



Phase transitions and dimensional cross-over in layered confined solids

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The nature of solid phases and cross-over of order–disorder phase transitions from two-dimensional (2D) layers to three-dimensional (3D) bulk in confined atomic systems remain largely unexplained. To this end, we consider noble gases and aluminum confined between graphene sheets at different pressures and temperatures. Using crystal structure search methods and molecular dynamics based on machine-learned potentials with quantum-mechanical accuracy, we identify structures of multilayer confined solids that deviate from simple close packing. Upon heating, we find that confined 2D monolayers melt according to the two-step continuous Kosterlitz–Thouless–Halperin–Nelson–Young theory. However, multilayer solids transition continuously into an intermediate layered-hexatic phase before melting discontinuously into an isotropic liquid. This intermediate phase persists at least up to 12 layers studied here. This change can be qualitatively understood based on the cross-over from 2D topological defects toward 3D ones during melting as the number of layers increases.

melting | multilayers | defects | dislocations | disclinations

Spatial dimension is one of the main factors influencing the existence and nature of phase transitions, and this issue has inspired innumerable mathematical and physical studies (1). The Hohenberg–Mermin–Wagner theorem (2, 3) states that continuous symmetries cannot be spontaneously broken at any finite temperature in $d \leq 2$ dimensions. However, the Kosterlitz–Thouless theory (4) proposes a topological phase transition in two-dimensional (2D) systems that is driven by the unbinding of a small concentration of topological. As a fundamental physical phenomenon, melting also shows dimensionality dependence (5). The classical theory of three-dimensional melting indicates a first-order phase transition from solid to liquid. In contrast, in 2D, the Kosterlitz–Thouless–Halperin–Nelson–Young (KTHNY) theory (4, 6, 7) suggests a continuous two-step melting scenario with an intermediate hexatic phase between solid and isotropic liquid. The 2D hexagonal solid first melts by the unbinding of dislocation pairs to the intermediate hexatic phase which has some free unbound dislocations but bound disclination pairs, followed by the unbinding of these to a normal isotropic liquid phase. In addition to topological defects, the relevant translational and orientational order parameters can be used to quantitatively identify the different states.

A similar intermediate phase with four-fold tetragonal orientational order, the tetratic phase, was also reported to exist in a 2D lattice and living tissue (8–11). However, the nature of the hexatic-liquid transition in 2D melting, which is continuous in the KTHNY theory, has been long debated, since experiments and simulations deviate from the KTHNY theory in certain instances. These include a discontinuous first-order transition of the hard disk model (12) and the direct sublimation of graphene (13). This might be due to several factors, including interparticle interactions (14), particle shape (15, 16), and out-of-plane fluctuations (17). Recent work using a soft-disk model with up to $1,024^2$ disks (18) has emphasized that the order of the liquid-hexatic transition is strongly influenced by finite-size effects and the difficulties in equilibrating large systems. Even in three-dimensional melting, various transition pathways can occur, involving diverse defect dynamics beyond those predicted by classic nucleation theory (19).

Experimental verification of the 2D melting scenario often relies on confined systems (20–25) and theoretical simulation studies (8–10, 14, 18, 26–31) introduce confinement as an unavoidable constraint in investigations of 2D melting. In experiments, most systems comprise μm colloidal particles, usually confined between two glass coverslips. Some experiments have used an air–water interface to constrain the particles (22, 23). The latter setup can be characterized by a smooth potential that just holds the particles at the interface which avoids complications due to glass confinement, ensuring more reliable results.

Significance

Noble gases (He, Ne, and Ar) and aluminum typically form only close-packed structures, even under the extreme conditions of white dwarf stars. However, machine learning–assisted crystal structure search and molecular simulations reveal tetragonal-packed configurations in their 2D layered structures confined within graphene (up to 6 layers). Confined monolayers melt via the continuous Kosterlitz–Thouless–Halperin–Nelson–Young theory, while multilayers undergo a continuous transition to a layered-hexatic phase before melting discontinuously. This shift in melting behavior arises from a qualitative evolution of defects, transitioning from purely 2D topological to 3D-type ones.

