I. INTRODUCTION

Phenomenological classification of liquids as glassforming or crystal-forming liquids was introduced in the past when the most common way of making a glass was cooling of viscous liquids fast enough to avoid crystallization. Crystalline phase is more stable than the glassy state and the system always reaches this state if the cooling rate is slow enough to follow the equilibrium path.

However, nearly all materials with every class of bonding can be frozen into a glassy solid or a crystalline state depending on the various routes used in the process of solidification.1 The development of techniques that give faster cooling rates such as laser quenching, cold compression of crystal, chemical vapor deposition, solvent evaporation, and many others1–3 has led to the enormous progress in materials science and the discovery of new glasses. Many engineering materials of technological significance such as plastics, optical fibers, and some metallic substances and alloys can be produced as amorphous solids.

Water is a typical crystal-like liquid under normal conditions, but if it is quenched exceptionally fast, the glassy state is obtained.5 In contrast, methylcyclohexane is regarded as a typically “good glassformer” according to the empirical rule \( T_v/T_m > 2 \),1 where liquids with melting temperature \( T_m \) less than half their vaporization temperature \( T_v \) are usually sufficiently viscous at their melting points to avoid crystallization. In our recent paper6 we showed that methylcyclohexane in the undercooled liquid phase may form an either crystal or glassy state which strongly depends on the quenching rate. We have identified the characteristic temperature \( T^* \) that is a no-return point between crystallization and amorphization.

The properties of glass and crystal-forming liquids continue to draw basic research attention in chemistry and condensed-matter physics.7–13 There is no theory that accurately describes the behavior of any liquid over the full temperature range in which the relaxation times cover 15 orders of magnitude. An analysis of the glass transition viewed from the liquid side at higher temperatures is based on the mode coupling theory (MCT).14,15 MCT theory predicts the ergodic non-Arrhenius behavior above a critical temperature \( T_c \) that marks the crossover from liquidlike to solidlike transport properties. At \( T = T_c \), the system undergoes a phase transition to a state with frozen density fluctuations. The relaxation time shows a characteristic power law, \( \tau \sim \left| T - T_c \right|^{-\gamma} \). The physical picture is related to the particle performing the rattling motions in the cage formed by the particles of the environment. Unfortunately, this phase transition at \( T_c \) cannot be identified with the calorimetric glass transition \( T_g \) or the temperature \( T_o \) (from the Vogel–Tamman–Fulcher equation), because \( T_o \) is sufficiently larger (\( T_o > T_c > T_g \)). Moreover, the MCT theory cannot explain the slow dynamics below \( T_c \). The slow processes below \( T_c \) are better described by the idea of barrier-dominated behavior on the potential energy hypersurfaces,16 known as the “energy landscape” approach.8 The “energy landscape” approach applies a statistical mechanical formalism for metastable states, specifically undercooled liquids, to clarify the static and dynamic properties that arise in formation of the glassy state at the molecular level. Much of this analysis is at present largely qualitative and reflects the fact that precise computation of how viscous liquids sample their landscape has become possible only recently.8

In this paper we will study the glass transition and crystal–liquid transitions viewed from the liquid and from the solid side during the processes of cooling and warming to check if this path is irreversible and if the temperature changes in the opposite directions generate the hysteresis. We have...
chosen the CH$_2$ rocking mode of methylcyclohexane as a probe encouraged by our recent results.$^6$ We have identified the characteristic temperature $T^*$ that is quenching rate dependent which is the no-return-point between crystallization and amorphization. Below this temperature the undercooled methylcyclohexane exists in either the liquid state that is out of equilibrium and represents nonergodic behavior that leads to glassforming or in the metastable equilibrium ergodic state that leads to crystallization.

We will show that vibrational static properties and vibrational dynamics of the internal modes combined with the low frequency phonon Raman spectra studied by the low temperature Raman spectroscopy are powerful indicators of the phase transitions. There are much more sensitive molecular indicators of transition anomalies than viscosity, dielectric relaxation, heat capacity or diffusion coefficients. We have identified for the first time the premelting crystal structure of MCH in the temperature range of 140–147 K that proceed the melting both for the glassy state and the equilibrium crystal state.

