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1 Thermo-Physical characterization of Hexadecane during 2 the solid/liquid phase change

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7 Abstract

8 In this study we provide a multi-physical and multi-scale characterization
9 of an organic Phase Change Material (PCM), i.e. hexadecane, for both its
10 liquid and solid phase and during the phase transition. Macroscopic ther-
11 mal and physical properties provided are density and viscosity in the liquid
12 phase and thermal conductivity and heat capacity in each phase. Further
13 macroscopic measurements were done by differential scanning calorimetry
14 (DSC), which was used to obtain a first estimation of temperatures at which
15 the solid/liquid phase transition occurs. DSC results present a thermal hys-
16 teresis between melting (T_m) and solidification (T_s) temperature. A similar
17 hysteresis was also collected during rotational and oscillatory rheometry at
18 the phase change, where T_s is found to depend on the applied cooling rate.
19 Moreover, near T_s the forming solid structure is continuously affected by
20 conditions imposed by the rheometer (i.e. applied shear rate or stress) and
21 the breakage of crystals takes place even at the weak imposed stress tested
22 (0.001 Pa). Beside the bulk behavior, the local melting and solidification
23 were studied at microscopic scale through Raman spectroscopy. The local
24 melting temperature is very close to what found by DSC and by rheome-
25 try. On the other hand, crystallization onset is found at higher temperatures
26 for long waiting times, thus considerably reducing the thermal hysteresis.
27 Finally, we highlight a key influence of interfaces on the phase transition.
28 Variations in boundary conditions (thermal and/or kinematical conditions)
29 are found responsible for the way hexadecane's solidification occurs.

30 *Keywords:* Phase Change Materials, Hexadecane, Solidification, Melting,
31 Multi-scale characterization

1. Introduction

Continuous increase in fossil energy consumption and in energy supply leads to crucial impact on the climate change. Therefore, major efforts have been made in recent years to promote a more responsible use of the extracted energy. A promising way to do so concerns the optimization of technological processes via recovery and further reuse of waste heat produced. These latter constraints require the development of efficient and low-cost thermal energy storage (TES) systems.

Among the available ways to store thermal energy, the heat energy generated/absorbed during phase transition is one of the most widely used [1, 2]. Phase change materials (PCMs) which theoretically exhibit significant latent heat per unit of volume are the basic components of such thermal energy storage devices. Such materials allow to store the latent heat during the melting and release that energy during the solidification process. The main advantages of PCMs based systems lie in (i) a quasi-constant temperature at which the phase transition occurs (for mono-component PCMs or eutectics) [2, 3, 4], and (ii) the reversibility of storage/release cycles as long as the materials do not present significant ageing effects [5] or thermal instabilities [6].

The usage of PCMs can have a strong impact also on the environmental health care. In sustainable architecture, PCMs are employed for example to maintain indoor steady temperatures near the thermal comfort for long periods [5]. This decreases the need of heating, ventilating and air conditioning systems, which account to more than half of the total energy consumed in buildings [7], and therefore decreases the energy consumption and the emission of greenhouse gas, playing an important role in the decarbonization. Similarly, PCMs are involved in a large range of smart engineering processes, e.g. in the transport of food or pharmaceuticals such as vaccines [8, 9], in electronic systems [10], in smart textiles [11], etc. PCMs are also a key topic in geophysics where a clear knowledge of how thermal and mechanical properties of partial melted rocks vary near phase transitions is essential to properly model crustal magmatic systems [12].

Commercially available PCMs differ from each other in physical-chemical characteristics, thermal properties and phase transition temperatures [13, 14]. They are commonly divided in organic PCMs, inorganic PCMs and a combination of the two. Beside their usually higher latent heat and low cost, inorganic PCMs undergo corrosion, decomposition and thermal stability defi-

69 ciency, making them less attractive than the organic counterpart [5]. Organic
 70 PCMs, e.g. paraffin and fatty acid, have much more stable thermo-physical
 71 properties and more suitable phase transition temperatures for a wide range
 72 of applications. However, their main drawback falls in a quite low thermal
 73 conductivity (e.g. $\lambda \sim 0.2 \text{ W m}^{-1}\text{K}^{-1}$ for liquid paraffin waxes), that leads
 74 to slow charging and discharging rates [4, 5, 15]. There are several ways
 75 to improve the heat transfer, for instance: (1) by using micro-encapsulated
 76 PCMs [16, 17], (2) by triggering the phase change in convective regime [10],
 77 and (3) through the usage of composite shape-stabilized PCM systems that
 78 increase their thermal conductivity [18]. Micro-encapsulated PCMs (1) have
 79 the main advantage of increasing the surface to volume ratio of PCM, i.e. the
 80 effective surface where heat transfer occurs [19]. The PCM is stored as core
 81 of microcapsules and is coated with a polymer layer. This solution allows to
 82 avoid leakage and to reduce reactions with the external environment during
 83 phase transition. The second way (2) to enhance heat transfer consists in
 84 performing the phase change with convection. When, in the liquid PCM,
 85 the dominant heat transfer mode is convection, the melting rate increases
 86 and the melting interface moves faster [20]. The most common composites
 87 PCM systems (3) consists in inserting PCMs in a porous matrix with high
 88 thermal conductivity. A large amount of experimental and numerical studies
 89 has been carried out for different combination of PCMs with porous supports
 90 (e.g. metal or graphite foams, beads, etc.). A recent and extensive review
 91 on the topic is given by Zhang *et al.* [2]. Compared with the case of a pure
 92 PCM, heat is in this case more efficiently transferred away from the heating
 93 source because of the higher thermal conduction of the porous medium [21].
 94 Although any combination of methods (1) to (3) is possible, in some cases
 95 they can counteract each other. For instance, solid foams with high thermal
 96 conductivity can drastically delay the occurrence of natural convection in
 97 liquid phase [22, 23] since relative buoyancy driven forces are smaller than
 98 diffusive (dissipative) effects. As this example points out, it becomes essen-
 99 tial to understand the physical mechanisms at stake as well as being able
 100 to quantify them. This involves a detailed knowledge of materials proper-
 101 ties. Above this specific case, given the wide use of PCMs in engineering
 102 processes it is of utmost importance to properly determine their thermo-
 103 physical properties. This concerns PCMs thermal properties (e.g. thermal
 104 expansion, thermal diffusivity, melting and solidification temperatures etc.)
 105 and physical properties (e.g. viscosity) within specific time scales (e.g. fast
 106 or long runs, transient or steady state conditions), both at the phase transi-

tion and for each phase. These properties are not always easily measurable as they strongly depend on the methods/protocols involved [24, 25, 26]. An inaccurate estimation of their value or the way they vary close to the phase transition can lead to wide discrepancies in the description of the materials behavior. On the importance of the correct definition of PCMs properties, Arkar *et al.* [27] show how the thermal response of a TES system depends on the accuracy of the properties measured. The authors highlight the importance in taking into account variations of PCMs apparent heat capacity with the cooling/heating rate to which they are subjected to. These variations are critical in their models as they study the transient response of a TES system.

Beside the specific heat capacity, in problems driven by temperature variations, another crucial material property is the thermal conductivity λ . For the specific case of paraffin, if the thermal conductivity for the liquid phase alone is usually well known [e.g. 25, 28, 29], there are not many studies that report the variation of thermal conductivity between liquid phase and solid phase embracing also the phase transition region. Only recently Vélez *et al.* [15] reported an experimental study on thermal conductivity and diffusivity of three paraffins in both their liquid and solid phases by using the hot wire technique. They have found that the thermal conductivity is larger in the solid phase than in the liquid phase for any tested paraffins. Moreover, λ is found nearly constant for temperatures much lower than the melting temperature, while it slowly decreases for temperature close to the melting one. The evolution of thermal conductivity with temperature is then characterized by a sharp discontinuity once the melting temperature is reached. Even though the data at the transition show a larger dispersion of λ due to the latent heat that may have affected the temperature in the setup, Vélez *et al.* [15] always recorded a sudden jump in λ values characterizing the phase change. In the same paper, they also performed DSC measurements in order to measure the heat transfer involved during the phase change. This allows in the first place to evaluate the temperature at which the solid-to-liquid and the liquid-to-solid transitions take place. For the paraffin with a least number of carbon atoms used (i.e. hexadecane), they display a thermal hysteresis between melting and solidification temperatures of about 1 °C. This value of thermal hysteresis varies between different authors. For instance, for the same paraffin and always by measuring the transition temperatures with DSC but with faster temperature variations, Fang *et al.* [30] obtain an hysteresis of 4.6 °C whereas Moulahi *et al.* [31] and Chriaa *et al.* [32] one of

145 11.6 °C. The absolute value of such hysteresis strongly depends on the ex-
 146 perimental conditions. Moreover, the rate of cooling also plays a major role
 147 on supercooling effects [33, 34]. Supercooling takes place during the liquid-
 148 to-solid phase transition and leads to a delay in the crystallization onset,
 149 that is the material remains liquid even at temperatures smaller than the
 150 freezing temperature. Short experimental times, e.g. an increase in cooling
 151 rate, would result in an increase in the degree of supercooling, defined as the
 152 temperature difference between the melting and crystallizing temperatures,
 153 as shown by Safari *et al.* [33].