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In contrast to 3D (32–35) and 2D substrate adsorption structures (36), confined systems exhibit several unique features. For example, the packing of confined colloidal particles follows an intriguing pattern with increasing confinement width perpendicular to the individual layers (37–39), from a monolayer triangular or hexagonal lattice (denoted here as $1\blacktriangle$) to a bilayer stacking with a square or tetragonal lattice (denoted here as $2\blacksquare$). The full characteristic sequence of morphological transitions for confined colloids with increasing confinement width is established as $n\blacktriangle \rightarrow (n+1)\blacksquare \rightarrow (n+1)\blacktriangle$, where n is the number of stacking layers. Layering transitions are typically first-order with increasing particle number density (40). It has also been found that liquids confined between two plates exhibit spatially nonuniform features in the perpendicular direction (41, 42). Recently, new phases of atomistic systems under confinement were found, including, e.g., buckled tetragonal arrangement of He under diamond confinement (43) and square ice between graphene nanocapillaries (44, 45), accompanied by rich thermodynamic behavior and phase diagrams of nanoconfined ice (46, 47). An interesting question then arises as to how the confinement strength determines the elemental phase diagrams and order–disorder phase transitions and how the confined atomic system evolves from 2D toward 3D with increasing confinement width. To answer these questions, we perform extensive structure searches and atomistic simulations of elemental novel phases under varying 2D confinement provided by ideal graphene sheets. For computational efficiency and accuracy, we choose selected noble gases, which exhibit simple structural properties without confinement even under extreme conditions (32, 33) and when adsorbed on surfaces (36). To verify the universality of our conclusions, we also consider aluminum as a canonical example of a metallic substance (35). We systematically scan the crystal structures of these elements as a function of graphene confinement strength and lateral pressure (up to 10 GPa) using machine-learning and graph theory–assisted universal structure searcher (MAGUS) (48) in combination with quantum mechanical density functional theory (DFT) calculations. In large-scale systems, the interactions between the confined atoms are modeled realistically by the neuroevolution potential (NEP) approach (49), which is a machine-learning model that can simultaneously achieve an accuracy of the underlying DFT reference data and a computational efficiency comparable to typical empirical potentials. This efficient approach as implemented in the Graphics Processing Units Molecular Dynamics (GPUMD) package (49) enables machine-learning molecular dynamics (MLMD) simulations of systems consisting of millions of atoms for up to hundreds of nanoseconds in this work to minimize finite-size effects and to obtain equilibrium structures for the different materials.

We first find that multilayer systems possess ground states whose symmetries deviate from simple close-packed ones. We present complete phase diagrams of ground states up to $n = 12$ layers. Following this, we verify the two-step continuous KTHNY melting scenario for all the confined monolayer materials studied here. After that, we focus on the details of the order–disorder transitions for systems with increasing number of layers. Detailed analysis of the relevant thermodynamic quantities and configurations reveals that a continuous transition to a layered hexatic (LH) phase exists at least up to $n = 12$. The temperature range of this phase becomes narrower with increasing n , indicating eventual cross-over to a single first-order 3D bulk melting transition. We find that in our systems, the LH melting transition becomes first-order already for $n = 2$ and beyond. Further,

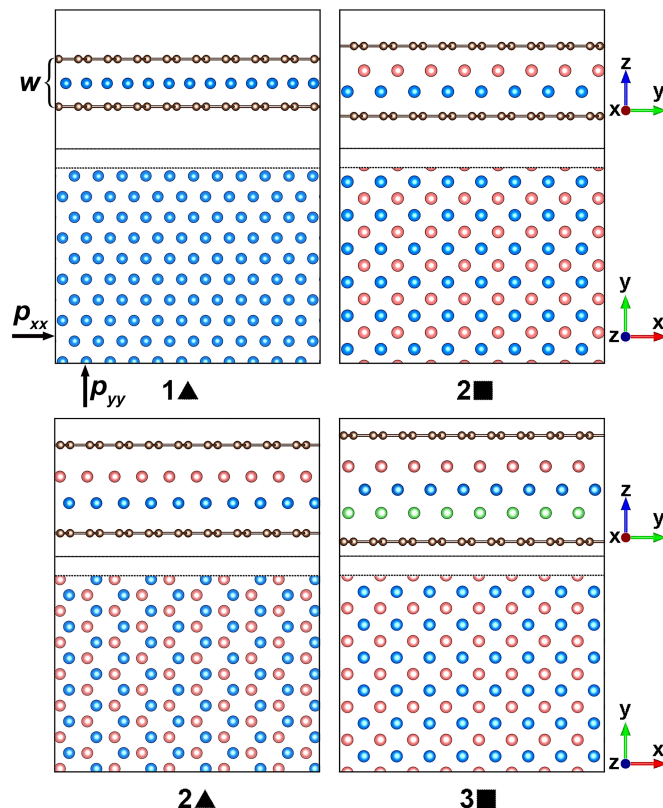


Fig. 1. Stable crystal structures of graphene-confined He under a lateral pressure $P_{\text{lat}} = 5$ GPa and different confinement widths ($w = 4, 6, 7$, and 8 Å) as viewed from the lateral (Top) and perpendicular (z) directions (Bottom). The structural transformation pattern with increasing confinement width follows $n\blacktriangle \rightarrow (n+1)\blacksquare \rightarrow (n+1)\blacktriangle$, where n is the number of atomic layers. He atoms in different layers are marked with blue, pink, and green. Brown atoms and bonds highlight the graphene sheet.

the melting temperature decreases with increasing number of layers with changes in the structure of the defects in the LH phase, highlighting the role of confinement and increasing dimensionality in phase transitions.

