic changes from the x-ray data. Fig.2 discloses several remarkable issues: The $L_{\beta'}$- and the L_{α}-Phase have a very

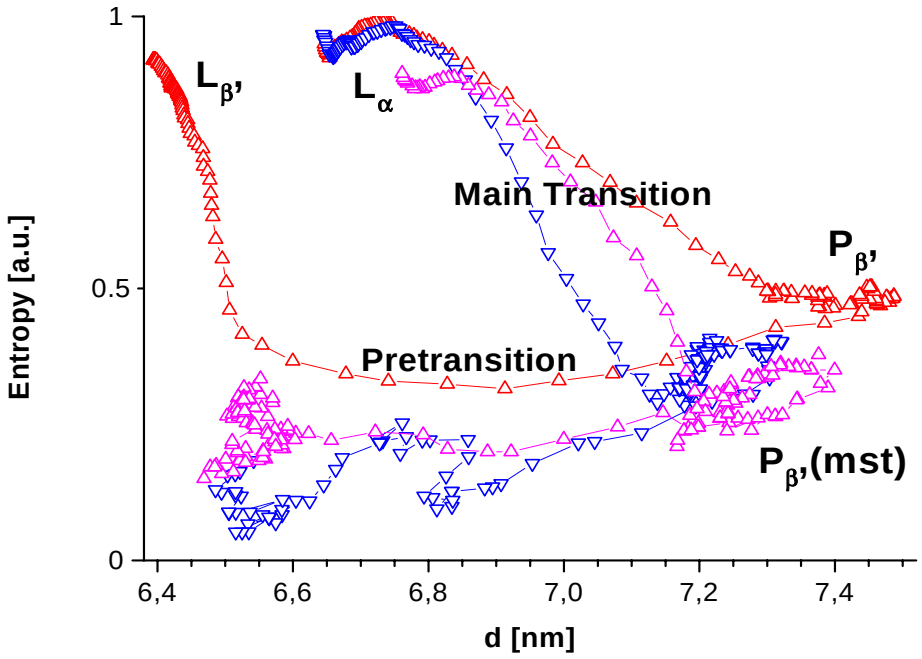

Figure 2: Structural vs. thermodynamic changes in DPPC; Symbols as in Fig.1

similar entropy, i.e. degree of stability. The stable ripple phase $P_{\beta'}$ is literally more stable than the metastable ripple phase $P_{\beta'}$(mst).

Over the main transition, the change of the lattice parameter is in good approximation linear to the change in entropy, independent of the degree of stability on the low temperature side of the main transition. On the other hand, the physics of the pretransition appears to be different: before the sample undergoes the pretransition, the entropy decreases. The lattice parameter, i.e. the structure, changes in the pretransition. The metastable ripple phase does not show any strong changes in entropy anymore though the structure changes upon cooling. It appears, that the decoupling of structural and thermodynamic changes are intimately related to hysteresis and metastability.

References

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