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Abstract: Phase transitions between different aggregate states are omnipresent in nature and technology. Conventionally, a crystalline phase melts upon heating as we use ice to cool a drink. Already in 1903, Gustav Tammann speculated about the opposite process, namely melting upon cooling. So far, evidence for such "inverse" transitions in real materials is rare and limited to few systems or extreme conditions. Here, we demonstrate an inverse phase transition for molecules adsorbed on a surface. Molybdenum tetraacetate on copper(111) forms an ordered structure at room temperature, which dissolves upon cooling. This transition is mediated by molecules becoming mobile, i.e., by mobilization upon cooling. This unexpected phenomenon is ascribed to the larger number of internal degrees of freedom in the ordered phase compared to the mobile phase at low temperatures.

A phase transition describes a reversible change in the state of matter upon varying external conditions, typically pressure or temperature.[1,2] As an example, commonly we expect a crystal to melt upon heating and a liquid to crystallize upon cooling.

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/anie.202105100.

Already in 1903, Gustav Tammann, a chemist at the University of Göttingen, speculated about the inverse process, a rather counterintuitive phase transition termed "inverse melting".[3,4] In inverse melting, a crystalline phase melts upon cooling. While Tammann himself never found evidence for the existence of such a peculiar phase transition in real materials, his ideas inspired the quest for inverse phase transitions in nature. So far inverse phase transitions were only observed in specific three-dimensional (3D) systems under extreme conditions (extremely low temperatures and high pressures), or for rather exotic 3D systems.[5–7] For instance, inverse melting was found for helium atoms under pressures above 20 bar and low temperatures (< 1 K).[6]

Metal alloys, the major research interest of Tammann, show a similar phase transition from a crystalline to a disordered state upon cooling; however, the disordered state in this material is amorphous (immobile) rather than liquid (mobile).[7–12] Likewise, evidence for an inverse transition from an ordered to an amorphous state has been presented for polymeric systems.[13–16]

For molecules adsorbed on a surface, phase transitions can be observed in a similar manner as for 3D bulk material.[2] Molecules confined to a surface may form two-dimensional (2D) ordered arrangements with a strong intermolecular interaction. In the other extreme, molecules with negligible molecule–molecule interaction might be able to freely diffuse over the surface. These systems can differ from 3D bulk materials not only in the dimensionality, but also by the fact that the underlying surface is involved and molecule–surface interactions need to be considered. These molecule–surface interactions can enrich the phase diagram as will be demonstrated herein.

For such 2D systems, an inverse order–disorder transition has been observed for an organic overlayer adsorbed on a silver(111) surface.[17] However, even for this model case, it is yet unclear whether the disordered state at low sample temperature corresponds to a surface-confined mobile phase or to an amorphous solid structure.

Here, we present a system of adsorbed molecules on a surface that shows an inverse phase transition from a 2D ordered to a mobile state. At room temperature, an ordered phase is observed. Upon cooling, a large fraction of the molecules becomes mobile on the surface. To the best of our knowledge, this is the first demonstration of mobilization upon cooling on a surface. Variable-temperature scanning tunneling microscopy (VT-STM) images allow for investigating the system in real space. This enables us to directly follow the transition by observing the change in relative surface coverage of the two phases. In this way, the low-temperature

phase can be unambiguously assigned to mobile species, i.e., we provide a direct proof that the disordered state corresponds to mobile molecules rather than to an amorphous solid state.

As a model system for our study, we investigate dimolybdenum tetraacetate $Mo_2(O_2CCH_3)_4$ (MoMo, Figure 1a) on the (111) plane of copper (Figure 1b) in ultrahigh vacuum using STM (experimental details in Supporting Information). For this system, it was previously shown that different phases
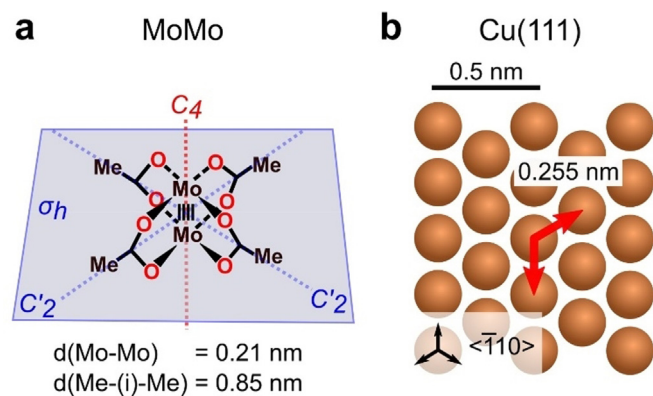

Figure 1. Model of the dimolybdenum tetraacetate $Mo_2(O_2CCH_3)_4$ (MoMo) molecule (a) and the Cu(111) surface to illustrate the surface geometry and directions (b).