Results

Solid Noble Gases and Aluminum Confined Between Graphene Layers. First, we consider situations in which selected solid noble gases (He, Ne, and Ar) are confined between graphene (Gr) layers using confinement crystal prediction methods as implemented in MAGUS (48). Details of the methodology can be found in *SI Appendix*. To explore the phase diagrams, we vary the lateral pressure $P_{\text{lat}} = (P_{xx} + P_{yy})/2$ and the confinement width w along the z -axis between the two graphene layers (cf. Fig. 1). For all the systems with n layers, the series of structural transformations $n\blacktriangle \rightarrow (n+1)\blacksquare \rightarrow (n+1)\blacktriangle$ is observed either with increasing w or P_{lat} . An example for He under the condition of fixed $P_{\text{lat}} = 5$ GPa and increasing w is shown in Fig. 1. Interestingly, similar structural transformation patterns have been observed previously in micrometer-sized colloidal particle systems (37).

The automated process of MAGUS allows us to accurately and comprehensively scan phase diagrams of confined noble gases under different conditions (Fig. 2). We calculate enthalpies of these structures to locate the most stable phase at given P_{lat} and w . We consider P_{lat} up to 10 GPa and w up to 20 Å (*SI Appendix*, Fig. S3). Since He crystallizes only at pressures above 25 atm

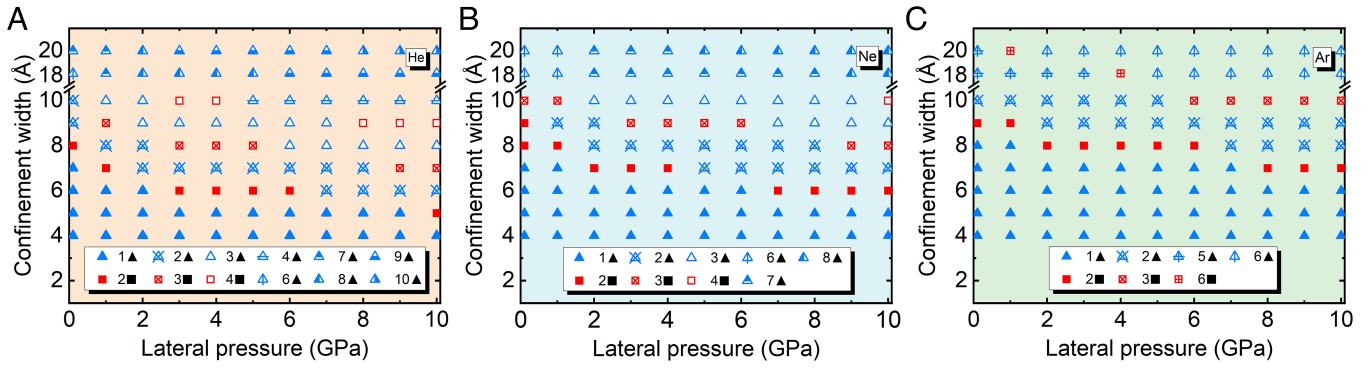


Fig. 2. (A–C) Confinement phase diagrams of He, Ne, and Ar (from Left to Right) as a function of P_{lat} and w based on minimization of enthalpy. $n\blacktriangle$ and $n\blacksquare$ represent n -layer hexagonal and tetragonal lattices, respectively. For clarity, data between $w = 10$ Å and 18 Å are not shown here (see *SI Appendix, Fig. S5* for complete phase diagrams).

(≈ 0.0025 GPa), the minimum P_{lat} is set to 0.1 GPa. The phase with the lowest enthalpy corresponds to the most stable crystal structure in the confinement condition. Using this methodology, we can accurately compute the w vs. P_{lat} phase diagrams of confined He, Ne, and Ar (Fig. 2 A–C). To verify the generality of these results, we also consider the case of Al which displays similar structural evolution $n\blacktriangle \rightarrow (n+1)\blacksquare \rightarrow (n+1)\blacktriangle$ under Gr confinement (*SI Appendix, Fig. S4*). We also validated that our conclusions are not affected by the inclusion of the quantum-mechanical zero-point energy in the enthalpy calculations (*SI Appendix, Fig. S7*).

There are several interesting common features in the phase diagrams for confined systems. First, the structural transformation pattern $n\blacktriangle \rightarrow (n+1)\blacksquare \rightarrow (n+1)\blacktriangle$ applies to structures with less than 5 to 7 layers, consistent with previous observations in colloidal systems (37). Beyond a certain number of layers, systems enter their stable 3D bulk phases without tetragonal structures. Second, the frequency of occurrence of tetragonal structures decreases as the number of layers increases. Third, the gradual increase in the atomic radius of noble gases from He to Ar reduces the number of layers at given w . In addition, there are some intermediate buckled-layer structures located at a narrow range of phase transition points between $\blacktriangle$ and $\blacksquare$, which were also observed in previous colloidal particle studies (50). To clarify their role, we have performed further enthalpy and phonon calculations that suggest that these buckled states are always metastable (*SI Appendix, Fig. S8*). Considering the fact that the noble gas elements and aluminum here adopt close-packed lattices even under TPa pressures (32) in 3D bulk, the emergence of new phases under the (quasi) 2D conditions highlights the crucial impact of confinement.