II. EXPERIMENT

Spectrograde methylcyclohexane (MCH) and deuterated methylcyclohexane (MCH-d$_{14}$) was purchased from Aldrich and used without further purification. The melting temperatures $T_m$ of methylcyclohexane and deuterated methylcyclohexane are 147 K, the calorimetric glass transition temperature $T_g$ is about 85 K.$^{17}$

The Raman spectra of the CH$_2$ rocking mode of methylcyclohexane as a function of temperature and cooling rate were measured in the cryostat (Oxford Instruments Limited) with Ramanor U1000 (Jobin Yvon) and Spectra Physics 2017-04S argon ion laser operating at 514 nm. The vibrational assignment of the modes in methylcyclohexane were taken from Ref. 18. More experimental details are given in our recent paper on this subject.$^6$

III. RESULTS

In this section, we present the results of the Raman studies on vibrational dynamics and static vibrational properties of methylcyclohexane and deuterated methylcyclohexane as a function of temperature and cooling rate. The frozen solid phases, glassy or crystalline that have been generated in the cooling process at 10 K are slowly warmed and the Raman spectra are recorded as a function of temperature.

We have shown$^6$ that the Raman spectra for methylcyclohexane generated at various cooling rates differ drastically indicating that even the moderate differences in the cooling rates may generate solids that are topologically distinct. When the sample of MCH is cooled slowly (0.5 K/min) the liquid state becomes undercooled below the melting temperature $T_m=147$ K down to $T_{ms}=110$ K. With further cooling the undercooled liquid transforms to a crystalline form. In contrast we observe quite a different history of the sample when cooled rapidly (3 K/min) down to $T^*=125$ K for MCH. This temperature have been identified as the characteristic temperature $T^*$ that is quenching rate dependent which is the no-return-point between crystallization and amorphization.$^6$ In this case the Rayleigh wings typical for liquids have been observed down to the calorimetric glass transition of MCH at $T_g=85$ K.$^{17}$ At about 85 K methylcyclohexane transforms into an amorphous solid glassy phase with no signature of the crystal ordering down to 10 K.$^6$

To check if the histories of the samples are reversible we have recorded the Raman spectra (VV and VH spectra) in the region of 15–200 cm$^{-1}$ as a function of temperature. (a) Warming of the solid crystal (α crystal) phase that has been generated during slow cooling (0.5 K/min). (b) Warming of the solid glassy phase that has been generated during rapid cooling (3 K/min).

![FIG. 1. VV Raman spectra of methylcyclohexane in the lattice region of 15–200 cm$^{-1}$ as a function of temperature. (a) Warming of the solid crystal (α crystal) phase that has been generated during slow cooling (0.5 K/min). (b) Warming of the solid glassy phase that has been generated during rapid cooling (3 K/min).](image-url)
temperature structure. We have called this premelting structure the crystal \( \beta \) to distinguish it from the equilibrium structure at lower temperatures (crystal \( \alpha \)). Even more exciting results are observed for the warming process of the glassy state in Fig. 1 (b). Structureless broad spectra recorded during the warming of the sample with no signature of the crystal lattice peaks show the identical features as those for the cooling in the temperature range of 10–110 K.\(^6\) However, at 140 K the spectra begin to demonstrate the crystalline premelting structure that becomes clear at 147 K and is identical with that observed in Fig. 1 (a) for slow cooling.

To obtain a more illuminating picture to elucidate the origin of the mechanisms that control the phase transitions in methylcyclohexane we have monitored the Raman spectra of the internal vibrational mode of \( \text{MCH} \) represented by \( \text{CH}_2 \) rocking mode that has the vibrational frequency of 545.7 cm\(^{-1}\) at 293 K.

Figures 2(a) and 2(b) show the VV Raman spectra of the \( \text{CH}_2 \) rocking mode as a function of temperature for the warming process from 10 K to 293 K. One can see that the bands between 10 K and 140 K are significantly broader for the glassy phase [Fig. 2(b)] than for the crystal phase [Fig. 2(a)]. At the temperatures close to the melting temperature around 147 K the bands both for the crystal and glassy phases become significantly redshifted, and the bandwidth of the glassy phase exhibits dramatic narrowing. Above 147 K the normal liquid phase is represented in both Figs. 2(a) and 2(b) by identical broad bands shifted again to higher frequencies.

