

Instability of Vacancy Clusters in Solid ^4He

Y. Lutsyshyn · C. Cazorla · J. Boronat

Received: 26 June 2009 / Accepted: 1 October 2009 / Published online: 10 October 2009
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Abstract The behavior of pairs and clusters of vacancies in solid ^4He crystals is studied with diffusion Monte Carlo method. We use a trial function suitable for describing solid ^4He with long range order, arbitrary number of unoccupied sites and explicit Bose symmetry. It is found that vacancy clusters are unstable and collapse in all considered systems. We find no signature of stability of bound vacancy clusters of any size. Vacancies are found to exhibit weak attraction and a rough estimation of the binding energy is reported.

Keywords Supersolid · Defects · Vacancies · Clusters

PACS 67.80.-s · 64.75.-g · 61.72.J-

1 Introduction

Properties of the ground state of solid ^4He have gained interest due to discovery of a decoupled, non-classical moment of inertia fraction (NCRIF) and other seemingly accompanying effects in helium crystals that are attributed to an onset of “supersolidity” [1–3]. For a review, see Refs. [4–6]. Numerous theoretical works have since considered helium solids [7–17], especially with finite temperature [12–17] simulation methods. The latter have the conceptual difficulty of trying to investigate the properties of hypothesized supersolid without the knowledge of where the transition

Y. Lutsyshyn (✉) · J. Boronat
Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya,
Campus Nord B4-B5, 08034, Barcelona, Spain
e-mail: yaroslav.lutsyshyn@upc.edu

C. Cazorla
Earth Sciences Department, University College London, London WC1E 6BT, UK

temperature is precisely located. Experimentally, NCRIF effects do not appear at temperatures slightly above 0.2 K, and even less in crystals of higher quality [18]. It may also be the case that the true supersolid phase exists at temperatures as low as 50 mK, and effects observed at higher temperatures are reminiscent of this phase [19]. Unfortunately, results of simulations at finite temperatures below 0.1 K are scarce at present. Existing methods, such as the path integral Monte Carlo (PIMC), are also known to suffer a considerably reduced performance as the temperature is lowered to the relevant range. It is therefore important to consider these systems with first principles zero-temperature methods. In this work we employ diffusion Monte Carlo (DMC) to study the problem. Another suitable ground state method, Shadow Path Integral Ground State (SPIGS) has also been applied to solid helium [8, 9].

Defects are believed to be necessary for any existing supersolidity effects in helium. While various defect candidates and defect interaction scenarios have been nominated for this role, there is not yet a consensus on which is the dominant one. It is generally agreed however that the presence of vacancies will induce supersolidity. Unfortunately, vacancies in the experimental samples, especially at relevant low temperatures, are not well characterized. Theory still lacks the answer whether small concentration of vacancies may be present in the ground state of the helium crystal, as originally proposed [20] (activation energy of a *single* vacancy is found to be rather large, in the range of 10–20 K). Whether or not vacancies are present in the ground state of helium crystals, current experiments are likely to use samples with various defects created during the growth. Whether these remain in the crystal in a ground or a metastable state is unknown. It has been suggested [15] that vacancies will tend to cluster and “bubble away”, thus removing themselves from the crystal. In this paper we present our work, based on quantum Monte Carlo (QMC), on the stability of introduced clusters of vacancies in solid ^4He at zero temperature.

2 Method

We have investigated the behavior of vacancy clusters with the DMC method [21–23]. DMC is an exact ground-state method for bosonic systems and has proven indispensable in investigating the properties of superfluid and solid helium.

To apply DMC, one needs to use an importance sampling function that guides the system away from the configurations that have suppressed probability. In case of solids, it can also be used to help the simulation to discover the configurations with crystalline order. Even with a non-precise importance sampling function, DMC samples the properties of the ground state. Unless severely constrained by the sampling function Ψ_T , the method yields the exact ground-state energy $E_0 = \langle \phi_0 | \mathcal{H} | \phi_0 \rangle$, ϕ_0 being the ground-state wavefunction of the system. Estimates for operators that do not commute with the Hamiltonian (such as density profiles) may be computed using mixed estimators $\langle \phi_0 | \mathcal{A} | \Psi_T \rangle / \langle \phi_0 | \Psi_T \rangle$. In particular, results for the vacancy pair correlation function and for cluster size distribution, presented in the following sections, were obtained with mixed estimators mostly for efficiency reasons. While using pure estimators would provide definitive answers [24, 25], it is unlikely that it would change the conclusions that we draw from our results.