Figure 2. Phases adopted by MoMo adsorbed on Cu(111). At room temperature, an ordered chain phase is formed that is composed of upright-standing molecules. Upon cooling, a coexisting fuzzy phase evolves on the surface, which is ascribed to flat-lying molecules that are mobile on the surface. Further cooling results in the formation of yet another phase, the mesh phase composed of ordered flat-lying molecules. Imaging parameters: $I_t = 90$ pA; $V_B = -0.8$ V (a); -1.5 V (b and c).

form depending on the substrate temperature.[18] When the copper substrate is held at room temperature (300 K), a so-called chain phase exists on the surface, which consists of upright-standing molecules that arrange in ordered chains aligned next to each other (Figure 2, left-hand side). Upon cooling the substrate below a temperature of approximately 220 K, another ordered phase evolves, revealing a mesh phase (Figure 2, right-hand side). In the mesh phase, the molecules lie flat on the surface. The structural investigation of the chain and the mesh phase has been in the focus of previous STM investigations,[18] and the existence of a so-called fuzzy phase in the intermediate temperature regime from 300 K to about 220 K has been observed and reported. However, the details of the phase transition in the intermediate temperature regime have not been addressed so far. Herein, we provide a detailed experimental investigation of this phase transition and discuss the thermodynamic aspects of the phase transition when cooling from room temperature to 220 K. The molecular phase present in this intermediate temperature regime is characterized by a fuzzy appearance (Figure 2, middle panel). As shown in the following, the streaky features seen in this fuzzy phase can be ascribed to mobile molecules. Thus, it can be concluded that an ordered structure present at room temperature is transformed into mobile molecules upon cooling. From a theoretical point of view, however, a direct assignment of these molecular structures on the surface to a gas, liquid, or crystalline phase is strictly speaking not possible as a 2D crystal cannot exist due to the Mermin–Wagner theorem.[19,20] Therefore, the here observed inverse transition cannot be directly assigned to the 3D case of
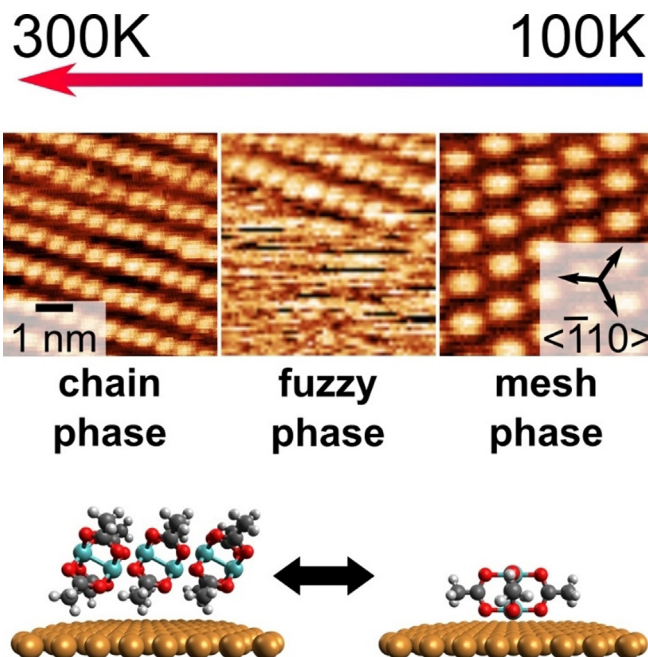
inverse melting. Instead, we refer to this inverse transition as "mobilization upon cooling".