154 Thermo-physical properties have to be carefully determined with tem-
 155 perature variations since Boussinesq approximation is only valid in a narrow
 156 temperature range. Hence, properties such as viscosity η , density ρ and co-
 157 efficient of thermal expansion β must also be measured as the temperature
 158 varies, especially in the case of coupling heat transfer and fluid flows. To
 159 our knowledge, the viscosity of paraffin has been scarcely studied close to
 160 the phase transition temperature or even across the phase transition. The
 161 rheological behavior of octadecane was studied by Delgado *et al.* [35] who
 162 performed rotational and oscillatory tests at different heating/cooling rates.
 163 They found that the viscosity can span over several order of magnitudes (up
 164 to six) during the phase change. From oscillatory rheological tests performed
 165 with different temperature ramps, they were able to measure variations of the
 166 complex viscosity, i.e. the viscosity derived from measured values of storage
 167 and loss moduli, during the phase transition. As for DSC, also rheological
 168 analysis shows a thermal hysteresis between melting and solidification pro-
 169 cesses that depends on the temperature ramp imposed during the experiment
 170 [35, 36]. Similar results were obtained performing a set of intercomparative
 171 tests with different rheometers on octadecane [37] and on RT25 paraffin [38].

172 More precise analysis of phase transition requires the measurement of lo-
 173 cal state close to the melting/solidification temperature. Such insight can
 174 be obtained with the use of various spectroscopic approaches, which, from
 175 microscopical point of view, give access to vibrational properties of molecules
 176 inside the system. Such vibrations depend on the types of atoms, their inter-
 177 actions, and the distance between them; and therefore their study allows to
 178 detect structural changes with a quite good accuracy. In such way, Raman
 179 spectroscopy has been already applied for the investigation of phase transi-
 180 tion of paraffin by Marchetti *et al.* [39] and Corsetti *et al.* [40]. Specifically,
 181 they shown that from the temperature-dependent Raman spectra some well
 182 recognizable patterns can be used to decompose the contributions of the

183 liquid and solid phase. In this way, the phase transition can be detected
184 through convectional analysis of spectra with respect to wavenumbers shifts
185 and intensity ratio between specific peaks and by using principal component
186 analysis (PCA). They found that by combining these analyses, the tempera-
187 ture at which the paraffin starts to change phase is well resolved by spectra
188 changes.

189 PCMs characterization is fundamental. The literature is clearly abundant
190 on this topic, however results are scattered, mostly partial and experimental
191 conditions/protocols are often insufficiently detailed. In the present paper,
192 we propose a fully characterization of an organic PCM, i.e. hexadecane.
193 To do so, different techniques were employed and different protocols were
194 tested, leading to the determination of the main macroscopic thermo-physical
195 properties both for the two phases and during the phase change. In parallel,
196 structural information are also provided by using Raman spectra analysis.
197 They allow us to investigate accurately the crystallization and the melting
198 processes and to provide local measurements of transition temperatures.

199 Hexadecane is a straight-chain alkane hydrocarbon with 16 carbon atoms
200 and chemical formula $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$. Two properties make it attractive
201 for experiments dealing with PCMs: its high latent heat and the fact that
202 the temperature at which the phase change takes place is near the room
203 temperature [15].

204 Although widely used, literature on hexadecane lacks of experimental
205 studies regarding both a proper investigation of its thermal properties and
206 rheological behavior near the phase transition. By covering the phase tran-
207 sition region we provide, in section 2, novel values of thermal conductivity
208 for both solid and liquid phase. Moreover, we discuss the impact that ex-
209 perimental conditions may have on the proper measurement of transition
210 temperatures since the thermal hysteresis between melting and solidification
211 processes is found to be dependent on the heating/cooling rate. Afterward
212 we provide in section 3 the first experimental rheological analysis for hexade-
213 cane during the phase change. As pointed out in [35], there are surprisingly
214 only few experimental studies dealing with the rheological behavior of *n*-
215 alkane, none of which employ hexadecane. Similarly to Delgado *et al.* [35],
216 we performed rotational and oscillatory tests with varying heating/cooling
217 rates where the role played by either the shear rate or the stress is high-
218 lighted. Carrying out oscillatory tests in addition to standard rotational
219 tests is crucial to provide rheological properties of PCMs when a solid phase
220 develops. This is because, for small solicitations, oscillatory tests modify the

sample's structure as little as possible and let the crystals grow. In the same section we propose further original rheological tests during the phase change where we followed the time evolution of the bulk deformation and viscoelastic moduli at constant temperature. The structural investigation of the PCM is provided in section 4 by exploring locally the phase change by Raman spectroscopy. A systematic analysis of temperature dependent patterns in Raman spectra of hexadecane is then given by showing the main differences recognizable during both the melting and the crystallization of the sample. Discussion and conclusions end the paper in the last section 5.

2. Hexadecane physical and thermal properties at the macroscopic scale

The samples of hexadecane were supplied by Sigma-Aldrich (CAS number 544-76-3). They were labeled as 99% pure and with a phase change temperature of $T=18$ °C. They were used as received, i.e. without any further purification or removing impurities.

2.1. Density and thermal expansion

The temperature dependence of density was measured for hexadecane (sample volume ~ 1 mL) at ambient atmospheric pressure with a DMA 5000M Anton-Paar densimeter which allows measurements only for liquid materials. For hexadecane, data were collected every 1 °C from temperature $T=40.0$ °C to $T=16.0$ °C. For the latter temperature the sample was still liquid, we attribute this to undercooling effects. The waiting time for measurement stabilization was about five minutes. Without phase change, this stabilization time was sufficient given the small volume of fluid employed, and results were reproducible with a maximum variation of 5×10^{-6} kg m $^{-3}$. The resulting dependence of density on temperature is shown in Fig. 1 where it is also linearly fitted by the equation

$$\rho(T) = -0.6854 T + 787.2 \text{ kg m}^{-3}, \quad (1)$$

with T in °C. Equation (1) is obtained from our experimental data only and, by considering other measurements provided in [41] and [42], it is also valid for a wider range of temperature (Fig. 1).

The coefficient of volumetric thermal expansion is linked to the density through $\beta(T) = -\rho^{-1}(\partial\rho/\partial T)$. From our density measurements within the

257 *2.2. Thermal conductivity*

Figure 2: Hot tube device used to measure the thermal conductivity. (a) Photo of the entire setup where (I) indicates the hot tube device; (II) the current generator; (III) the temperature data logger (Almemo 2890-9, Ahlborn); (IV) an homemade device to measure the difference in voltage between the two thermocouples; and (V) the thermal Bath (Julabo eco). (b) Schematic representation of the hot tube device alone. The device consists of two co-axial cylinders of height $H=200$ mm. The inner stainless-steel-cylinder has an internal radius $r_0=2.54$ mm and an external radius $r_1=2.76$ mm. The outer cooper-cylinder has an internal radius $r_2=6.00$ mm and an external radius $r_3=7.00$ mm and it is in contact with a water flow.