The trial function that we use allows for a good account of pair correlations between atoms. It also introduces the crystalline order *and* explicitly enables Bose exchange symmetry. It avoids glassy states that may show up in QMC simulations as a result of sampling problems. This approach was successfully tested on solid ^4He and is described in Ref. [11]. The function has the form

$$\Psi_{\text{SNJ}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_p}) = \prod_{i < j}^{N_p} f(r_{ij}) \left(\prod_{J=1}^{N_s} \sum_{i=1}^{N_p} g(|\mathbf{r}_i - \mathbf{R}_J|) \right) \quad (1)$$

where N_p is number of particles in the system, located at the positions \mathbf{r} , and N_s is number of lattice sites that are assumed at the positions given by \mathbf{R} . Function $g(r)$ helps to guide an atom to a single but arbitrary (due to the symmetrization) lattice site. This localizing term is usually chosen to be a Gaussian $g(r) = \exp[-1/2\gamma r^2]$. The two-body term $f(r)$ is the pair correlation function and has been chosen to be of McMillan form $f(r) = \exp[-1/2(b/r)^5]$. Both parameters b and γ were optimized variationally. Disregarding their density dependence, we used $b = 2.86 \text{ \AA}$ and $\gamma = 1.15 \text{ \AA}^{-2}$. We find that Ψ_{SNJ} allows to handle well simulations with vacancies in solid ^4He . In particular, the vacancies are properly mobile.

3 Cluster Collapse

To get an insight on whether a macroscopically large cluster of vacancies may be stable in solid helium, we performed series of DMC calculations with various lattice configurations. The calculations were performed with both hcp (180 atoms) and fcc (256 atoms) lattice symmetries. Vacancy cluster sizes varied from 21 to 64 atoms (comparing to a filled commensurate system). Such a large number of vacancies puts the system near or below the melting point [26]. Clusters did not form during the simulations regardless of how filled the system was. For this reason we started the calculations with clusters already present in the initial conditions. Periodic sheets of different width and spherical configurations were tried out for cluster geometry. In all cases, an imminent collapse followed, that is, the vacancies dispersed throughout the simulation volume. The resulting state did not melt and was still crystalline as could be inferred from clear peaks in the static structure function $S(k)$. In the case of 21-vacancy simulation described in more detail below, the main peaks' amplitude decreased by a factor of 0.5 and the structure remained sharp.

Sampling during Monte Carlo simulations does not by any means represent actual dynamics. However, the configurations that are being sampled during DMC do tend towards the lowest allowed state and may give some insight into the properties of the system. In all simulations we observed that even if present in the initial conditions, the cluster collapsed, that is the vacancies "evaporated" into the solid. An example of this behavior is shown in Fig. 1. Left panel on this figure shows the initial configuration for one of the simulations and a randomly chosen snapshot among the DMC walkers at a later imaginary time. The initial configuration was created with a large vacancy sheet occupying two atomic planes. The sheet collapsed in the beginning of the simulation. The configuration shown on the right panel of Fig. 1 is representative

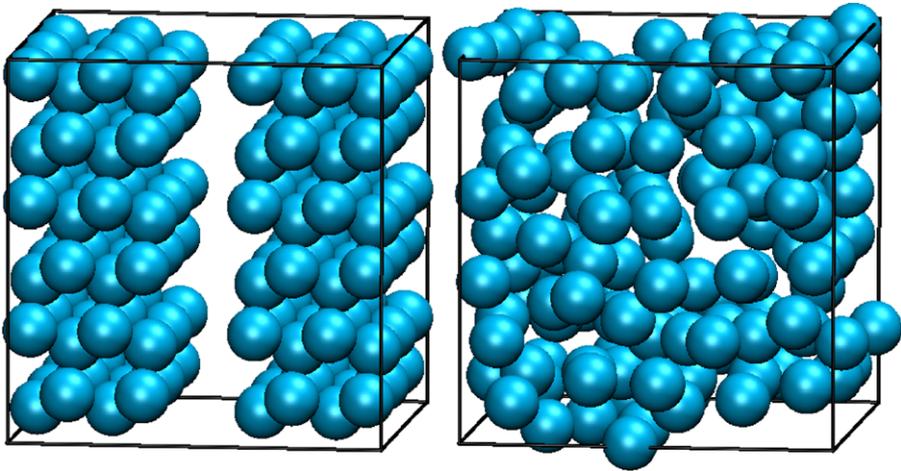


Fig. 1 (Color online) Initial configuration (*left*) and a runtime snapshot (*right*) for an hcp crystal with a two-layer vacancy sheet. This configuration had 144 atoms and 180 lattice sites. Images were generated with VMD package [27]

of the configurations sampled after the collapse, during the equilibrated part of the simulation.

Because these systems have such a large number of vacancies introduced into them, it is natural to ask if there exists a tendency to form vacancy clusters of certain size. We defined the vacancy positions as location of the lattice sites that do not have an atom in their Wigner-Seitz cell. Two vacancies are considered to be in the same cluster if there could be found a chain of vacancies connecting the two, such that each pair of the vacancies in the chain is separated by less than some cutoff distance r_c . The resulting distribution of cluster sizes is a rapidly and monotonically decaying function without any preferred cluster size regardless of the choice of r_c . We conclude that the vacancies disperse rather evenly and while there may be some grouping they do not tend to form isolated compact clusters with more than just a few vacancies.