To elucidate this transition in more detail, representative STM images taken at different temperatures are presented in Figure 3. Throughout this study, a fixed absolute molecular coverage of 2/3 ML was chosen (1 ML corresponds to a full monolayer coverage of the chain phase). At a substrate temperature of 300 K, only the chain phase is present (Figure 3a, a detailed view is given in the inset). Upon cooling the substrate to 220 K (Figure 3b), the chain phase dissolves in some areas. In these areas, the fuzzy phase becomes apparent. The mobility of the structures at this temperature of 220 K is illustrated by an image series in Figure 3c. Here, consecutive images are shown with a time lapse of 3.5 min between two successive images. From this series it becomes evident that the chain phase dissolves and reforms at different positions over time by detachment and attachment of molecules at the chain ends. This indicates a reversible transition. Moreover, we observe the formation of a further modification of the chain structure, a single curved chain (referred to as single-chain phase). Further cooling to 150 K (Figure 3d) results in the appearance of the above-mentioned mesh phase, which coexists with the chain phase. At this temperature of 150 K, few fuzzy features can still be recognized, indicative of the mobile molecules. Upon cooling down to 106 K (Figure 3e), the fuzzy structures vanish completely, and the surface is covered by the chain and mesh phase exclusively.
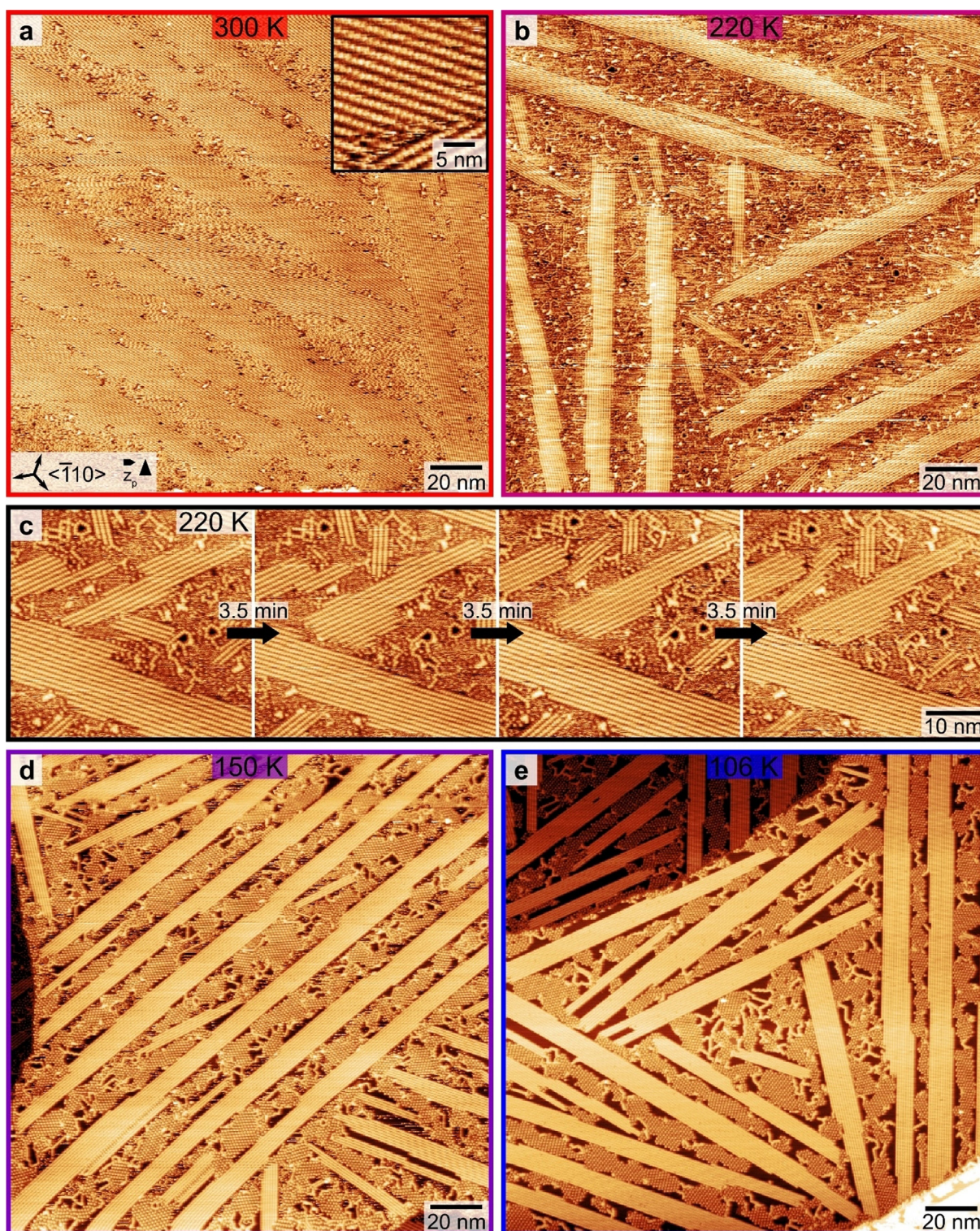
Figure 3. Mobilization upon cooling. Scanning tunneling microscopy images of MoMo adsorbed on Cu(111) held at different temperatures. a) At room temperature, the molecules form the chain phase. The top-right inset provides a detailed view of the chain phase. Very few mobile molecules exist on the surface, which are imaged as streaky features in the areas where no chain phase is present. Further details as well as another image (Figure S1) taken at room temperature are given in the Supporting Information. b) Upon cooling to 220 K, the chain phase dissolves in part and the fuzzy phase evolves. c) Sequential images illustrating the mobility of the molecules at 220 K. d) Further cooling to 150 K results in the appearance of the mesh phase. At this temperature, the fuzzy phase has nearly vanished. e) At 106 K, only the chain and the mesh phase remain on the surface. The chain phase is seen in six orientations, which arrives from the fact that the chains are oriented with an angle of $+/-23°$ with respect to the close-packed row direction of the substrate. Imaging parameters: $I_t = 90$ pA; $V_B = -1.5$ V (a–d) and $I_t = 80$ pA; $V_B = -1.4$ V (e).

