Structure of metastable 2D liquid helium

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Abstract – We present diffusion Monte Carlo (DMC) results on a novel, superfluid phase in two-dimensional \(^4\)He at densities higher than 0.065 Å\(^{-2}\), which is very close to the freezing density. The new phase has anisotropic, hexatic orbital order, but the single-particle density remains constant. By increasing density the hexatic superfluid forms a metastable state, which lies above the crystal ground state in energy. This implies that the liquid-solid phase transition takes place in two stages: a second-order phase transition from the isotropic superfluid to the hexatic superfluid, followed by a first-order transition that localizes atoms into the triangular crystal order.

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Metastable states are transient, excited states that have a relatively long lifetime, and may appear in the absence of an external disturbance that would trigger the transition to the ground state. Three-dimensional helium has a metastable high-density (pressure) liquid phase, observed in laboratory experiments by Ishiguro et al. \([1]\) and Werner et al. \([2]\). The liquid phase is measured up to 160 bars — far above the liquid solid freezing pressure of 25.3 bars. Also Pearce et al. \([3]\) observed metastable liquid at pressures up to 40 bars in helium immersed in gelsil pores. These types of metastable states are typical for a first-order phase transition, where the excess energy must be released to make the transition from liquid to solid phase. Diffusion Monte Carlo (DMC) simulations by Vranjes et al. \([4]\) confirmed that a metastable state is superfluid with a finite condensate fraction and has a roton minimum in the excitation spectrum up to 275 bars, but no upper limit in pressure to this behavior is proposed.

Variational calculations of both 2D and 3D liquid helium suggest that the isotropic low-density liquid state becomes unstable against formation of an anisotropic liquid state before the solidification pressure is reached \([5,6]\). The energy required to create hexatic orbital order into the liquid phase diminishes with increasing density and becomes zero at the transition density. The liquid undergoes a smooth, second-order phase transition into the hexatic phase. Gernoth \([7]\) has made a detailed group theoretical analysis of the possible scenarios of the phase transition from the high symmetry liquid phase through the reduced symmetry point group of the hexatic phase to the low symmetry space group of the solid phase.

In this article we present results on the DMC simulation of the two-dimensional \(^4\)He at zero temperature and study the high-pressure metastable liquid phase. We show that this zero-temperature phase is “hexatic”, i.e. it has the hallmarks of long-range orientational order and short-range positional order. The phase transition from liquid to solid has two stages when the pressure increases. It is triggered by a second-order transition from an isotropic liquid to the hexatic phase, and then followed by a first-order transition from the hexatic phase to a solid with the full space group symmetry of the crystal structure. In the first-order transition the constant single-particle density of the hexatic phase acquires triangular lattice order. Yet, the hexatic phase can exist as a metastable state up to very high densities.

The ground-state properties of zero temperature 2D \(^4\)He have been studied using Monte Carlo methods by Giorgini et al. \([8]\) and by Whitlock et al. \([9]\), who find that the ground state at high densities is a triangular solid phase. Helium layers on a substrate, such as graphite, and in porous media have been thoroughly studied using theory \([10–12]\) and experiments \([13]\). The full phase diagram at finite temperature has been calculated using the path integral Monte Carlo by Gordillo and Ceperley \([14]\). Also the change in the angular order in the liquid-solid transition has been discussed using the variational shadow wave function \([15]\). Our new result complements those properties with a metastable superfluid state, which has the hexatic two-particle structure.

We first describe how structural properties were obtained from the simulation. Diffusion Monte Carlo \([16]\)
is a zero-temperature method that uses a large number (in this work \(\sim 500-1000\)) of independent \(N\)-atom simulations, walkers, to statistically represent an imaginary time (marked \(\tau\)) evolution process to a wave function \(\Psi(\tau)\). In principle this projects out the excited states and one proceeds to sample the properties of the ground state \(\phi_0\). In a simulation metastability arises if it is improbable that one sees the asymptotic result \(\Psi(\tau) \rightarrow \phi_0\) within the limited simulation time. In other words, there may only be a very narrow random-walk path that takes the evolution to the true ground state. Statistics is always improved with importance sampling and a chosen trial state. With importance sampling one biases the random walk, usually to the effect that the ground state is reached faster. For example, if one imposes a triangular solid periodicity on the simulation we use a square simulation box with edges along the \(x\) and \(y\) axes, and choose the direction \(\hat{e}_0\) to point to the \(x\)-direction. With this choice the trial wave function (1) has six maxima, one at the \((x, y)\)-direction \((1,0)\). The \(g_m(r)\) data is collected as a distance histogram multiplied by \(\cos(m\theta_{ij})\), where \(\theta_{ij}\) is the angle defined in the trial wave function (1). Cosine is used here to keep the measurement and the trial wave function angles in phase —this poses only a calculational limitation to the external direction \(\hat{e}_0\).