270 Temperatures were measured by two K-type thermocouples positioned at
 271 the interfaces between cylinders and PCM sample; i.e. the first one (mea-
 272 suring T_1) was positioned at $r = r_1$ and the second one (measuring T_2) at
 273 $r = r_2$, both at half of the the cylinders height in order to avoid any up-down
 274 wall effects.

275 Within this framework, the thermal conductivity can be calculated from
 276 the following expression:

$$\lambda = \frac{\rho_e I^2 \ln(r_2/r_1)}{2\pi^2(r_1^2 - r_0^2)(T_1 - T_2)}, \quad (2)$$

277 where ρ_e is the specific electrical resistivity of stainless steel and I the elec-
 278 trical intensity. Within our experiments, the temperature difference $T_1 - T_2$
 279 varies from 3 °C to 10 °C. Figure 3 shows how the thermal conductivity of
 280 hexadecane evolves as a function of the mean temperature between the two
 281 cylinders, i.e. $\bar{T} = (T_1 + T_2)/2$. Measurements were carried out within a range
 282 of $\bar{T}$ between 6 and 37 °C. Thermal conductivity data and corresponding
 283 temperatures measured by thermocouples are summarized in supplementary
 284 material.

285 The first measurement of λ was carried out in the solid phase at $\bar{T}=6.3$ °C.
 286 The temperature was much smaller than the melting temperature suggested
 287 by the manufacturer in order to ensure that the entire sample volume was
 288 solid. Each step in solid and liquid phase lasted 20 minutes, long enough to
 289 guarantee that the difference in temperature between the two thermocouples
 290 reached steady state. Steps were longer (around two hours) during the phase
 291 transition.

292 In the solid phase, results are displayed in Fig. 3 (blue symbols). The
 293 thermal conductivity is found mainly constant with an averaged value of
 294 $\lambda=0.341$ W m⁻¹K⁻¹. Measurements were carried out about 2 or 3 times in
 295 order to verify the reproducibility of the results. It is all the more important
 296 to repeat runs since the volume decreases during the liquid-to-solid transition.
 297 In the case of hexadecane the volume shrinkage is moderate, preventing then
 298 any thermal resistance through the PCM layer and at the interfaces between
 299 PCM and tube - at least at half the height of the setup. Finally, a good
 300 agreement in the thermal conductivity of the solid phase is obtained with
 301 the value provided by Vélez *et al.* [15] which used another method, i.e. the
 302 transient hot wire method.

303 We proceeded afterward toward the melting of the sample by increasing
 304 the temperature through different steps. In our experiments, the thermal

conductivity varies strongly in the $\bar{T}$ range of 15-20 °C, i.e. close to the melting temperature T_m . Results in this second temperature range should correspond to a case where both a liquid substrate (near the heat source) and a solid one (far from the heat source) coexist inside the PCM layer (green symbols in Fig. 3).

When both T_1 and T_2 are above T_m , the resulting thermal conductivity corresponds to the one of the liquid phase (red symbols in Fig. 3). A third and quasi constant value of λ is obtained ($\lambda=0.150 \text{ W m}^{-1}\text{K}^{-1}$) in the $\bar{T}$ range between 20 °C and 37 °C.

Both values of λ in solid and liquid phases are in good agreement with values given by Vélez *et al.* [15]. The deviations between our values of λ and those of Vélez *et al.* are 6% and less than 1% in liquid and solid phase, respectively. However, our measurements are quite different to those proposed by Holmen *et al.* [44]. In this latter work, authors followed the freezing or melting front velocity in a layer of PCM presenting two superimposed phases. In this configuration, they proposed theoretical expressions for thermal conductivity of both phases by considering a thermal gradient only in the appearing phase. In our opinion, this assumption is quite difficult to reach experimentally. Beyond this aspect, their theoretical expressions for λ highlight a strong dependency on other main parameters (e.g. melting point, interface evolution with time) whose measurements are not trivial and can lead to relative large errors. In particular, the melting point can vary with experimental conditions. Holmen *et al.* reported a total error in measuring λ of about 18% for both liquid and solid phase. These sources of inaccuracy can explain the differences obtained between their results and ours and those of Vélez *et al.*. Deviations between our values of thermal conductivity λ and those proposed by Holmen *et al.* [44] are indeed about 15% and 33% in solid and liquid phase, respectively.

As a remark, we mention that the temperature that triggers the solid-to-liquid transition as well as the one at which the sample freezes entirely are badly resolved with our hot tube setup since it does not allow any optical access. Furthermore, the thermal conductivity is obtained via a temperature variation across the PCM layer. For this reason, we would expect a PCM layer composed of a liquid part and a solid part around the phase change temperature. Methods presented in the following sections are more relevant for this purpose.

Figure 3: Thermal conductivity λ of hexadecane as a function of temperature. $\bar{T}$ is the mean temperature between the inner and outer cylinders.

2.3. Melting and solidification temperatures, latent heat and specific heat capacity

Differential scanning calorimetry (DSC) is a common thermal analysis technique employed to measure heat transfer involved in a small volume of material subjected to temperature variations. It allows to determine the melting and solidification temperatures, T_m and T_s respectively, as well as the latent heat ΔH_m and ΔH_s associated with melting and solidification phase transitions. Furthermore, it is useful also for measuring the specific heat capacity c_P at atmospheric pressure in the solid and liquid phases. For this purpose, we used a SETARAM μ DSC3 evo calorimeter in order to characterize hexadecane within a temperature range of 10-37 °C. A sample mass of ~ 200 mg was placed within a small crucible, the latter with a surface of average roughness of $R_a = 0.16 \mu\text{m}$ (measured with a Taylor Hobson Surtronic S116 surface roughness tester). For DSC measurements, we adopted two different protocols, one to better resolve the phase transition temperatures, and another one to estimate the heat capacity.

In the first case, the heat flux was recorded as a function of time to obtain the melting and solidification temperatures with temperature increments of about 0.5 °C for both melting and freezing processes. Each increment lasted

~2 hours in order to ensure that the heat flux had vanished, the following increment was then reached with a rate of 0.2 °C/min. Figure 4 shows the measured heat flux (in blue) for the different temperature increments (in red) both during temperature rise (Fig. 4a) and drop (Fig. 4b).

From Fig. 4a, the melting temperature of hexadecane is found between 17.2 and 17.7 °C. This interval of T_m includes values of melting temperature reported in other studies, most of which report temperatures that are within $18.0\text{ °C} \pm 1.7\%$ (for instance $T_m=18.1\text{ °C}$ in [45], 17.75 °C in [15], 18.3 °C in [46] and 18.0 °C in [47]). Despite this good agreement of T_m , the solidification temperature is not well defined in these articles, and only few studies explicitly report it. From Fig. 4b, we evaluate the bulk solidification temperature of hexadecane between 15.0 and 15.5 °C, leading to an apparent thermal hysteresis of about 2 °C between the melting and the solidification of the sample. Our result of T_s deviates of about 8-10% from others DSC measurements with 2 °C/min [15] and 10 °C/min [31] cooling rates. A possible reason of such a large discrepancy can be either found in their higher solidification rates or their small amount of sample used during the DSC scans (less than 10 mg in [15] and [31]).

Heat capacity and latent heat were measured within the temperature range of 11.2 and 37.5 °C. Temperature increments were in this case of about 2 °C, and they were obtained with a cooling/heating rate of 0.2 °C/min. The apparent heat capacity is displayed in Fig. 5. Within this temperature range, we obtain a constant value of heat capacity in liquid phase, i.e. $c_p=2.24\text{ kJ kg}^{-1}\text{K}^{-1}$. In solid phase the heat capacity increases with temperature and we do not obtain a constant value within our experimental conditions. This was also observed in other works, e.g. [15] and [48]. In addition, in Fig. 5 the phase change is clearly observed since heat flux (or apparent heat capacity) varies strongly at the transition. We obtain a latent heat of melting $\Delta H_m=232.55\text{ kJ kg}^{-1}$ and a latent heat of solidification $\Delta H_s=235.95\text{ kJ kg}^{-1}$.

3. Rheological behavior

We performed rheological analysis on both liquid hexadecane and during the liquid-to-solid transition. A stress-controlled AR-G2 rheometer (TA Instruments) was used in rotational and oscillatory modes.