To confirm reversibility of the phase transition, we performed experiments upon cooling and also upon heating the copper substrate. The data shown in Figure 3 are independent of the direction of temperature change, confirming the reversibility of the presented phase transition. Moreover, we also ensured that no desorption took place during the experiments. This can be reliably checked upon evaluating the coverage at low temperatures when all molecules become immobile.

The temperature-dependent phase transition is quantified by analyzing the surface coverage of the respective phases. With the knowledge of the molecular surface density in the chain and mesh phase, 1.79 and 0.71 molecule nm^{-2}, respectively,[18] and knowing the fact that no desorption takes place, the fraction of the molecules that constitute the chain, fuzzy, and mesh phase at a given temperature is calculated (Figure 4). The data shown in Figure 4 are taken from about 40 independent images. Further information about the data collection is given in the Supporting Information along with a diagram showing the surface coverages of the respective phases as a function of temperature (Figure S2). As can be seen, at a temperature of 300 K, the majority of the molecules exist in the chain phase (nearly 100%), while the few remaining molecules are mobile (fuzzy phase). Upon decreasing the temperature to 220 K, the fraction of molecules in the chain phase decreases to about 70%, while the fraction of molecules that are mobile increases to 30%. These numbers corroborate the above-reported finding of molecules in the ordered chain phase becoming mobile upon cooling, i.e., mobilization upon cooling is observed in the temperature window from 300 to 220 K (marked in blue in Figure 4). Upon further decrease of the temperature, the mesh phase forms,
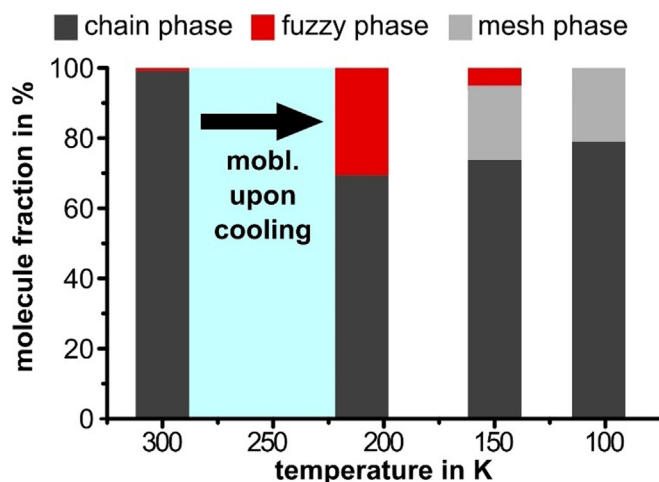

Figure 4. Coexisting molecular phases for MoMo on Cu(111) at different temperatures. For all temperatures shown here, a fixed absolute coverage of 2/3 ML with respect to the chain phase was chosen. At room temperature, almost only the chain phase is present on the surface. When cooling to 220 K, the number of molecules in the chain phase decreases and mobile molecules evolve (fuzzy phase). The data in the temperature window from 300 to 220 K (shaded blue) give evidence for mobilization upon cooling. Upon further cooling, the mesh phase evolves. At 100 K, both the chain and the mesh phases coexist on the surface.

and the number of mobile molecules is reduced again. We note that the formation of the mesh phase is a further interesting aspect of this system, however, the emphasis of this work is on the phase transition from the chain to the fuzzy phase.