If the trial state is still a liquid, why should the angular part make any difference? The angular part serves a dual purpose, in close relation to the way quantities are measured in DMC. First, a well-known fact is that if the trial state is not too far from the eigenstate \(\phi_0\), one can approximate the expectation values of operator \(A\) by the so-called extrapolated estimator, \(\langle \phi_0 | A | \phi_0 \rangle \approx 2\langle \phi | A | \phi_T \rangle - \langle \phi_T | A | \phi_T \rangle\), where \(\langle \phi | A | \phi \rangle\) is what we want to know, \(\langle \phi | A | \phi_T \rangle\) is what the average over walkers gives, and \(\langle \phi_T | A | \phi_T \rangle\) is the value in the trial state. This implies that even if there is no angular order in \(\phi_0\), the walkers simulate roughly half of the order we put in the trial state \(\phi_T\). As a result the trial state gently biases the walkers to favor a given globally oriented local anisotropy. In this respect the trial state acts as a perturbation. The extrapolation or the forward-walking algorithm discussed below removes this perturbation from the final expectation values.

The second reason for using the angular part is that it enables us to measure how this “perturbation” affects the high-density liquid in coordinate space. To see why, let us first assume that the metastable liquid indeed has a global angular order with respect to some fixed external (laboratory) direction, but we use a spherically symmetric trial state. Then in the DMC simulation each walker picks up a different, randomly chosen orientation, which, over a large number of walkers, averages to zero. This is the reason why we need a non-zero angular order in the trial state in order to see one in \(\phi\) when using a coordinate space observable. The fact that a trial state, or importance sampling in general, can be used to actually make a quantity observable in a Monte Carlo simulation is not frequently mentioned in standard texts. If available, we always use unbiased estimators, since extrapolated estimators are known to give systematic errors, especially for structural quantities like the pair distribution. In this work we apply the algorithm based on forward walking described in ref. [17]. One keeps track on how many asymptotic off-springs a given walker will have, and weights the present situation accordingly. Although the name indicates that these results are unbiased by the trial state, this is not entirely true: as discussed above, without the trial state angular structure there is no chance of observing coordinate space angular order. In our case the unbiased estimators are more like conditional results, valid for a certain fixed amplitude of the angular

\[\varphi_T = \prod_{i<j} \exp \left[ \alpha \frac{\cos(m\theta_{ij}) - 1}{r_{ij}} \right] \exp \left[ - \beta \frac{r_{ij}}{r_0} \right]. \] (1)

The variational constants are \(\beta \sim 3.3\) Å and \(\mu = 4\). Here \(m\) is an even integer and the angle between atoms at \(r_i\) and \(r_j\) is defined \(\cos(\theta_{ij}) = \frac{r_i \cdot r_j}{r_{ij}}\), with respect to a reference direction \(\hat{e}_0\) and \(r_{ij} = |r_i - r_j|\) is the distance between the atoms \(i\) and \(j\). The amplitude of the trial angular structure is \(\alpha \sim 0.6\) (see footnote 1). This wave function has no crystalline order and atoms are not fixed to lattice sites, contrary to the Nosanow-type solid trial state. Also the anisotropic trial state is not the same as using, say, a substrate potential, because the liquid structure cannot ignore the latter and a potential induces a global order, and not just a local one, around each atom. Here we are not forcing anything upon the 2D liquid itself, merely adding a possibility to measure the degree of anisotropy from the simulation. Within statistical error, the energy and the radial distribution function of the metastable state are independent of the trial state.

The reference direction \(\hat{e}_0\) is set externally, which enables us to see if the high-density liquid orients itself to the direction set by the trial wave function. In short, we estimate how strongly the liquid binds to the globally defined orientation. From the simulation we determine the pair distribution, expanded as

\[g(r) = \sum_{m=0}^{\infty} g_m(r) \exp(i m \theta), \] (2)

where \(m\) is even and \(\cos(\theta) = \mathbf{r} \cdot \mathbf{e}_0\). In this work we keep terms up to \(m = 12\). We measure the pair distribution rather than the momentum space static structure function,
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Fig. 1: (Colour on-line) The total energy of 2D helium as a function of density. The present data and the data by Giorgini et al. [8] are computed using DMC with the revised Aziz HFDHE2 potential [18] (“Aziz II”). For comparison we show the energies of liquid and triangular solid by Whitlock et al. [9], who used the 1979 version of the Aziz HFDHE2 potential (“Aziz I”) [19].

Fig. 2: (Colour on-line) The $g_{m=6}(r)$ component of the pair distribution as a function of density, computed using the trial state with the amplitude $\alpha = 0.6$. For reference, the points labeled “VMC” show the input trial state $g_{m=6}(r)$ amplitude. The lines are just guides to the eye.

Fig. 3: (Colour on-line) The amplitude of the $g_{m=6}(r)$ component of the pair distribution as a function of density, computed using the trial state with the amplitude $\alpha = 0.6$. For reference, the points labeled “VMC” show the input trial state $g_{m=6}(r)$ amplitude. The lines are just guides to the eye.