Melting of a Confined Ne Monolayer. Having identified a series of confinement-induced layered structures, we next focus on their thermodynamic behavior. In 2D, the KTHNY theory explains melting with a two-step continuous topological phase transition, first from solid to hexatic with the breakdown of translational order, and then from hexatic to liquid as the orientational order disappears (21, 51). The atomic translational order parameter is defined as $\varphi_{\mathbf{k}}(\mathbf{r}_j) = e^{i\mathbf{k}\cdot\mathbf{r}_j}$, where i is the imaginary unit, and $\mathbf{r}_j = (x_j, y_j)$ is the intralayer atomic 2D coordinate of atom j . $\mathbf{k}$ is a vector in the reciprocal lattice corresponding to the Bragg peak of the ordered phase with a maximum in the static structure factor $S(\mathbf{k})$. The n -fold atomic local orientational order parameter

is defined by $\varphi_n(\mathbf{r}_j) = (1/N_b^j) \sum_m N_b^j e^{-in\theta_{jm}}$, where N_b^j is the number of the nearest neighbors (bonds) to atom j , and θ_{jm} is the angle between the bond vector $\mathbf{r}_m - \mathbf{r}_j$ and the fixed x -axis. For hexagonal and tetragonal intralayer lattices $n = 6$ and 4 , respectively. The global order parameter of a single configuration is the spatially averaged order parameter summed over all N atoms as $\phi_\alpha = \sum_{j=1}^N \varphi_\alpha(\mathbf{r}_j)/N$, where α denotes either $\mathbf{k}$ or n . To identify structural transitions in the 2D layer, the correlation functions and susceptibilities corresponding to the two order parameters are defined as

$$g_\alpha(|\mathbf{R}|) = \left\langle \frac{1}{N} \sum_{j=1}^N \varphi_\alpha^*(\mathbf{r}_j) \varphi_\alpha(\mathbf{r}_j + \mathbf{R}) \right\rangle; \quad [1]$$

$$\chi_\alpha = \langle |\phi_\alpha|^2 \rangle - \langle \phi_\alpha \rangle^2, \quad [2]$$

where $\langle \dots \rangle$ represents the ensemble average. Going from the 2D solid to the hexatic phase, the translational order correlation function changes from a quasi-long-range form $g_{\mathbf{k}}(|\mathbf{R}|) \propto |\mathbf{R}|^{-\eta_{\mathbf{k}}}$ to short-range correlations given by $g_{\mathbf{k}}(|\mathbf{R}|) \propto \exp(-|\mathbf{R}|/\xi_{\mathbf{k}})$. At the transition point from the solid to hexatic phase, $\eta_{\mathbf{k}} \leq 1/3$. Correspondingly, going from the 2D hexatic phase to liquid, the orientational order correlation function changes from quasi-long-range form $g_n(|\mathbf{R}|) \propto |\mathbf{R}|^{-\eta_n}$ to a short-range form $g_n(|\mathbf{R}|) \propto \exp(-|\mathbf{R}|/\xi_n)$. At the transition point from the hexatic to liquid, $\eta_n = 1/4$. $\xi_{\mathbf{k}}$ and ξ_n are temperature-dependent correlation lengths (6). Also, the corresponding susceptibilities $\chi_{\mathbf{k}}$ and χ_n diverge at the transition points from solid to hexatic and from hexatic to isotropic liquid, respectively. It has been shown experimentally that the susceptibilities are more robust in locating the transition points as compared to the correlation functions (51).

In the present work, we select Gr-confined Ne as a concrete example to quantify the critical behavior of confined layered structures. It should be noted that all the 2D solid phases in this work are perfect single crystals (24). Recent work highlights the importance of properly accounting for finite-size effects and thermodynamic equilibration during 2D melting using up to $1,024^2$ particles (18). Therefore, we have carefully checked these by performing MLMD simulations in the isothermal-isobaric ensemble up to millions of atoms and hundreds of nanoseconds. Details can be found in *SI Appendix*.