Figures 3(a), 3(b), and 4(a), 4(b) summarize the results for the maximum peak positions and the VV Raman bandwidths \( \Delta_{1/2} \) (FWHH) of the \( \text{CH}_2 \) rocking mode of methylcyclohexane as a function of temperature; \( \circ \), slow cooling (0.5 K/min) (Ref. 6); \( * \), slow warming (0.5 K/min); -, hard collision theory (Ref. 6).

\( T_m = 110K \quad T_m = 147K \)

FIG. 2. VV Raman spectra of the \( \text{CH}_2 \) rocking mode of methylcyclohexane as a function of temperature. (a) Warming of the solid crystal phase (crystal \( \alpha \)). (b) Warming of the solid glassy phase.

\( T_m = 110K \quad T_m = 147K \)

FIG. 3. (a) VV Raman maximum peak position of the \( \text{CH}_2 \) rocking mode of methylcyclohexane as a function of temperature. (b) VV Raman bandwidth \( \Delta_{1/2} \) (FWHH) of the \( \text{CH}_2 \) rocking mode of methylcyclohexane as a function of temperature; \( \circ \), slow cooling (0.5 K/min) (Ref. 6); \( * \), slow warming (0.5 K/min); -, hard collision theory (Ref. 6).
when the crystal $\alpha$ transforms into the premelting structure (crystal $\beta$) shortly before $T_m = 147$ K, where one observes the sudden redshift of the CH$_2$ rocking mode maximum position.

For the case when the glassy phase of MCH has been generated [Fig. 4(a)] the maximum peak positions are identical for the cooling and warming branches in the full temperature range of 293–10 K except the region around $T_m = 147$ K where the glass transforms suddenly into the crystal premelting structure (crystal $\beta$) signalized by the significant redshift that is identical to that observed in Fig. 3(a).

Figures 3(b) and 4(b) represent the similar pattern of behavior. The cooling and warming branches for the bandwidths are identical except the region $T_{ms} < T < T_m$ for the crystal phase MCH, and the premelting region around $T_m = 147$ K for the glassy MCH.

IV. DISCUSSION

The picture that emerges from the analysis to this point shows that the vibrational dynamics (related to the bandwidth) and the average potential of interaction (related to the maximum peak position) are very sensitive indicators to specify the phases and phase transitions of methylcyclohexane at the molecular level. Combining the results for the low frequency Raman spectra with the results for the internal normal modes we can easily distinguish between the normal liquid, undercooled liquid, crystal equilibrium structure (crystal $\alpha$), crystal premelting structure (crystal $\beta$), and glassy state generated in MCH.

The second important finding of this paper is evidence of existing of the premelting structure of MCH in the temperature range 140–147 K that precedes the melting process. The basic question we wish to address is if the nature of this premelting structure can be identified on the basis of its spectroscopic properties.

The premelting structure exhibits evidently crystalline ordering [Figs. 1(a) and 1(b)] that differs from that for the equilibrium stable crystal (crystal $\alpha$) generated in MCH at low temperatures [Fig. 1(a)] and the amorphous nonequilibrium structure without translational ordering for the glassy state of MCH [Fig. 1(b)]. Moreover, the CH$_2$ mode peak position increases abruptly at $T_{ms} = 110$ K (undercooled MCH-crystal $\alpha$ transition) during cooling while it decreases significantly at around $T_m = 147$ K (crystal $\beta$-normal liquid MCH transition) during warming [Fig. 3(a)]. The magnitude of the maximum peak position is much lower than the magnitudes for the normal liquid, undercooled liquid, crystal phase $\alpha$ [Fig. 3(a)] and glassy MCH [Fig. 4(a)]. The dramatic redshift in Figs. 3(a) and 4(a) is accompanied by the abrupt narrowing of the bandwidths in the glassy phase of MCH [Fig. 4(b)]. In contrast, no significant changes are observed in vibrational dynamics illustrated by the bandwidths [Fig. 3(b)] between the crystal $\alpha$ at low temperatures and the premelting crystal structure (crystal $\beta$). It is obvious that these changes must illustrate the change of the mechanisms of vibrational dynamics (vibrational relaxation) and the changes of the average potential of interaction between the oscillator and the environment due to structural reorganization that occurs during the process leading to melting.