The two slightly different He-He potentials used in the QMC calculations. Our results agree well with the liquid energies computed by Giorgini et al. [8] available up to $\rho < 0.065 \text{Å}^{-2}$. For testing we also reproduced the Aziz-I potential liquid energies reported by Whitlock et al. [9]. Trial states with $\alpha$ in the range 0–0.6 gave the same total energies within statistical error bars. Also the spherically symmetric component of the radial distribution function $g(r) \equiv g_{m=0}(r)$ is the same for any trial state angular parameter $\alpha$. The phase transition from the isotropic to anisotropic liquid generates angular dependence into the pair distribution function $g(r)$. The transition is continuous and the amplitude of the angle dependence increases with increasing density. The angular behavior is determined by the $m = 6$ component of the expansion in eq. (2), which is in agreement with the point group symmetry of the triangular lattice. Figure 2 shows the component $g_{m=6}(r)$ at three densities near the freezing density, computed using exactly the same trial state. While the stable liquid ($\rho = 0.060 \text{Å}^{-2}$) is insensitive to the trial state, the metastable liquid shows a clear externally oriented angular structure. The amplitude of the short-distance oscillations in $g_{m=6}(r)$ increases with increasing density, but in long distances these oscillations vanish, which means that the system remains in the liquid state. The phase transition is made more apparent in fig. 3, where we plot the maximum value of $g_{m=6}(r)$ i.e. the amplitude of the first oscillation. We use the same trial wave function at all densities and fig. 3 shows also the “input amplitude”, computed using variational Monte Carlo (VMC). While the trial wave function gives rise to an angular amplitude that slowly increases as the density increases, the DMC data shows a clear onset of the angular structure. Above the density $0.065 \text{Å}^{-2}$—remarkably close to the expected freezing density—the $g_{m=6}(r)$ component

term in the trial state, and we note in passing that the unbiased and the extrapolated estimators agree well. We have also checked that the period we follow the walkers is long enough so that the asymptotic regime is reached. Sarsa et al. [20] compared the pair structure of 3D liquid helium obtained using the Path Integral Ground State (PIGS) method and the forward-walking DMC algorithm and found that the two methods produce very accurately the same result. We have done simulations using a quadratic DMC algorithm, using mainly 64 or 120 atoms. Figure 1 shows the total energy vs. density in the high-density 2D liquid and triangular solid. Notice
Fig. 4: (Colour on-line) Typical results for the absolute values of the radial distribution $|g_0(r)−1|$ and the angular distribution $|g_6(r)|$ are shown at the density 0.075 Å$^{-2}$. The decay of the oscillations in the radial distribution function as a function of distance can be accurately fitted to an exponential curve, while the oscillations in the angular distribution decay with a power law.

 increases anomalously, yet much less than what would be observed in freezing$^2$. The fact that the DMC algorithm reduces the amplitude from above 0.12 in the trial wave function to less than 0.02 at low densities shows how little bias there is, and that the forward-walking DMC algorithm is indeed able to remove the trial state angular structure if it is favorable.

The full spatial crystal order requires releasing of the excess energy leading to the triangular structure in the single-particle density$^[21]$. Here the single-particle density stays constant. Figure 4 shows that the oscillations in the positional order, measured by the radial distribution function $g_0(r)$, decay exponentially typical for the 2D liquid, while the oscillations in the $m=6$ orientational order, measured by $g_6(r)$, decay with a power law — these properties are summarized by calling this liquid phase hexatic.

In the high-density, metastable $^4$He the angular component $g_{m=6}(r)$ of the pair distribution function grows above the freezing density, unlike any other component. To exclude the possibility that this is an artifact due to the $m=6$ symmetry put into the trial state, we repeated the calculation using a four-fold symmetry in $\varphi_T$; in that case there is no anomalous increase in $g_{m=4}(r)$. In our DMC calculations we used a periodically repeated square box, which is not commensurate with a triangular lattice and also will not spuriously enhance the sixfold symmetry component.

According to our results the metastable state is superfluid. In fig. 5 we show the results for the condensate fraction $n_0$, which decays monotonously from 15% at 0.05 Å$^{-2}$ to 1% at 0.08 Å$^{-2}$ as a function of density. We have fitted our results with a simple quadratic formula

$$n_0 = 0.228 - 0.456x + 0.234x^2,$$

where $x = (\rho - \rho_0)/\rho_0$ and $\rho_0 = 0.0421 \text{ Å}^{-2}$ is the saturation density. No abrupt change in the condensate fraction is observed at the onset of the phase transition density 0.065 Å$^{-2}$. The DMC method is not ideal for measuring the long-range order in the one-particle density matrix, since here one cannot use the unbiased estimator. The sensitivity of the long-ranged tail to the extrapolated estimator is illuminated in fig. 6.

$^2$We also saw few cases of freezing with rapid increase in the angular order, similar to one reported in ref. [15].
In conclusion we have shown that a novel metastable state in two-dimensional $^4$He exists at high densities. It has a hexatic orbital symmetry, but homogeneous single particle density. This metastable state may be created in a crystal growth process in rapid freezing of $^4$He, and should disappear slowly in annealing. We like to draw attention to a similar metastable state in three-dimensional $^4$He [4], where the ultrasound shock-wave experiments pressurized $^4$He far beyond the freezing density, and yet $^4$He remained superfluid [1,2]. Whether also the three-dimensional metastable state has angular structure is an interesting open question.

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