The first structure is the $1\blacktriangle$ at a confinement width of 4 Å and a lateral pressure of 5 GPa. From the order parameter correlations and susceptibilities, a typical two-step melting behavior with

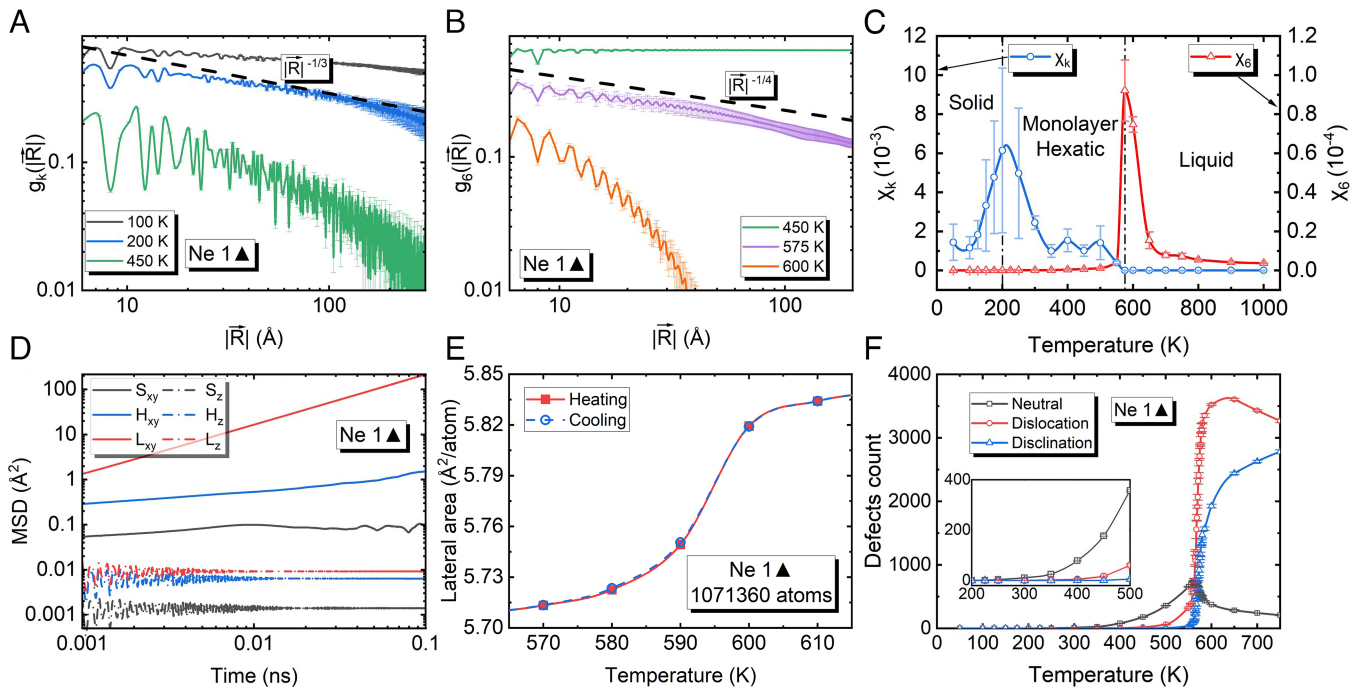


Fig. 3. Thermodynamic properties of 1Å ($P_{\text{lat}}=5$ GPa, $w=4$ Å) at various temperatures. (A–C) Intralayer quantities: Translational order correlation function (g_k), orientational order correlation function (g_n), and corresponding susceptibilities (χ_n) within the KTHNY theory framework. Error bars show the SD from three independent trajectories. (D) Mean squared displacements (in log-log scale) along the xy plane and z -axis at 100 K (solid, S), 450 K (hexatic, H), and 600 K (liquid, L). (E) Equilibrium lateral areas per layer atom during cooling and heating around the melting point, showing no thermal hysteresis. (F) Defect counts vs. temperature, determined by nearest neighbor counting and Voronoi diagrams (details in [SI Appendix](#)).

an intermediate hexatic phase dictated by the KTHNY theory can be clearly identified as shown in Fig. 3. In Fig. 3A, we show the translational correlation function at three selected temperatures in a log-log plot. At about 200 K, we find a well-defined power law $g_k(|R|) \propto R^{-1/3}$ indicating a change of the ordered phase to a hexatic phase. Further, at a higher temperature of 575 K, $g_6(|R|) \propto R^{-1/4}$ in Fig. 3B, which indicates a change of the hexatic phase to the 2D liquid phase. The phase transition sequence is evident in the corresponding susceptibilities χ_k and χ_6 in Fig. 3C, which develop sharp and distinct peaks at the transition temperatures. Further, the phase transitions can be seen in the mean-square displacements (MSDs) at different temperatures in Fig. 3D. The MSDs along the z -axis at different temperatures are saturated with thermal vibrations due to strong confinement. In contrast, the MSDs in the xy plane remain virtually constant in the solid phase at 150 K, while they indicate small amounts of particle diffusion in the hexatic phase at 450 K, and eventually much higher diffusion rates in the liquid phase at 600 K. The temperature range of the hexatic phase in this work, similar to that of monolayer-confined water (46), is about 400 K which is large enough to make it experimentally observable.