Next, we will generally discuss inverse phase transitions to understand why mobilization upon cooling is possible. The phase behavior of a material is often depicted in a diagram as a function of temperature T and pressure p (Figure 5a). At the phase boundary, where two phases coexist, the difference in the chemical potential of the two states vanishes. From this equilibrium condition, the slope of any boundary in the phase diagram of a 3D material can be calculated, which is known as Clapeyron equation. For a melting transition, the system is transformed from a crystal (index c) to a liquid (index l) [Eq. (1)].

$$\frac{dp}{dT} = \frac{S_{m,l} - S_{m,c}}{V_{m,l} - V_{m,c}} = \frac{\Delta S_m}{\Delta V_m} \tag{1}$$

Here, S_m and V_m denote the molar entropy and molar volume, respectively. For a conventional melting transition (see arrow in Figure 5a), the molar entropy and the molar volume increase upon melting. Hence, such a transition has a positive slope ($dp/dT > 0$) in the pT-diagram as present in region I in Figure 5a. However, materials exist for which the molar volume decreases upon melting, with water being the most prominent example for such an anomalous melting transition (see arrow in Figure 5a). Such a transition is associated with a negative slope in the pT-diagram (region II in Figure 5a). As already pointed out by Gustav Tammann,[3] the melting curve might curl down again, which results an inverse melting transition in region III (see arrow in Figure 5a). This transition is associated with a decrease in both the molar volume and the molar entropy upon inverse melting, resulting again in a positive slope of the melting curve. Analogously, the melting curve might curl up at small pressure and low temperature[5] (not shown in Figure 5a for reasons of clarity), which results in another type of inverse melting. This type of inverse transition is associated with a decrease in molar entropy and an increase in molar volume.

This discussion shows that inverse transitions require the molar entropy to decrease upon melting. The fact that the entropy of the crystalline phase is larger than the entropy of the liquid phase appears, at first glance, counterintuitive.[4,5] This is because we often associate the high positional order in a crystal with a low entropy. This view is, however, limited, as in molecular systems further degrees of freedom, e.g., oscillations and rotations, can additionally contribute to the entropy. These contributions can compensate or even over-compensate the reduction of entropy due to immobilization. Therefore, an ordered phase consisting of immobile molecules might have a higher entropy than a liquid or gaseous phase consisting of mobile molecules.

Finally, we want to address the question why an inverse transition is seen for the specific 2D system of adsorbed MoMo molecules on a copper(111) surface studied here. In view of the general discussion presented above, one condition for mobilization upon cooling is that the ordered phase has
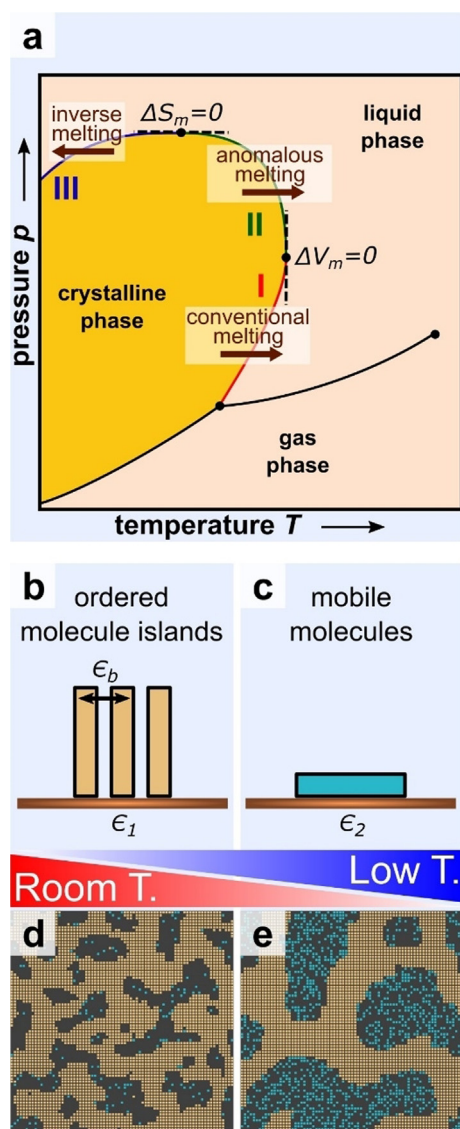
Figure 5. Schematic phase diagram illustrating inverse melting. a) Phase diagram showing the phase boundary between a crystalline, a liquid, and a gaseous phase; adapted from ref. [4]. In normal melting (region I), both the molar entropy and the molar volume increase upon a phase transition from the crystalline to the liquid phase, which results in a positive slope of the phase boundary. Substances for which the molar volume decreases upon melting—such as water—show so-called anomalous melting with a negative slope (region II). When both the molar volume and the molar entropy decrease upon melting, inverse melting takes place, which is again associated with a positive slope (region III). b,c) Conformational transition of MoMo molecules, from upright-standing in an ordered phase (b) to flat-lying mobile in an unordered phase (c), which is accompanied by a loss of single-molecule entropy. The parameter ϵ_b denotes the lateral binding energy between two standing molecules, while ϵ_1 and ϵ_2 denote the binding energy of the molecules with the substrate in the standing and lying configuration, respectively. e,d) Simulation snapshot of a lattice gas at reduced temperature d) $T/\epsilon_b = 0.3$ and e) $T/\epsilon_b = 0.2$. The upright-standing molecules are colored in light brown, while the flat-lying molecules are colored in blue.