For fully liquid hexadecane we used both cone-plate and plate-plate geometries to obtain viscosity. Given the low viscosity of the material in liquid

Figure 4: Heat flow rate measured from the DSC (in blue) and imposed temperature steps (in red) as a function of time. (a) Melting of hexadecane. (b) Solidification of hexadecane.

Figure 5: Apparent specific heat capacity as a function of the mean temperature of each temperature step, for both melting and solidification processes.

396 phase we used a large diameter (60 mm) for both plate and cone in order
 397 to increase the accuracy of measurements. More specifically, in cone-plate
 398 we used a 60 mm wide plate with a cone angle of 2° and a standard gap
 399 of $70 \mu\text{m}$. Both geometries lead to same results. Cone-plate geometry was
 400 used only to investigate viscosity of hexadecane in the liquid phase. At the
 401 phase change, when a solid structure develops and crystals grow, the small
 402 gap imposed by the cone-plate geometry limits the measurements (the size
 403 of solid components should not exceed the 10% of the gap to guarantee rep-
 404 resentative measures). For this reason, during the phase transition it is more
 405 appropriate to choose and use a plate-plate geometry in which the gap be-
 406 tween plates can be adapted. For plate-plate geometry we used plates of
 407 diameter of 32, 40 and 60 mm and gaps of 1000 and $1200 \mu\text{m}$. These gaps
 408 were found as the best compromise between ensuring isothermal conditions
 409 (i.e. low temperature differences through the sample) and guarantee an ad-
 410 equate distance between plates. Gaps of 500 and $2000 \mu\text{m}$ were also tested.
 411 Both of them did not provide suitable results: in the first case the gap was
 412 too small compared with the size of the crystal structure, while in the second
 413 case we always observe a temperature gradient through the PCM layer.

414 Temperature was controlled by a Peltier plate which was covered by the

415 fluid sample, the volume of which depends on the gap between the plates.

416 3.1. Liquid phase

417 Hexadecane's rheological properties were first determined in the liquid
418 phase at different temperature values. We found liquid hexadecane being
419 Newtonian with a temperature-dependent viscosity (η). The latter was in-
420 vestigated in more details from temperatures close to the transition to 40 °C
421 (Fig. 6). Within this interval of temperatures, viscosity of hexadecane ex-
422 ponentially decreases with increasing temperature following an exponential-
423 type dependency that writes

$$\eta(T) = a e^{b(T-T_0)}, \quad (3)$$

424 with $a=3.3 \times 10^{-3} \text{ Pa s}^{-1}$, $b=-1.9 \times 10^{-2} \text{ }^\circ\text{C}^{-1}$ and $T_0=20.0 \text{ }^\circ\text{C}$, as represented
425 by the continuous line in Fig. 6b.

426 3.2. Phase transition

427 The phase transition was first analyzed following the evolution of hex-
428 adecane rheological properties during different temperature ramps (in both
429 rotational and oscillatory modes). This procedure allows to investigate vari-
430 ations in viscosity (rotational mode) and in viscoelastic moduli (oscillatory
431 mode) when crystallization starts and a solid structure develops.

432 Afterwards, we report the analysis of results obtained performing time
433 sweep tests at steady temperature.

434 3.2.1. Temperature ramps

435 We first carried out rotational tests at fixed value of shear rate $\dot{\gamma}$ dur-
436 ing which the sample was subjected to a temperature ramp (1.0, 0.5 or 0.2
437 °C/min) from an initial value of 20 °C down to temperatures below the so-
438 lidification one (T_s).

439 We used a plate of 32 mm in diameter with a constant gap (equal to
440 1000 μm), while different shear rates were tested, i.e. $\dot{\gamma}=0.1, 1, 10$ and 50
441 s^{-1} . Figure 7 shows the evolution of viscosity as a function of temperature.
442 One can observe how viscosity increases of about 4 orders of magnitude
443 from liquid to solid phase, with a transition temperature close to the one
444 obtained by DSC which, however, depends on the chosen temperature ramp.
445 As expected, for large temperature ramp (i.e. 1.0 °C/min), we always observe
446 solidification temperatures lower than what obtained with the smallest ramp

Figure 6: Viscosity of liquid hexadecane as a function of temperature obtained for different rheometer geometries. For measurements with plate-plate geometry (circles) we used a 60-mm-wide plate, the gap was fixed and equal to $1000 \mu\text{m}$ and the imposed shear stress was 0.1 Pa . In measurements with cone-plate geometry (squares), the cone angle was 2° , the gap was $70 \mu\text{m}$ and the imposed shear stress was 0.1 Pa . The black line is the data fit.

447 (i.e. 0.2 °C/min). Moreover, in Fig. 7c the ramp 0.2 °C/min leads to a
 448 slightly smaller hysteresis than the one observed with DSC (grey region in
 449 the figure).

450 Beside the fact that a lower cooling rate can decrease the hysteresis be-
 451 cause it ensures more time for crystals to nucleate and grow, one can also
 452 expect a dependence of T_s on the imposed shear rate. Although shear flow
 453 can lead to a homogenization of temperature by advection (here the flow does
 454 not lead to recirculation), its main impact remains linked to the breakage of
 455 solid clusters and weak crystals. This is similar to what happens in weakly
 456 sheared hard-sphere colloids, where at low supersaturation, crystallization
 457 rate decreases as the strain rate increases [49]. This occurs when the forces
 458 exerted by the shear flow overcome the driving force of crystallization, lead-
 459 ing to the breakage of the forming solid clusters. However, in the case of
 460 Fig. 7, we do not observe any relevant shifts of hexadecane’s solidification
 461 temperature when varying $\dot{\gamma}$. A possible explanation is that even the low-
 462 est shear rate tested here ($\dot{\gamma}=0.1 \text{ s}^{-1}$) affects the system by breaking down
 463 crystals and weakening the forming solid structure as should be the case for
 464 higher $\dot{\gamma}$.

465 A way to reduce the influence of measurements on the phase transition
 466 process is to proceed to oscillatory tests. We carried out time sweep tests for
 467 both solidification and melting processes by imposing small stress amplitudes
 468 and by using a 40-mm-wide plate. Both the gap between plates (here equal
 469 to 1200 μm) and the frequency ($\omega=10 \text{ rad s}^{-1}$) are kept constant. Tests
 470 started from a liquid sample previously pre-sheared for around 5 minutes at
 471 $T=20 \text{ °C}$. In order to solidify the sample a decreasing temperature ramp of
 472 1 °C/min was then applied until the temperature reached 12 °C. When the
 473 latter was achieved, the same increasing temperature ramp was applied from
 474 12 °C to 20 °C in order to melt again the sample. In Fig. 8 we show the
 475 results obtained for an imposed amplitude stress of $\sigma=2 \text{ Pa}$ (Fig. 8a) and
 476 $\sigma=0.2 \text{ Pa}$ (Fig. 8b). Similarly, in Fig. 9 we show results achieved with a
 477 smaller temperature ramp (0.2 °C/min) and smaller stresses.

478 Within these experimental conditions, we clearly obtain in both cases a
 479 temperature hysteresis around the phase change. While the melting tempera-
 480 ture is always close to that obtained with DSC, the solidification temperature
 481 varies considerably depending on the applied conditions. For a large temper-
 482 ature ramp (Fig. 8), T_s is quite small and is found to be around 13 °C for
 483 both tested stresses. The resulting hysteresis is thus larger than the one from
 484 DSC. Similarly to what observed in rotational mode, by applying a slower

Figure 7: Variation of viscosity η as a function of temperature T from rotational test during the solidification of hexadecane. Three temperature ramps were used: a decrease of (a) 1.0 °C/min, (b) 0.5 °C/min and (c) 0.2 °C/min. The gray box shows the interval of solidification temperature T_s obtained from DSC (i.e. in between 15.0 and 15.5 °C). Different symbols represent different shear rates, $\dot{\gamma}=[0.1, 1.0, 10, 50]$ s⁻¹. Data points represent the average of at least three runs with the same conditions.