Moreover, there is an interesting question regarding the order of the 2D hexatic-liquid transition, and some studies have found that the transition may become discontinuous depending on, e.g., the particle-particle interactions (12–15, 17, 18, 20, 22, 23). In particular, recent work (18) has shown that for purely repulsive soft disks in 2D, there is a change from a second-order to discontinuous melting with increasing inverse power law. In the present case of noble gases, we expect the KTHNY scenario to be valid for one-layer melting, as supported by power-law behavior of the correlations at the susceptibility peaks. We have further tested for possible thermal

hysteresis of the 2D confined 1Å during cooling and heating around 580 K in Fig. 3E. The lack of any discernible hysteresis supports a continuous hexatic-to-liquid transition without a free energy barrier.

Perhaps even more direct evidence about the nature of the transition can be obtained from statistical analysis of the topological defects in Ne 1Å shown in Fig. 3F, including dislocations and disclinations in the KTHNY theory. The emergence of dislocations occurs as the system goes to the hexatic phase, and the unbinding of bound disclination pairs to free disclinations is characteristic of the transition to an isotropic liquid. Details of defects classification can be found in [SI Appendix](#).

Melting of Multiple Layers Under Confinement. Considering our clear evidence for the KTHNY melting in the 1Å Ne, we next focus on cases where there are multiple (but not many) layers under Gr confinement. Previous work (24) on the melting of confined colloidal crystals has indicated the absence of the KTHNY two-step melting in multilayer systems. They found evidence on first-order melting in thick films beyond 4 layers, while thin films between 2 and 4 layers melt continuously in a single step. However, recent work (10) proposed an intermediate antiferromagnetic tetragonal phase in a confined bilayer hard sphere tetragonal structure which suggests that two-step melting might still occur in multilayer systems.

To tackle the case of multilayer melting, we again consider Gr-confined Ne as the model system. In the case of 2■ Ne ($P_{\text{lat}}=3$ GPa, $w=7$ Å) and 2▲ Ne ($P_{\text{lat}}=8$ GPa, $w=7$ Å), the intralayer correlation and susceptibility data clearly show that two-step melting still exists in these systems ([SI Appendix, Fig. S19](#)). The melting behavior of 2▲ Al also indicates a two-step melting scenario ([SI Appendix, Fig. S25](#)).