To distinguish between preferred configurations and sampling “phantoms” or even sampling problems in Monte Carlo methods in general, one needs to pay attention to energies of the resulting states. We can also compare the resulting energy with energies of alternative configurations, prevented from projecting to the ground state by properly selected restrictive guiding functions. In our case we force each atom to be bound to its own lattice site by using Nosanow-Jastrow (NJ) function. The function has the form

$$\Psi_{NJ}(\mathbf{r}_1, \dots, \mathbf{r}_{N_p}) = \prod_{i < j}^{N_p} f(r_{ij}) \prod_{i=1}^{N_s \equiv N_p} g(|\mathbf{r}_i - \mathbf{R}_i|),$$

with the same notation as in (1). Ψ_{NJ} yields correct energy of the commensurate system as exchange effects turn out to have negligible impact on the energy of the solid [11, 28]. However, it explicitly breaks the Bose symmetry and lacks intersite

Table 1 Energy per particle for commensurate and incommensurate crystals. The last two lines show corresponding energies obtained with Nosanow-Jastrow function, which does not allow for proper simulation of systems with vacancies but instead constrains them to the excited state where the vacancy cluster is nearly intact. Difference between the second and fourth entry provides estimate for cluster evaporation energy at 2.97 ± 0.14 K per vacancy. The last column is energy per particle in each case

Ψ_T	Geometry	N_s	N_p	ρ_{lattice} , sites/nm ³	ρ_{He} , atoms/nm ³	E/N_p , K
SNJ	filled	180	180	29.30	29.30	-5.291 ± 0.006
SNJ	vacancies	180	159	29.30	25.88	-4.723 ± 0.017
NJ	filled	180	180	29.30	29.30	-5.282 ± 0.004
NJ	vacancies	180	159	29.30	25.88	-4.331 ± 0.006

hopping. For a system with vacancies, Ψ_{NJ} is in a sense pathological and may only be used as a rough reference point, as described below. Since each atom is tied to its own site, an intentionally created cluster must remain stable during the simulation if the NJ trial function is used. (Structure relaxes significantly even in the case of clusters constrained with the NJ function.)

Table 1 shows an example of energies for a simulation of a 21-vacancy, 180-lattice sites system, with vacancies initially arranged in a spherical cluster. The density of this system once the vacancies are introduced equals to 25.88 nm^{-3} . This is below the melting density for ^4He , but above the solidification point. Therefore, four phase possibilities need to be considered: with vacancies separated into a cluster with remaining volume filled by crystal structure, with the vacancies dispersed through the solid structure, with solid rebuilt into commensurate lattice at particle density (hence without vacancies), and finally the liquid phase. From the energy and previous work [26] we can deduce that the liquid phase is the most stable one, followed by the commensurate solid. This is consistent with findings by Clark and Ceperley [12] that large concentration of vacancies melts solid ^4He structure. Melting of the crystal is however in some disagreement with the hypothesis of Boninsegni et al. [15]. It is worth reminding that we know from evidence and calculations that these phases do not allow for voids in the ground state all the way down to their spinodal densities.

The remaining two phases are subject of the current work. Our DMC calculations with SNJ sampling function are placing the solid into a metastable regime at this density. From our past calculations, we have good reasons to believe though that the metastable regime is described well in this way. It is at these densities that one would expect the system most likely to separate into a solid and a vacancy cluster. Instead we observe that vacancies are dispersed over the lattice. We can additionally assure ourselves considering the forced clusters with the NJ calculations. While Ψ_{NJ} simulations fix the system into an excited state and may contain systematic biases, the cost of holding a vacancy in a cluster turns to be about 3 K per vacancy. This is sufficiently large to conclude that the vacancy cluster will necessarily evaporate into the solid. Once again, even if the resulting phase is to melt, there will still be no voids (“vacancy clusters”) in the resulting overpressurized liquid.

4 Pair Binding

In order to investigate the effective interaction between vacancies, we computed the vacancy-vacancy correlation function $g_{vv}(r)$. We considered system that is two atoms short of filling a 180-atom hcp lattice, at densities of 0.0290 \AA^{-3} and 0.0308 \AA^{-3} . Such system remains crystalline and hence has two vacancies and possibly interstitial-vacancy pairs. For the statistical analysis, the vacancy location is assigned to a lattice position that has zero occupation number either in a given step or in a fraction or all of several consecutive steps. We only consider the cases that have exactly two vacancies present, which is meant to exclude most of the interstitial-vacancy pairs. We observe that $g_{vv}(r)$ is a decaying function and the rate of decay is consistent with the results currently published in the literature, in particular those obtained by Pollet et al. [16] and the SPIGS results of Rossi et al. [8].