485 ramp instead (Fig. 9), the hysteresis significantly reduces and T_s moves to a
 486 temperature around 16 °C. However, it is still not easy to infer whether this
 487 thermal hysteresis is a real material property or it is mainly due to the chosen
 488 cooling rate and applied shear rate or stress. Differences between Fig. 8 and
 489 Fig. 9 remain crucial and they need to be taken into account once dealing
 490 with processes with fast temperature variations rather than with slow ones.

491 The complex viscosity, $\eta^* = (G'^2 + G''^2)^{1/2}\omega^{-1}$, and the viscosity, η , ob-
 492 tained from oscillatory and rotational measurements, respectively, are shown
 493 in Fig. 10 for a cooling rate of 0.2 °C/min. Here we present curves for ro-
 494 tational measurements with imposed strain rate of 0.1 and 50 s⁻¹, together
 495 with those ones for oscillatory measurements with imposed stress of 0.2 and
 496 0.02 Pa. For this temperature ramp, between the two methods we observe
 497 only small differences in the temperature below which crystallization begins
 498 (less than 1 °C). However, a larger discrepancy arises when looking at the
 499 value of viscosity achieved after the liquid-to-solid phase change: here it can
 500 span up to three orders of magnitude at, for instance, $T=14.0$ °C < T_s . These
 501 evidences suggest that even for such small shear stresses in oscillatory mode
 502 and strain rates in rotational mode, the conditions imposed by the rheome-
 503 ter have some significant influences on the nucleation and/or crystallization
 504 process.

505 3.2.2. Steady temperature

506 To avoid issues related with a too large temperature ramp we performed
 507 oscillatory time sweep tests at fixed temperature. This procedure allows to
 508 follow the transient behavior of the material at a given temperature and to
 509 obtain insights about time scales of the phase transition.

510 We focused on a short range of temperatures around the solidification
 511 temperature T_s obtained by DSC, where very fine oscillatory tests with an
 512 imposed shear stress of 0.001 Pa were carried out. Although such a small
 513 imposed stress was chosen to investigate the beginning of crystallization and
 514 the solidification of the sample, we do expect it to be too small to obtain
 515 reliable data in liquid phase because of the low viscosity of liquid hexadecane.
 516 This is the reason of noisy results in liquid hexadecane in what follows. We
 517 worked with a frequency of $\omega=10$ rad s⁻¹, a gap of 1000 μ m and a 40-mm
 518 diameter plate. Given the long duration of each run, during the measurement
 519 we used an anti-evaporation device that covered the moving plate and the
 520 sample. Each experiment started with a liquid sample of hexadecane at
 521 initial temperature $T_0=20.0$ °C to which a single temperature step was then

Figure 8: Hexadecane's temperature dependence of storage G' (blue symbols) and loss G'' (red symbols) moduli during melting (crosses) and solidification (circles) processes, for imposed stress of 2.0 Pa (a) and 0.2 Pa (b). The initial liquid sample was first solidified and then remelted by using a temperature ramp of $1^{\circ}\text{C}/\text{min}$.

Figure 9: Hexadecane's temperature dependence of storage G' (blue symbols) and loss G'' (red symbols) moduli during melting (crosses) and solidification (circles) processes, for imposed stress of 0.2 Pa (a) and 0.02 Pa (b). The initial liquid sample was first solidified and then remelted by using a temperature ramp of 0.2 $^{\circ}\text{C}/\text{min}$.

Figure 10: Temperature dependence of viscosity η and complex viscosity η^* for solidification processes with temperature ramp of $0.2\text{ }^{\circ}\text{C}/\text{min}$. The complex viscosity is retrieved for oscillatory tests with imposed stress of 0.2 and 0.02 Pa. For rotational tests we show the cases with constant shear rate of 0.1 and 50 s^{-1} .

522 applied, i.e. temperature was decreased from T_0 directly to the desired value
523 (see an example in the inset of Fig. 11a).

524 In Fig. 11 we show for an imposed temperature of $T=15.0$ °C the time
525 evolution of G' and G'' and the one of the normal force exerted by the sample
526 on the upper plate of the system. Three main material responses can be
527 observed from the curves of the moduli (Fig. 11a). The first step (i) regards
528 a noisy stage that lasts a couple of minutes in which the sample is still fully
529 liquid. In the second step (ii), that starts after about three minutes, the
530 structure seems to change and the material response shows an overall liquid
531 behavior where its viscous component is larger than the elastic one ($G'' > G'$).
532 The last step (iii) starts around 8-10 minutes after the beginning, when
533 the crossover between G' and G'' takes place. Here the sample behavior is
534 prevailed by its solid-elastic response with values of storage modulus ($G' \sim 25$
535 Pa) and loss modulus ($G'' \sim 18$ Pa) that remain constant till the end of the
536 run. The same behavior is shown in Fig. 12 at three other temperatures,
537 i.e $T=14.5$, 15.5 and 16.0 °C. For each case we see the same three stages
538 described above, with a solid-elastic behavior that becomes more pronounced
539 with time. We were able to detect the crossover between G' and G'' until
540 $T=16.0$ °C, but not for higher temperatures. Although for $T=16.0$ °C the
541 difference between G' and G'' remains very small (only few Pa), this latter
542 temperature is much like the apparent solidification temperature obtained
543 from rotational and oscillatory tests with temperature ramp of 0.2 °C/min
544 (Fig. 10).

545 Changes also occur in the slope of the normal force during the mention
546 stages (Fig. 11b and Fig. 12b). For instance, during stage (ii) the nor-
547 mal force decreases due to the sample volume reduction caused by sample
548 crystallization (Fig. 11b). However, in stage (iii) the reduction in volume is
549 countered by an increment of normal force. The latter can be related to crys-
550 tals being formed that push against the upper plate of the rheometer. After
551 this increment, the value of normal force seems also to vary cyclically around
552 a mean constant value. These cycles are characterized by periods where the
553 normal force decreases almost linearly with a step-like behavior. We point
554 out that the period of such cycles is around a couple of minutes, thus it
555 is not linked to the oscillation period of the rheometer that is $2\pi\omega^{-1}=0.63$
556 s. Such variation of normal force most likely highlights phenomena at the
557 plate-sample interface. Indeed, at $T=16.0$ °C we observed by eyes the sample
558 being in its solid phase except on its upper surface where a thin layer of liquid
559 phase persists. This thin liquid layer was very likely due to the friction with

560 the moving plate.

561 These evidences indicate that even at this weak imposed stress (0.001 Pa),
562 corresponding to low strains (ranging from 10^{-3} to 10^{-5} after the crossover
563 point between G' and G''), and long waiting time, an imposed oscillation
564 affects constantly the solidification process by breaking the forming crystals
565 at least nearby the moving plate for temperatures near the transition. This
566 results in a weaker structure compared to that obtained for lower tempera-
567 tures, as highlighted by the low values of G' and G'' observed in Fig. 11a
568 with respect to those obtained with small temperature ramps in the solid
569 phase (e.g. in Fig. 9).

570 4. System at rest and local investigation with Raman spectroscopy

571 The onset of hexadecane’s phase change was also investigated for the sys-
572 tem at rest (i.e. without any imposed deformation) by Raman spectroscopy.
573 This spectroscopy technique is based on the inelastic scattering of light and
574 it allows the investigation of spectra that are directly linked to vibrational
575 modes of the chemical bonds present in the analyzed sample’s molecules.

576 In order to collect scattered light at different temperatures, a setup con-
577 sisting of a copper plate laying on a Peltier element was used (Fig. 13). A
578 15.0 mm-deep and 37.7 mm-wide square cavity was made in the center of
579 the plate. The cavity lateral surface has an average roughness of $R_a=0.60$
580 μm , while the average roughness of the bottom surface is $R_a=1.60$ μm . The
581 cavity was filled by around 16 mL of hexadecane to form a ~ 11 mm-high
582 fluid layer with a free upper surface. Isothermal conditions were obtained
583 in the bulk sample by adding a thick layer of insulating foam around the
584 lateral walls of the device and a glass surface on the top of the system as
585 represented in Fig. 13. This latter glass plate has a thickness of 0.55 mm
586 and a transmittance of 90.5% at the laser wavelength (see supplementary ma-
587 terials). Hexadecane was then cooled or heated to the chosen temperature
588 and kept at that constant temperature for several hours before acquiring the
589 spectra. Temperature was recorded by a PT100 platinum resistance ther-
590 mometer placed inside the lower part of the copper plate as indicated in Fig.
591 13. The distance between the bottom of the sample reservoir and the central
592 axis of the thermometer is 3.8 mm. When the liquid sample was solidified,
593 crystallites formed far from cavity walls were usually small (mm-scale) and
594 randomly oriented.