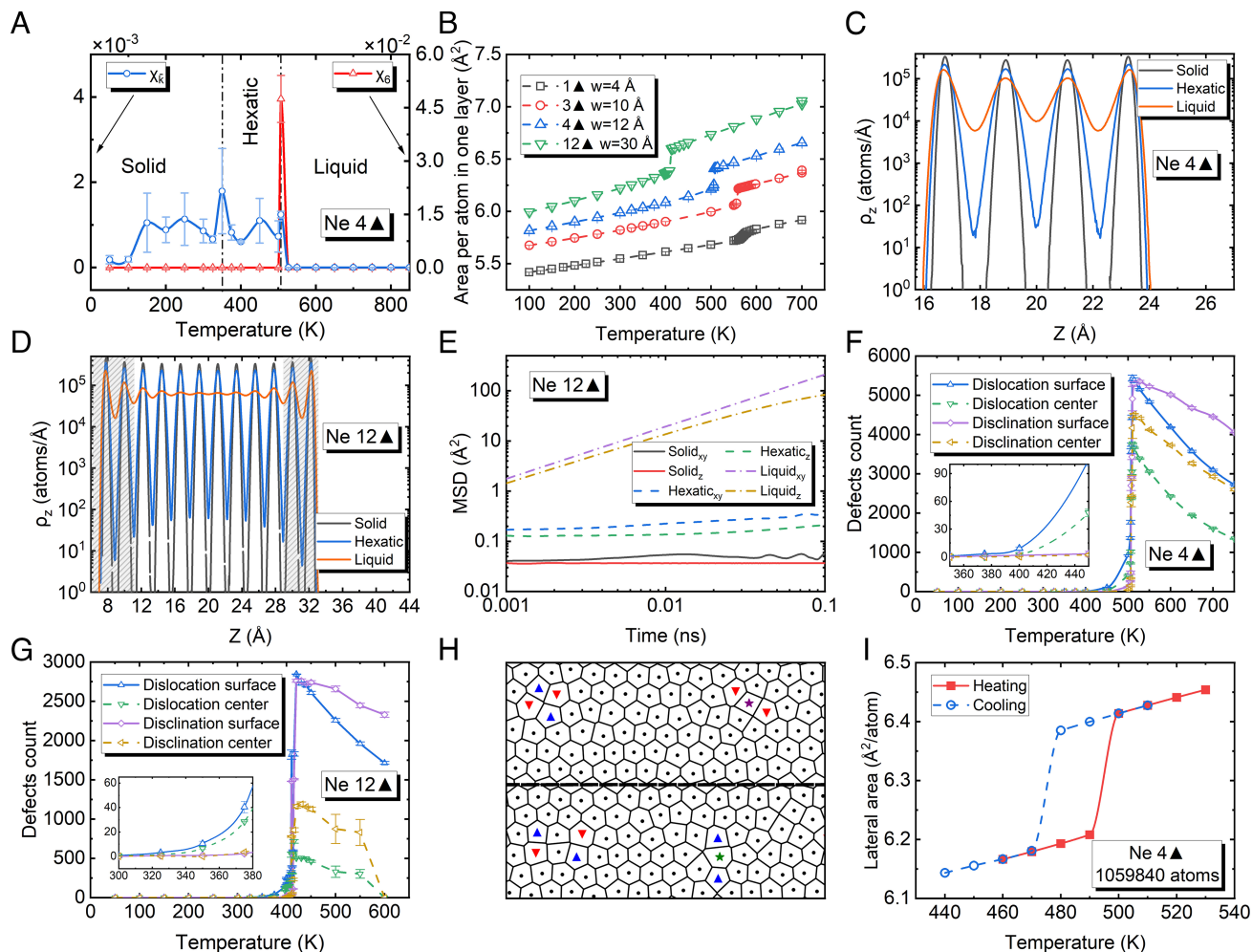


Fig. 4. Thermodynamic properties of multilayer structures Ne at $P_{\text{lat}} = 5$ GPa. (A) Temperature-dependent susceptibilities χ_k of 4▲ ($w = 12$ Å); (B) Atomic area per layer at different temperatures and layer numbers; (C and D) Interlayer z -axis density distribution ρ_z of 4▲ (solid at 200 K, layered hexatic at 450 K, liquid at 600 K) and 12▲ ($w = 30$ Å, solid at 200 K, layered hexatic at 350 K, liquid at 600 K), with shaded areas in (D) indicating the surface region; (E) Mean squared displacements corresponding to d (in log-log scale) along xy and z axes; (F and G) Defect statistics vs. temperature in 4▲ and 12▲; (H) Voronoi diagram of layered hexatic 4▲ surface layer, with atoms having 4–8 neighbors marked by purple, blue, black, red, and green, respectively. The dashed line separates different regions from a large system; (I) Equilibrium lateral areas per atom in 4▲ during cooling and heating around the melting point, showing thermal hysteresis.

To highlight the interesting features that emerge with the increasing number of layers beyond a monolayer, we discuss the details of the two-step transitions for 4▲ and 12▲ in what follows. More data for $n = 2$ and 3 can be found in *SI Appendix*. We naturally expect that when the number of layers increases, the melting crosses over to the relevant limit in 3D, with a single first-order transition. Our main result here is that already for $n = 2$, the critical behavior of the melting scenario changes. There is a continuous order–disorder transition to a LH phase as in monolayers, but the hexatic–liquid transition becomes first-order (cf. *SI Appendix*, Figs. S19 and S20). This is also evident for 4▲ Ne ($P_{\text{lat}} = 5$ GPa, $w = 12$ Å), for which the susceptibilities are shown in Fig. 4A. The transition from a solid to an LH phase (52) seems to be present but becomes weaker in transitional susceptibility with increasing n . For melting, the orientational susceptibility peak moves to a lower temperature becoming sharper. These conclusions apply to the 3-layer (*SI Appendix*, Fig. S21).

Additional data in Fig. 4B for the evolution of the equilibrium transverse xy areas from 1▲ Ne to $n = 12$ Ne at $P_{\text{lat}} = 5$ GPa during heating further confirm that the melting temperature

decreases as the number of layers grows. However, this behavior is unexpected because generally we expect fluctuations to be enhanced in 2D, leading to a lower melting point than in 3D. To explain this puzzle, we consider the density profile of the Ne atoms in the z direction as well as the evolution of the intralayer (xy plane) defects in 4▲ and 12▲ ($P_{\text{lat}} = 5$ GPa, $w = 30$ Å) at different temperatures. The interesting finding here is that atoms can now start occupying interlayer positions upon entering the LH phase (Fig. 4C and D), corresponding to the changes in susceptibilities. The relative number of such atoms remains very low in the LH phase, which means that individual hexatic-like layers are still well-defined.

Confinement-induced ordering or layering between the walls (42) can be clearly seen in Fig. 4C and D. However, while 2D layers remain well-defined in the 4▲ liquid, for the case of 12 layers, the middle part of the system is almost homogeneous. For colloidal systems, it has been shown (24) that there is a difference in the melting of thin (≤ 4 layers) and thick films (> 4 layers). The data show that upon melting the concentration of interlayer atoms increases by at least two orders of magnitude, indicating the formation of 3D defects that can influence the nature of

melting. The MSDs of 12▲ (Fig. 4E) at different states also indicate atoms in the LH phase diffuse within the layers (on the xy plane) and between them (z direction) but at a much lower rate than in the fully molten liquid.