Statistical errors are currently too high to allow a clear determination of the binding energy and a clear distinction of whether the state is indeed bound. Determining the binding energy also requires knowledge of the effective mass which is not directly accessible. Pollet et al. [16] found that at density 0.0292 \AA^{-3} the effective mass m^* is isotropic and $m^* \approx 0.43m_{\text{He}}$. Using this result, we obtain that binding energy of vacancy pairs is equal to about 1.6K at both densities.

5 Conclusions

As a result of the present DMC calculations with large clusters of vacancies introduced into helium crystals, we find that vacancy clusters do not belong to the ground state of such systems. There is no indication of an existence of preferred vacancy cluster sizes. This disagrees with some of the previous PIMC calculations, which may be attributed to temperature effects. The ground state of the helium crystal with large number of vacancies, if such exists, consists of vacancies dispersed through the volume, whether in small groups or on their own. We, however, did not consider a possibility of phase separation between commensurate crystalline structure and crystals with very small vacancy concentrations. Such a calculation is beyond the scope of the present-day computer capabilities.

Various vacancy structures may form for purely combinatorial reasons and due to weak vacancy-vacancy attraction. Such attraction can be deduced from vacancy-vacancy correlation function. Results for the binding energy are at our current level a rough estimate. As such, they are consistent with the binding energies cited in the literature.

Acknowledgements This work was partially supported by DGI (Spain) Grant No. FIS2008-04403 and Generalitat de Catalunya Grant No. 2005SGR-00779.

References

1. E. Kim, M. Chan, Nature **427**, 225 (2004)
2. J. Day, J. Beamish, Nature **450**, 853 (2007)

3. Y. Aoki, J.C. Graves, H. Kojima, *Phys. Rev. Lett.* **99**, 015301 (2007)
4. S. Balibar, F. Caupin, J. Phys. Condens. Matter **20**, 173201 (2008)
5. D.E. Galli, L. Reatto, *J. Phys. Soc. Jpn.* **77**, 111010 (2008)
6. N. Prokof'ev, *Adv. Phys.* **56**, 381 (2007)
7. F. Pederiva, G.V. Chester, S. Fantoni, L. Reatto, *Phys. Rev. B* **56**, 5909 (1997)
8. M. Rossi, E. Vitali, D.E. Galli, L. Reatto, *J. Phys. Conf. Ser.* **150**, 032090 (2009)
9. D.E. Galli, L. Reatto, *Phys. Rev. Lett.* **96**, 165301 (2006)
10. B. Chaudhuri, F. Pederiva, G.V. Chester, *Phys. Rev. B* **60**, 3271 (1999)
11. C. Cazorla, G.E. Astrakharchik, J. Casulleras, J. Boronat, *New J. Phys.* **11**, 013047 (2009)
12. B.K. Clark, D.M. Ceperley, *Comput. Phys. Commun.* **179**, 82 (2008)
13. B.K. Clark, D.M. Ceperley, *Phys. Rev. Lett.* **96**, 105302 (2006)
14. M. Boninsegni et al., *Phys. Rev. Lett.* **99**, 035301 (2007)
15. M. Boninsegni et al., *Phys. Rev. Lett.* **97**, 080401 (2006)
16. L. Pollet et al., *Phys. Rev. Lett.* **101**, 097202 (2008)
17. M. Boninsegni, N. Prokof'ev, B. Svistunov, *Phys. Rev. Lett.* **96**, 105301 (2006)
18. A.C. Clark, J.D. Maynard, M.H.W. Chan, *Phys. Rev. B* **77**, 184513 (2008)
19. P.W. Anderson, *Science* **324**, 631 (2009)
20. A.F. Andreev, I.M. Lifshitz, *J. Exp. Theor. Phys.* **29**, 1107 (1969)
21. B.L. Hammond, W. Lester Jr., P.J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994)
22. A. Sarsa, J. Boronat, J. Casulleras, *J. Chem. Phys.* **116**, 5956 (2002)
23. J. Boronat, J. Casulleras, *Phys. Rev. B* **49**, 8920 (1994)
24. J. Casulleras, J. Boronat, *Phys. Rev. B* **52**, 3654 (1995)
25. K.S. Liu, M.H. Kalos, G.V. Chester, *Phys. Rev. A* **10**, 303 (1974)
26. L. Vranješ, J. Boronat, J. Casulleras, C. Cazorla, *Phys. Rev. Lett.* **95**, 145302 (2005)
27. W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graph.* **14**, 33 (1996)
28. D.M. Ceperley, *Rev. Mod. Phys.* **67**, 279 (1995)