Figure 11: Oscillatory time sweep with imposed stress of 0.001 Pa and gap of 1000 μm . Temperature is decreased by a single step from $T_0=20.0$ °C to $T=15.0$ °C and kept constant afterwards as shown by the inset in (a). (a) Time evolution of the storage modulus G' (blue) and loss modulus G'' (red). (b) Time evolution of the normal force.

Figure 12: Oscillatory time sweep with imposed stress of 0.001 Pa, gap of 1000 μm , and for temperatures of $T=14.5$ (circles), 15.5 (squares) and 16.0 °C (crosses). (a) Time evolution of the storage modulus G' (blue) and loss modulus G'' (red). (b) Time evolution of the normal force.

Figure 13: Heating and cooling system for Raman analysis. $T(t)$ indicates the point where temperature is recorded.

595 Laser beam with wavelength equal to 532 nm (power ~ 25 mW) was fo-
 596 cused on the top of the sample layer. The laser excited the sample only
 597 during the acquisition of the spectra (acquisition time of 1000 ms) in order
 598 to avoid any additional heating. The scattered light from the sample was
 599 finally collected by a spectrograph (HRS-750 Princeton Instruments) with
 600 entrance slit width of $200 \mu\text{m}$ and grating of 600 lines per mm. All spectra
 601 were here acquired with a 10x objective and with accuracy of 1.5 cm^{-1} .

602 The first way to identify the phase transition with Raman spectroscopy
 603 is through the observation of how peaks intensity and position change with
 604 temperature and time.

605 We focused our spectra analysis within the CH_2 and CH_3 stretching region
 606 of hexadecane's Raman spectra. It corresponds to the interval of Raman shift
 607 from around 2800 to 3100 cm^{-1} [50, 51]. Within this region, the band near to
 608 2850 cm^{-1} (P_1) and the one near to 2885 cm^{-1} (P_2) correspond to the CH_2
 609 symmetric and asymmetric molecule stretching, respectively. Bands near
 610 2930 cm^{-1} (P_3) and 2957 cm^{-1} (P_4) are instead due to the CH_3 symmetric
 611 and asymmetric stretching, respectively [40].

612 4.1. Raman spectra of solid and liquid phases

613 Peaks intensity within the CH region is displayed in Fig. 14 for solid
 614 hexadecane at $T=12.0 \text{ }^\circ\text{C}$ (Fig. 14a) and liquid hexadecane at temperature

615 $T=18.5, 19.7$ and 30.0 °C (Fig. 14b).

616 A main difference between spectra of solid (Fig. 14a) and liquid phase
617 (Fig. 14b) concerns peaks P_1 and P_2 . In solid phase, P_2 is always obtained
618 more intense than P_1 , leading to a ratio P_2/P_1 larger than one ($P_2/P_1=1.07$
619 for the case in Fig. 14a), while in liquid hexadecane P_2 becomes wider and
620 smaller than P_1 ($P_2/P_1=0.89$ in Fig. 14b). Similarly, peaks of CH_3 stretching
621 also change during the phase transition. Both peaks for the CH_3 symmetric
622 stretching (P_3) and CH_3 asymmetric stretching (P_4) are narrower and easier
623 to recognize in the solid phase than in the liquid phase. The evolution of
624 Raman peaks intensities can be used as a marker of phase transition, as
625 shown by Duričković *et al.* [52]. Indeed, they shown that the water-ice
626 phase change can be determined by following the ratio of intensities of main
627 peaks (i.e. the most intense one and the one that changes most significantly
628 during the transition) for different spectral bands. They shown that the
629 determination of solidification temperature and the identification of the two
630 phases was possible by following the peak intensities ratio obtained both
631 from the intensities at fixed wavenumbers and from integrated intensities of
632 wavenumbers ranges (as long as the characteristic wavenumbers of the two
633 phases were included). The same method was afterwards employed also to
634 determine the concentration of salt in aqueous solutions [53, 54].

635 4.2. Evolution of Raman spectra during solidification

636 Figure 15a shows the evolution of the ratio P_2/P_1 during the solidifica-
637 tion of hexadecane as temperature decreases. The initially liquid sample was
638 cooled by decreasing the temperature with steps of ~ 0.2 °C separated from
639 each other by several hours. Color bars in the figure refer to the time (in
640 hours) elapsed between the change in temperature and the acquisition of the
641 scan. All Raman scans were here performed at fixed position without moving
642 the setup throughout the duration of the experiment. The ratio between P_2
643 and P_1 for the liquid phase remains constant around 0.86 until the temper-
644 ature reaches $T=17.3$ °C. At this temperature, hexadecane locally begins to
645 crystallize since P_2/P_1 slowly increases. The difference from the ratio asso-
646 ciated to the purely liquid phase starts to be more clear after a waiting time
647 of around 24 hours from the previous temperature change. After around 72
648 hours P_2/P_1 reaches the value of 0.98, marking a significant difference with
649 the constant value obtained in the liquid phase for higher temperatures. A
650 similar trend is also observed at $T=17.1$ °C where P_2/P_1 further increases
651 with time and only after ~ 4 hours reaches a steady value. For $T \leq 16.9$ °C

Figure 14: Raman spectra of hexadecane within the CH region. (a) Solid phase at $T=12.0$ °C; (b) liquid phase at $T=18.5$, 19.7 and 30.0 °C. P_1 represents the peak associated to the CH_2 symmetric stretching ($\sim 2856 \text{ cm}^{-1}$), P_2 the peak associated to the CH_2 asymmetric stretching ($\sim 2883 \text{ cm}^{-1}$), P_3 the peak associated to the CH_3 sym. stretching ($\sim 2938 \text{ cm}^{-1}$), P_4 the peak associated to the CH_3 asym. stretching ($\sim 2968 \text{ cm}^{-1}$).

the dependence of P_2/P_1 on the waiting time seems to be no longer so relevant and the value of the ratio between peak intensities settles down around a new constant value.

Besides the intensity ratio, also the position of peak P_2 evolves both in time and temperature (Fig. 15b). In fact, although the intensity of a Raman peak depends on the concentration of the oscillators, the position of the peak is defined by the frequency of the oscillation. Therefore, peak's intensity and position correspond to different properties from a physical point of view, and both of them can be useful to identify the phase transition. In our case, a strong transition is recognizable for peak P_2 at $T=17.3$ °C where it moves from around 2896 cm^{-1} to around 2882 cm^{-1} . The transition at this temperature is not abrupt, instead with increasing waiting time the peak slowly proceeds toward the solid phase position in a similar way to what observed for P_2/P_1 .

4.3. Differences between melting and solidification

Reciprocally, similar experiments were conducted for the solid-to-liquid transition. Results are depicted in Fig. 16 in terms of P_2/P_1 as a function of temperature for different melting experiments (triangles) and different solidification experiments (circles). For the melting process, the local transition takes place at $T_m=17.7$ °C, i.e. when the ratio P_2/P_1 becomes smaller than 1. This transition occurs over shorter times than the crystallization process. The evolution of peaks within the CH region that we obtained during the solid-to-liquid transition is in agreement with experiments of Corsetti *et al.* [40], whom reported for the melting of hexadecane an almost instantaneous transformation in Raman spectra at $T=18.1$ °C.

As previously noted, within the experimental conditions of the first solidification process carried out (red circles in Fig. 16), solidification starts around $T=17.3$ °C if enough time is waited. Below this temperature we obtain $P_2/P_1 > 1$, meaning that the threshold value $P_2/P_1 = 1$ can be used as a criterion to distinguish between liquid and solid phase. In this way we observe a very small hysteresis between melting and solidification temperatures. This difference could be further reduced by inducing crystals nucleation via additional perturbations at interfaces. This latter point will be investigated deeply in a future work.