The maximum peak position of the vibrational band is the average frequency $\langle \omega \rangle$ over the frequencies of molecular oscillators in the statistical ensemble. The repulsive interactions give contribution to the blueshift of the peak position, while the attractive interactions lead to redshift of the maximum peak position. Our results in Figs. 3(a) and 4(a) show clearly that the interactions between the CH$_2$ rocking oscillator of MCH and the environment become more attractive (or less repulsive) in the premelting crystal structure (crystal $\beta$) than in the crystal $\alpha$ [Fig. 3(a)] or glassy [Fig. 4(a)] phases of MCH at lower temperatures. Moreover, this premelting structure is characterized by greater contribution from attractive (or less repulsive) interactions than in the normal liquid and undercooled liquid states.

Methylcyclohexane may exist in two conformations: equatorial (eq) and axial (ax)
with the equilibrium strongly shifted towards the equatorial form. The conformational free energy difference ($\Delta G^o$) for the process $\text{ax} \rightarrow \text{eq}$ was experimentally determined to be 1.74 kcal/mol at 300 K (Ref. 19) and 1.8 kcal/mol at 173 K.20

The steric interactions in methylcyclohexane have been the subject of a large number of publications.21–25 It was shown that the repulsive (gauche-butane, $g,b$) interactions dominate the overall energetics. It is clear that there are 2 $g,b$ repulsive interactions in the axial conformation of MCH, and no $g,b$ interactions in the equatorial conformation. In other words, the shorter distance between proximate protons of the ring and the axial methyl hydrogens (diagonal steric interactions) introduce more energetic van der Waals repulsion than do the corresponding nonbonded proton–proton interactions in an equatorial conformation. It denotes that the CH$_2$ rocking mode maximum peak position corresponding to equatorial conformation should be redshifted with respect to the axial one if we were able to observe both conformers. However, we failed to detect signals from the axial conformation of MCH in the whole temperature range which is not surprising taking into account that the very large equilibrium constant $K (\Delta G^o = -RT \ln K)$ favors entirely the equatorial conformer.

Let us now return to the striking feature of the premelting structure that reveals the significant redshift of the CH$_2$ rocking mode of MCH around $T_m = 147$ K. The repulsive steric effect of the axial conformer on the CH$_2$ protons that are involved in the CH$_2$ rocking vibration of MCH may suggest that the premelting crystal structure just simply represents the structure with the equilibrium shifted towards the equatorial conformers while the low temperature crystal represents the structure with the equilibrium shifted towards the axial conformers. However, this explanation seems to be unreasonable on the basis of thermally activated processes that predict stabilization of the equatorial conformer with temperature decrease. Moreover, this assumption would lead to the conclusion, that only the premelting structure represents the structure dominated by equatorial conformations while the other thermodynamic states including the normal liquid MCH at ambient temperatures are dominated by axial conformations which contradicts all experimental results and theoretical calculations26 obtained so far.

In order to rationalize the results presented so far and to answer the question that concerns the nature of the premelting crystal structure we have recorded the Raman spectra for the deuterated MCH. Figure 5 shows the Raman spectra of deuterated methylcyclohexane in the lattice region of 15–200 cm$^{-1}$. A comparison between Figs. 5, 1(a), and 1(b)
temperatures and the premelting structure.

We will consider if the vibrational dynamics of crystal phases at low temperatures closely resembles that of the premelting structures for non-deuterated MCH (crystal $\beta$). The small redshift is due to the isotope substitution effect.