To analyze the present case in more detail, as in Fig. 3F, the evolution of defects within the layers of the 4▲ and 12▲ structures (Fig. 4F and G) is scrutinized. At the transition point from LH to isotropic liquid in 1▲, the disclinations in the liquid state proliferate with increasing temperature, while the dislocations gradually disappear due to their unbinding. For 4▲ and 12▲, the number of all topological defects in the liquid decreases with increasing temperature because of the preferential formation of 3D interlayer defects (interstitials, vacancies). In the multilayer systems, the surface layers in contact with Gr have more topological defects than those in the middle. The topological defects disappear in the central homogeneous liquid of 12▲ at high temperatures. These features could be the underlying reason for the observed decrease in the melting temperature as the number of layers increases.

We have also examined the nature of the LH phases in more detail for multilayer systems. In Fig. 4H, we show defects in the surface layer of the 4▲ LH phase, classified using the Voronoi diagram method. The atoms with 4 – 8 nearest neighbors are marked by purple, blue, black, red, and green, respectively. According to the KTHNY theory, defects in the hexatic phase should be 5 – 7 disclination pairs unbinding from the 5 – 7 – 5 – 7 dislocation pairs of the triangular crystal. However, as shown in Fig. 4H, there are also some 5 – 8 – 5 and 7 – 4 – 7 dislocations in the LH phase. The emergence of such defects highlights the existence of interlayer interstitial atoms.

To summarize, the temperature-dependent evolution of susceptibilities, equilibrium areas, and defects in multilayer structures show a continuous transition from the solid to the intermediate LH phase at least up to $n = 12$. However, the melting of the LH phase is not compatible with the KTHNY scenario. Our data imply that all quantities change discontinuously at the LH-to-liquid transition in the thermodynamic limit. Perhaps the clearest evidence comes from the evolution of the area of the 2▲ and 4▲ phases during cooling and heating, shown in *SI Appendix*, Fig. S20 and Fig. 4I, where there is clear thermal hysteresis supporting a first-order melting transition. Moreover, the melting point determined by the hysteresis in multilayer systems (e.g., $T_m \approx 480$ K for 4▲) is larger than the typical LH temperature of 450 K, suggesting the LH phase is not metastable due to superheating.

Discussion

In this work, we have considered the influence of spatial confinement on monolayer and multilayer solids. Fundamental questions in such systems concern the nature of the solid phases and how the two-step monolayer melting with continuous transitions changes when the number of layers increases. To this end, we have used quantum-mechanically accurate machine-learned potentials for selected noble gases and aluminum combined with molecular dynamics simulations within the GPUMD software (49). We have explored in detail the ground-state phase diagrams for He, Ne, Ar, and Al and confined between graphene layers using the MAGUS structural search code (48). The structural transitions between hexagonal and tetragonal lattices observed in these layered structures violate the conventional rule that these elements only adopt close-packed crystal patterns. For monolayer Ne, we have further

confirmed the two-step melting as predicted by the KTHNY theory, with a continuous transition to an intermediate hexatic phase followed by another continuous transition to an isotropic liquid. We find a wide range of temperatures where the hexatic phase is stable, which makes it experimentally feasible to observe it. In contrast to monolayers, in multilayer systems of Ne up to $n = 12$ here, melting proceeds in two stages: First, there is a continuous transition from solid to a LH phase, followed by a discontinuous transformation from LH to an isotropic liquid. As the number of layers increases, the melting temperature decreases, and the intermediate LH temperature range narrows, indicating eventual cross-over to a single 3D first-order melting transition. Our detailed analysis of defects throughout the phase transitions reveals the strong influence of substrate effects for a small number of layers, while thicker films exhibit more bulk-like behavior in the middle layers. The key differences between monolayer and multilayer melting transitions may then be attributed to the different nature of defects between the pure 2D limit (dislocations and disclinations) and 3D systems where interstitials and more complicated defects appear.

Our results reveal the influence of dimensionality and defects on the melting pathways for confined systems. In more complex systems, such as confined ice (44, 46, 47) and polycrystals (24), even richer phase transition behaviors could be expected. Additionally, the structures of noble gases and aluminum identified in this work, which were hinted at in earlier experiments (43), offer promising platforms for exploring various physical phenomena and confirming our conclusions. The insights gained from the melting processes could be generalizable to other types of phase transitions (10), inspiring further exploration into the fundamental nature of these physical processes.

Materials and Methods

The crystal structures confined between graphene layers in this work were predicted using the MAGUS package (48). For these predicted structures, electronic structure calculations, structural relaxations, and ab initio molecular dynamics (AIMD) simulations were carried out based on DFT. The finite-temperature behavior of the predicted structures was further investigated using the GPUMD package (49). Machine-learning potentials for large-scale molecular dynamics were trained using the NEP module in GPUMD, based on datasets generated from the AIMD simulations. Further methodological and analytical details, along with supporting data, can be found in *SI Appendix*.

Data, Materials, and Software Availability. The data and the code for this work is available in Figshare (53), including the training dataset for constructing machine learning models, the source code of GPUMD with the implemented confinement potential for performing molecular dynamics simulations, and the MAGUS package used to predict confined crystal phases. More information can be obtained upon request from the corresponding author of this paper.

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