Following a similar solidification protocol but with larger temperature steps (green circles in Fig. 16), the increase in P_2/P_1 occurs at $T=17.0$ °C. As highlighted in Fig. 16, here at point 'A' the ratio P_2/P_1 is smaller

Figure 15: Evolution of Raman peaks intensity and position during hexadecane solidification. Starting from a liquid sample at $T=18.6^{\circ}\text{C}$, temperature was decreased to $T=16.3^{\circ}\text{C}$ with steps of around 0.2°C . Color bars indicate the waiting time (in hours) between the change in temperature and the acquisition of the scan. The longest waiting time is ~ 72 hours at $T=17.3^{\circ}\text{C}$. (a) Variation of the ratio between the intensity of the peak associated to the CH_2 asymmetric stretching (P_2) and the intensity of the peak associated to the CH_2 symmetric stretching (P_1) as a function of temperature and time. (b) Raman shift of peak P_2 as a function of temperature and time.

689 than 1 (corresponding to liquid phase), while at point ‘B’ it becomes larger
690 than 1 (corresponding to solid phase). This variation took place in ~ 5.5
691 hours, pointing out that the solidification process requires shorter times in
692 the subcooled region, i.e. below $T=17.3$ °C.

693 Additionally, although we observe that P_2/P_1 remains constant in the
694 liquid phase, it can take different values in the solid phase as shown in Fig.
695 16. This can be due either to (1) the formation of differently oriented crystals
696 [55], or (2) the presence of both crystalline and glass phase [56]. We deal
697 with this in the next section where a description of only the solid phase of
698 hexadecane is given. However, given the large variety of P_2/P_1 in the solid
699 phase that could affect a correct choice of the transition temperature, one
700 should also consider how other characteristics of the spectra vary and evolve
701 as temperature changes.

702 We carry out the principal component analysis (PCA) for all scan ac-
703 quired to evaluate if the entire set of Raman spectra in the CH-region changes
704 during the phase transition congruently with P_2/P_1 . PCA allows us to re-
705 duce dimensionality of a data set with large number of variables and to find
706 specific aspects that represent the variance of the data. By using PCA the
707 large number of variables needed to originally describe the data set (i.e. all
708 the wavenumbers) can indeed be reduced to just a few new variables (i.e. the
709 principal components) which account for the majority of its variability. Once
710 the principal components that characterize the entire set of acquired spectra
711 are extracted, each spectra can be represented in the principal component
712 space by its principal component scores. In the principal component space
713 the identification of similar spectra from the very different ones is done by
714 discerning how they are clustered together.

715 As pointed out by [39], the use of PCA over peak intensity ratio brings
716 some advantages in studying the phase transition of a PCM. For instance, to
717 calculate an intensity ratio representative of phase change one must identify
718 the correct spectral bands that characterize the transition (e.g. P_1 and P_2 in
719 the CH-region for hexadecane). This can introduce a threshold of subjectiv-
720 ity as it makes it necessary to correctly determine those peaks that properly
721 suite the analysis. Moreover, as shown in Fig. 15b, in addition of peaks
722 intensities the phase transition leads to variations in peaks position. Hence,
723 the accuracy in determining peak positions can also have an influence on the
724 correct estimation of intensity ratio. Although for hexadecane this seems to
725 not affect the identification of the transition, it may become necessary to
726 consider this shift when working with other PCMs. In this case, it should

Figure 16: Ratio of Raman peaks intensity P_2/P_1 as a function of temperature during the solidification (circles) and melting (triangles) of hexadecane. Colors refer to different runs of experiments. Red dashed line highlights the solidification temperature $T_s=17.3$ °C, defined when P_2/P_1 starts to increase from the constant value in the liquid phase. For the solidification process shown in green, letter ‘A’ and letter ‘B’ correspond to $T=17.0$ °C and a waiting time of ~ 3 hours and ~ 5.5 hours, respectively. Blue dashed line is the melting temperature $T_m=17.7$ °C obtained once $P_2/P_1 < 1$ in the melting processes.

be more appropriate to calculate an intensity ratio based on integrated intensities rather than on a single wavenumber. Furthermore, the variation in peak intensity ratio during the transition could be also covered from a small signal-to-noise ratio, which is not the case in our experiments. As a consequence, for a more optimized phase identification, for instance during on-line monitoring of which PCMs phase is present at a given temperature in TES systems, a PCA analysis should be considered.

The first principal component (PC_1) and the second principal component (PC_2) of all the acquired spectra are shown in Fig. 17a and Fig. 17b, respectively. Together they cover 99.5% of variability, with PC_1 that covers the 83.9% of it and PC_2 the 15.6%. The scatterplot of the scores for the first two principal components is given in Fig. 18. A main cluster of points is recognizable (bounded by the gray dashed line in Fig. 18) and corresponds to spectra of the liquid phase. Indeed, this cluster gathers together all those spectra acquired for $T \geq 17.7$ °C and even for $T > 17.3$ °C during a cooling procedure. Below these temperatures the sample is in solid phase but a main cluster is not recognizable.

The temperature values for which data points group together in the liquid phase cluster correspond to those found previously in Fig. 16 by looking at the variation of P_2/P_1 . The clustering in the principal component space of these spectra suggests that the use of $P_2/P_1=1$ as a method to discern between solid and liquid phase can be appropriate at least for hexadecane.

Moreover, similarly for what observed from the plot of P_2/P_1 as a function of temperature, also in Fig. 18 one can notice the dependence on the waiting time of spectra acquired during the solidification at temperature close to the transition. For instance, freezing hexadecane at $T=17.0$ °C $< T_s$ leads to a departure of the spectra from the liquid phase cluster only if a very long waiting time is waited before acquisition (more than 3 hours in our case). The same shift of spectra from the liquid phase cluster toward the solid phase can be followed for solidification at temperature $T = 17.3$ °C $> T_s$. For this case, while the first spectra acquired after waiting 8 hours falls in the liquid phase cluster, the others move further and further apart from it as the waiting time increases.

4.4. Polarized Raman in solid phase

Hexadecane crystals have a triclinic structure, that is unequal crystallographic axes that are non-orthogonal to each other. As others even-numbered

Figure 17: (a) First principal component PC_1 and (b) second principal component PC_2 for Hexadecane's Raman spectra in the CH stretching region.

Figure 18: PCA scores plot. Colors and symbols are those of Fig. 16. For the solidification process: filled symbols are defined for $T \leq 17.1$ °C while empty symbols for $T > 17.1$ °C. For the melting process: filled symbols are for $T < 17.7$ °C and empty symbols for $T \geq 17.7$ °C. The inset is a zoom on part of the liquid phase cluster. The latter is bounded by the gray dashed line. Letter 'A' is defined as in Fig. 16, i.e. $T = 17.0$ °C and a waiting time of ~ 3 hours.

763 n -alkanes with $n < 20$, solid hexadecane also does not present any intermedi-
 764 ate phases besides its crystalline triclinic phase and the liquid phase [40, 57].

765 We performed polarized Raman spectroscopy in a solid sample of hex-
 766 adecane to verify if the large variability of spectra in solid phase observed
 767 in Fig. 16 may be due to the different orientations of crystals in the sam-
 768 ple. By using the same setup described previously, we kept a thin layer of
 769 hexadecane (around 2 mm thick) at constant temperature $T=14.0$ °C for the
 770 entire analysis. Spectra were acquired after allowing the sample to crystallize
 771 completely (i.e. after more than 20 hours after setting the temperature) with
 772 a laser power of ~ 50 mW and a $40\times$ objective in order to focus on a small
 773 region. All other parameters were kept the same as those described at the
 774 beginning of this section.

775 We use the Porto notation based on the setup’s coordinate system (de-
 776 fined as depicted in Fig. 13) instead of the sample’s coordinate system to
 777 describe directions of incident and scattered light. Although this is a stan-
 778 dard procedure when working with liquids (i.e. isotropic samples), we keep
 779 it also for the solid phase since orientations of crystallites are here unknown.
 780 Four polarization tensors can then be examined. The first writes as $Z(YX)\bar{Z}$
 781 and indicates light incident along Z axis with laser polarized parallel to Y
 782 axis, and scattering light in the Z direction but in the opposite sense ($\bar{Z}$)
 783 with the analyzer aligned parallel to X axis. Thus the other combinations
 784 are $Z(YY)\bar{Z}$, $Z(XX)\bar{Z}$ and $Z(XY)\bar{Z}$.