Figures 6 and 7 show the VV Raman bandwidths and the maximum peak position of the CD$_2$ rocking mode of deuterated MCH. The temperature dependence for the bandwidths of the CD$_2$ rocking mode is very similar to that for the CH$_2$ mode presented in Fig. 3(b). In contrast, deuterated MCH shows the opposite trend in the temperature dependence of the maximum peak position (Fig. 7) in comparison to that for the CH$_2$ mode of nondeuterated MCH [Fig. 3(a)]. The crystal structure at low temperatures (crystal $\alpha$) of MCH shows the remarkable blueshifts with respect to the liquid phase while the crystal structure of deuterated MCH shows the significant redshift with respect to the liquid phase. However, it is worth emphasizing that the premelting structure of MCH that exists around $T_m$ [Fig. 3(a)] shows redshift similar to that observed in the deuterated MCH in Fig. 7.

Taking into account that the optical phonon spectra for the premelting structure of MCH [Fig. 1(a)] are very similar to those observed for the crystal phase of deuterated MCH (Fig. 5) we can state that they both represent the same crystal phase with the same symmetry and the type of crystal packing.

The results and conclusion just presented can be applied to rationalize the molecular mechanisms that take place with increasing temperature. Solid MCH exists in two stable crystal phases. The $\alpha$ phase is stable at low temperatures up to 140 K at which the crystal $\alpha$ phase is converted into the crystal $\beta$ phase. It is the crystal $\beta$ phase that prepares the system for melting at $T_m$. The deuterated MCH exists only in the $\beta$ crystal phase in the whole temperature range up to $T_m$.

In contrast to the mean field interactions represented by the maximum peak positions in Figs. 3(a) and 4(a), no significant changes are observed in vibrational dynamics illustrated by the bandwidths [Fig. 3(b)] for the crystal $\alpha$ at low temperatures and the premelting structure (crystal $\beta$). Here, we will consider if the vibrational dynamics of crystal phases and glassy phase of MCH presented in Figs. 3(b) and 4(b) can be rationalized in terms of the existing literature models. The models can be divided into two main groups. The first group is based on the idea of the thermal activation, the other one is based on the free-volume approach. We have used the extreme case of the free volume model that is based upon the hard-repulsive collision picture. We have introduced the thermal effects not through activation dynamics, but merely through the fact that the volume density is temperature dependent. The details of the calculations are presented in our previous paper. The comparison between the theoretical and experimental results are presented in Figs. 3(b) and 4(b). One can see that the hard-collision model reproduces perfectly the region of a normal liquid MCH down to the temperature around $T_c = 200$ K. It is not surprising as the normal liquid can be approximated by the dense gas model of the Enskog theory, which is successful in describing all the dynamical features, which are caused by free particle motions and binary collision events. This agreement between the experimental and theoretical results begin to deviate from the theoretical results predicted by the hard-collision model. The maximum of this deviation occurs at $T_m = 110$ K [Fig. 3(b)] and at around $T_g = 85$ K [Fig. 4(b)]. The temperature $T_g$ corresponds to the undercooled liquid MCH-crystal $\alpha$ transition, the temperature $T_m$ corresponds to the undercooled liquid MCH-glassy phase transition. The deviation from the free-volume model indicates that the additional dynamical features due to interactions of hydrodynamics fluctuations, viscoelastic effects, density fluctuations begin to dominate below $T_c = 200$ K in MCH. It is worth emphasizing that this temperature is significantly higher than the melting temperature for MCH $T_m = 147$ K. It strongly suggested that the system begins to prepare for solidification far before the melting point. The temperature $T_s = 200$ K may be related to the critical temperature at which the system undergoes a phase transition to a state with partially frozen density fluctuations. Using the language of thermally activated processes this phase transition is related to the transformation between ergodic Arrhenius--ergodic non-Arrhenius behavior. Our results in Figs. 3(b) and 4(b) show evidently that the region between $T_s = 200$ K and $T_m = 147$ K represents the ergodic behavior of the equilibrium structure as the results for cooling and warming directions are identical and independent on the cooling rate. At temperatures lower than $T_s = 200$ K the bandwidths in Figs. 3(b) and 4(b) begin to be more and more inhomogenous and their magnitudes reach the maxima at $T_m = 110$ K [Fig. 3(b)] and $T_g = 85$ K [Fig. 4(b)] with temperature decrease. This continuous increase of the bandwidths becomes especially pronounced in the undercooled liquid MCH region. It illustrates that the dynamics of density fluctuations in this region is governed by many-body interactions and the binary collisions model used in the paper is not sufficient to describe the cooperative rearrangement of the large clusters. Moreover, one can see that the results in Fig. 3(b) are not reversible in the cooling–warming cycle. They differ significantly for the