a higher entropy compared to the mobile phase. Fulfilling this condition can be rationalized by the following consideration: The molecules stand upright in the ordered chain phase

(Figure 5b) and are assumed to lie flat in the mobile phase (Figure 5c). Compared to the standing molecules, the flat-lying molecules exhibit a stronger binding towards the surface.[18] The molecule-surface bond formation is often associated with the conversion of translational and rotational degrees of freedom into vibrational degrees of freedom. The latter are typically harder to excite. As a consequence, these degrees of freedom cannot contribute to the heat capacity of the flat-lying molecules to the same extent as for the upright-standing molecules. Therefore, the ordered phase consisting of upright-standing molecules has a higher entropy than the mobile phase.

Next, we discuss why the mobile phase is formed at all, given that the ordered phase has a higher entropy. More specifically, what is the driving force of the transition from ordered molecules to mobile molecules upon cooling? In order to understand this, the internal energy U has to be considered. In a 2D system as studied here the structure with the minimal Helmholtz free energy F is formed in equilibrium [Eq. (2)].

$$F = U - TS \tag{2}$$

Generally, the influence of the entropy S to the Helmholtz energy F increases with higher temperature T. Consequently, as a rule of thumb, minimization of F drives the formation of the structure exhibiting the largest entropy (in our case the upright-standing molecules) at high temperature and the formation of the structure having the smallest internal energy U (in our case the flat-lying molecules) at low temperature.

The here presented measurements show that this transition happens to be around room temperature. In order to observe mobilization upon cooling, two conditions need to be fulfilled. The ordered phase needs to have a larger entropy S and the mobile phase needs to have a smaller internal energy U. The first condition was discussed above. Regarding the second condition, the strong binding of the flat-lying molecules to the substrate reduces the internal energy U and, hence, might explain the smaller internal energy of the mobile phase.

The latter picture is corroborated by Monte Carlo simulations of a lattice gas,[5,21] representing a minimal model in which molecules hop between discrete sites (theoretical details in Supporting Information). In addition, molecules can be transformed between two configurations: lying or standing. While the binding energy with the substrate is larger for the lying molecules, standing molecules are attracted by other standing molecules. As argued above, each standing molecule gains entropy from molecular degrees of freedom (vibrations etc.) that are suppressed in the lying configuration. Figure 5d,e shows typical snapshots at two temperatures. At the higher temperature (Figure 5d), extended domains of standing molecules (colored light brown in Figure 5d,e) form (here identified with the chain phase) and only few molecules have detached and lie (colored blue in Figure 5d,e) on the substrate. Upon cooling to a lower temperature (Figure 5e), a substantial fraction of molecules lies down. These molecules are highly mobile and move in the

space left by the compact chain phase, thus forming a mobile phase that can be identified with the fuzzy phase.

Our work thus demonstrates that the conditions for an inverse transition such as mobilization upon cooling in 2D systems are met when the transition is associated with a distinct change in the molecular adsorption geometry that strengthens the binding towards the surface in a way that it quenches vibrational and rotational degrees of freedom. We propose that molecules with many internal degrees of freedom might more frequently show inverse transitions as compared to simple atomic systems. This will pave the way towards tuning structure transition conditions and morphologies of low-dimensional molecular adsorbate systems.

Conflict of Interest

The authors declare no conflict of interest.

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