785 In Fig. 19 we report the variation within the CH-region of Raman spectra
 786 obtained in two distinct and fixed points of investigation. Although in all
 787 cases we observe $P_2/P_1 > 1$, meaning that no liquid phase is present, the
 788 value of P_2/P_1 depends on the geometry of polarization used to acquire the
 789 scan. It ranges between 1.57 and 2.28 in Fig. 19a and between 1.10 and 3.76
 790 in Fig. 19b. It is the same range of P_2/P_1 we collected and shown for solid
 791 phase during the melting and solidification processes (Fig. 16). Beside the
 792 variation of P_2/P_1 , the most pronounced difference observed when changing
 793 the polarization geometry regards peaks associated with the CH_3 stretching
 794 vibration modes. In Fig. 19a a strong increment in intensity is recorded for
 795 the CH_3 asymmetric stretching peak (P_4) when the $Z(XY)\bar{Z}$ geometry is
 796 employed. However, the same behavior does not occur at each acquisition
 797 spot, for instance in Fig. 19b both P_3 and P_4 remain always much less intense
 798 and developed than P_1 and P_2 .

799 To conclude, the variations of Raman spectra observed in the solid phase
 800 during heating/cooling processes are well recovered here by changing the po-

Figure 19: Polarized Raman spectra for the four geometries of polarization. Example for two different fixed positions of acquisition (a) and (b).

larization geometry. For this reason the variation of P_2/P_1 for solid phase in Fig. 16 is mainly caused by the different crystallites orientations. Moreover, the large variability in the PCA scores for the solid phase indicates spectra that differ statistically from one another. This variability can be related to structural changes in the sample, especially when the spectrum is acquired near the solidification point, but also to the differences observed for different orientations of crystallites. Formation of differently oriented crystallites could be explained by uncontrolled boundary conditions in terms of geometry or surfaces, where the roughness of the lateral surfaces of the sample reservoir here used is different from that of the bottom surface, or by any random heterogeneity. Finally, crystallization process and crystallites orientations depend on the surface tension since here the upper interface is a “free” surface in contact with air. Since this region is the last where crystallization occurs, it is also subjected to volume shrinkage that forms a heterogeneous, rough surface.

5. Discussion and conclusive remarks

In this work we provide a multi-physical and multi-scale characterization for hexadecane’s liquid and solid phases as well as for the phase change during

melting and solidification. Hexadecane’s thermo-mechanical properties are indeed investigated at macroscopic and microscopic scale as a function of temperature by achieving the phase transition with different techniques and protocols, i.e. transient or quasi-static temperature variations. The attempt is justified given the importance that such type of organic PCMs has in many industrial processes and by the lack in their proper characterization.

First, we have presented results for hexadecane’s thermo-physical properties at the macroscopic scale. The thermal conductivity λ of both liquid and solid phases were retrieved for the first time by the hot tube technique and compared with the available literature. λ in the liquid phase is found in good agreement with previous works (deviations within 6% with [15] and $\sim 18\%$ with [44]). Similarly, our value of λ in solid phase deviates by only 1.8% from the only other available measure [15]. The thermal conductivity of the solid phase is found larger than the one of the liquid phase, with a ratio between the two of ~ 2.27 .

Afterwards, differential scanning calorimetry (DSC) was used to determine the latent heat for both melting and solidification processes and the specific thermal capacity for liquid and solid phases. The same technique allows also to achieve the temperatures at which hexadecane melts (T_m) and starts to solidify (T_s). Their values are listed in Table 1 together with those obtained with the other analysis techniques. Even when using DSC with a relative small temperature ramp ($0.2\text{ }^\circ\text{C}/\text{min}$), we always recorded a thermal hysteresis of about $2\text{ }^\circ\text{C}$ between the onset of the phase change during melting and that during solidification. A similar thermal hysteresis was also collected during rheological analysis where T_s is found to depend on the chosen temperature ramp for both rotational and oscillatory tests. Processes involving fast temperature variations ($1.0\text{ }^\circ\text{C}/\text{min}$) are indeed characterized by a T_s that is considerably lower than what obtained for smaller cooling rate (up to $3\text{ }^\circ\text{C}$ difference in oscillatory mode), leading to a even larger thermal hysteresis. On the other hand, small cooling rates decrease supercooling effects and lead to a smaller difference between T_s and T_m even compared to DSC. Near the solidification temperature, the forming solid structure is continuously affected also by the conditions imposed by the rheometer. This is shown in oscillatory tests done at steady temperature. At $T \leq 16.0\text{ }^\circ\text{C}$ hexadecane’s transient behavior reaches a stage where the solid-like behavior dominates and, even though weakly, G' remains larger than G'' . Under this condition, the measured normal force displays periodic discontinuities that can be related to the breakage/growth of crystals along the plate-sample interface

Technique	Solidification temperature (°C)	Melting temperature (°C)
DSC	$T_s=15.0-15.5$	$T_m=17.2-17.7$
Oscillatory rheometer	$T_{G'>G''} \leq 16.0$	$T_m \sim 17.5$
Raman	$T_s=17.3$	$T_m=17.7$

Table 1: Phase change temperatures regarding different techniques.

even for the smallest imposed stress (0.001 Pa). Rheological tests highlight two counteracting phenomena when applying a weak strain or stress to the PCM: (1) it facilitates phase transition by homogenizing the temperature due to advection, (2) it leads to a weakening of the crystallites structure during the liquid-to-solid transition. Forces exerted by the imposed shear stress can overcome the driving forces of crystallization and lead to the breakage of the forming structure.

Melting and solidification at microscale were studied through Raman spectroscopy. These measurements regard the “local” phase change since the laser beam is focused on a μm -spot right below the sample top surface. Results show a local melting temperature ($T_m=17.7$ °C) close to what found by DSC and by rheology measurements (Table 1). This temperature deviates by only 2.2% from the values of T_m found by [40] for a much smaller sample of hexadecane. On the other hand, both the temperature evolution of the ratio between Raman’s peaks associated to the CH_2 stretching (P_2/P_1) and the PCA score plots show that, by waiting long enough, crystallization starts at $T=17.3$ °C, thus considerably reducing the thermal hysteresis to about 0.4 °C. It has been shown that an uniformly cooled liquid n -alkanes can undergo surface freezing by forming a crystalline monolayer on its surface at 3 °C above the bulk T_s [58, 59]. Although in our case boundary conditions for the temperature are different from those of [58, 59], this phenomenon could take place along the liquid-air interface of our sample and contribute to the mismatch between the local T_s obtained by Raman spectroscopy and the bulk T_s obtained for small temperature ramps with DSC. Furthermore, a large value of roughness can contribute to favor the occurrence of freezing, as in the case for the cavity surfaces used to contain the PCM during our Raman analysis. In our case, while solidification was measured locally by Raman spectroscopy, a solidification within the whole volume was observed.

Variations in boundary conditions, such as thermal conditions and/or

886 kinematical, dynamical conditions can significantly affect the way hexade-
887 cane’s solidification occurs. In addition, mechanical or even some physico-
888 chemical conditions can favor crystallization by inducing nucleation. This
889 has in turn a strong impact on how much efficiently energy is generated and
890 absorbed during the phase change and it needs to be taken carefully into
891 account when designing new thermal energy storage systems. For these rea-
892 sons, PCM interactions at interfaces are of utmost importance because they
893 can modify the sample bulk properties as well as equilibrium states.

894 Our ongoing work is currently dedicated to reduce PCMs supercooling.
895 One interesting route to address this issue is to provide nucleation sites to
896 favor crystallization, e.g. by using porous materials which increase the avail-
897 able solid surface to create sites for nucleation. In this case a complete
898 investigation on structural properties and phase transition mechanisms of
899 PCMs inside porous network will be mandatory to evaluate the ability of the
900 system to trigger crystals nucleation.

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