![Graph](image-url)
cooling branch (undercooled MCH) and the warming branch (solid crystal MCH) between $T_m$ and $T_{ms}$. One can see from Fig. 3(b) that the results obtained during the warming of the sample are reproduced perfectly for the crystal phase by the free-volume model like the results in the liquid phase above $T_c = 200$ K. It is obvious that the hard-collision events at low temperatures cannot be described as free particle motions and they should be understood as the repulsive interactions between the molecules due to close packing and performing the rattling motions hindered by lack of volume with decreasing temperature. The comparison between the experiment and theory in the region between $T_m$ and $T_{ms}$ in Fig. 3(b) strongly suggests that the cooperative rearrangements due to many-body interactions and density fluctuations are much more pronounced in the metastable state represented by the undercooled liquid MCH than in both crystal phases (crystal $a$ and the premelting structure of the crystal $b$). The vibrational dynamics of the both crystal phases seem to be governed by the binary repulsive interactions due to the close crystal packing.

The picture that emerges for the glassy MCH [Fig. 4(b)] differs remarkably from that for the crystal MCH in Fig. 3(b). The binary hard-collision model reproduces the experimental results only for the normal liquid MCH down to $T_c = 200$ K and for the premelting structure (crystal $b$). The other temperature regions are governed by molecular processes that strongly deviate from the binary hard repulsive interactions. In contrast to the crystal phase in Fig. 3(b), the density fluctuations reflected by the bandwidths increase up to the temperature $T = 85$ K. At around this temperature the density fluctuations seem to be entirely frozen as the bandwidths become independent of temperature. The deviation from the free-volume model for the glassy phase makes it reasonable to guess that models based upon the thermal activation idea or energy landscape approach are better to describe the vibrational dynamics of glasses. The results in Fig. 4(b) show that the bandwidths are very similar in the temperature range 10–140 K for the cooling–warming cycle, while they differ drastically around the melting point $T_m$. It is reasonable to guess that the molecular motions in the region 10–110 K are impeded primarily by insufficient thermal energy to jump across the barrier to another basin with the local energy minimum. With temperature increasing the height of the barriers separating sampled adjacent energy minima seems to be decreased abruptly at 140 K and the particle may execute more frequent jumps over the barrier. The abrupt change in the bandwidth in Fig. 4(b) at around $T_m$ may illustrate the crossover between landscape-dominated and landscape-influenced behavior according to the classification in Ref. 8. For MCH this crossover occurs somewhere between 140 and 147 K.

V. CONCLUSIONS

The present paper has illustrated important aspects of the complex behavior of methylcyclohexane below and close to the glass transition as well as to the melting transition viewed from the liquid and the solid sides. We have shown that methylcyclohexane commonly regarded as a model glassforming liquid can be transformed into the variety of equilibrium and nonequilibrium thermodynamical states including crystal phases, glassy phases, and undercooled liquid.27–29

The essential findings can be summarized as follows:

1. We have found that solid MCH may exist in two crystal forms (we called them $a$ and $b$) as well as in the glassy phase.
2. We have found for the first time that both glassy phase and the crystal phase (crystal $a$) of MCH are transformed into the premelting crystal structure (crystal $b$) at around 140 K that exists until the melting process is completed at $T_m = 147$ K.
3. The $b$ crystal premelting phase is characterized by the least repulsive interactions between protons involved in the CH$_2$ rocking mode and the environment in comparison to the $a$ crystal, glassy phase, undercooled liquid, and normal liquid.
4. Solid deuterated methylcyclohexane may exist only in the $b$ crystal phase in the studied temperature range and at the studied cooling rates.

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