Noble Gas Clusters

DOI: 10.1002/anie.200802743

Accurate Melting Temperatures for Neon and Argon from Ab Initio Monte Carlo Simulations**

*Elke Pahl, Florent Calvo, Love Koči, and Peter Schwerdtfeger**

Although studied experimentally for centuries, the melting of solids is still a fascinating phenomenon whose underlying mechanisms are not yet well understood.[1] Predicting melting points is a nontrivial task: The standard computational method relies on analyzing the free energies of the solid and liquid phases obtained independently by thermodynamic[2] or Gibbs–Duhem[3] integration; this approach suffers from the difficulty of calibration. Alternatively, in coexistence methods the interface between the two phases must be described explicitly;[4] this interface is often hard to stabilize.[5] An alternative idea, which we pursue herein, is to obtain information about the melting transition by studying finite clusters and extrapolating the results to infinitely large systems. Here we present for the first time calculated melting temperatures reaching experimental accuracy obtained from Monte Carlo simulations of Ne_N and Ar_N clusters consisting of a "magic number" N of atoms ($N = 13$, 55, 147, 309, 561, 923) and of bulk samples. This was achieved by the use of accurate interaction potentials obtained from precise ab initio data having the same computational efficiency as the widely used empirical Lennard-Jones (LJ) potential, and without any experimental input whatsoever.

Argon and neon adopt the face-centered cubic (fcc) periodic packing in the solid state, but their clusters with $N <$ 1000 are most stable as complete Mackay icosahedra. The number of atoms in the first six shells of the cluster corresponds to the "magic numbers": $N = 1 + 2\sum_{k=1}^{n}(5k^2+1) = 13$, 55, 147, 309, 561, and 923.[6] These "magic numbers" have been provided by mass spectra in free-jet expansions of rare-gas clusters.[7,8] The unusual stability of these clusters is explained by the structure in which one to six completed shells of atoms surround a central atom (see the inset of Figure 1).[6]

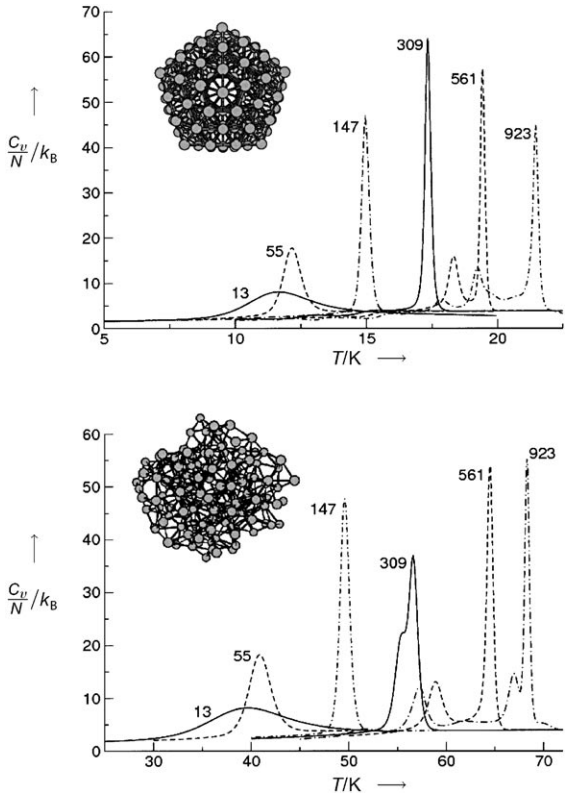

Figure 1. Heat capacities per atom for the Ne_N (top panel) and Ar_N (bottom panel) "magic number" clusters with $N = 13$, 55, 147, 309, 561, and 923. The insets show typical configurations of the 147-atom cluster in the solid (top) and liquid (bottom) state.

Previous work on determining melting curves for rare-gas clusters include Monte Carlo (MC) simulations by Labastie and Whetten[9] ($N = 13$, 55, 147). They found a well-defined single peak in the heat capacity, which becomes higher more intense and narrower as the cluster size increases. The apparent convergence towards the bulk limit was, however, questioned by Noya and Doye,[10] who found an additional premelting peak for the 309-atom cluster. As we show below, even though complicated premelting phenomena remain for all clusters with more than 309 atoms, the melting peak itself always turns out to be well defined. Furthermore, and to our knowledge, the 309-atom system is the largest rare-gas cluster studied so far for melting. To determine the bulk melting point T_m by extrapolation to the macroscopic limit, inclusion of two more shells is required, as we demonstrate in this work.

[*] Dr. E. Pahl, Prof. P. Schwerdtfeger
Center for Theoretical Chemistry and Physics
The New Zealand Institute for Advanced Study
Massey University Auckland, Private Bag 102904
North Shore City, 0745 Auckland (New Zealand)
E-mail: p.a.schwerdtfeger@massey.ac.nz
Dr. F. Calvo
LASIM, Université Claude Bernard Lyon 1
Bât. A. Kastler, 43 Bd du 11 novembre 1918, 69622 Villeurbanne (France)
Dr. L. Koči
Condensed Matter Theory Group, Physics Department
Uppsala University, Box 530, S-751 21, Uppsala (Sweden)

[**] We thank K. Szalewicz for providing the routines for the SAPT three-body potential and A. Hermann for technical support. This work was supported by the Royal Society of New Zealand (Marsden grant 07-MAU-016), the Swedish Research Council (VR), and the Durmont d'Urville PHC programme (15883VC) of the French and New Zealand governments.

Both the aforementioned papers, as well as the majority of papers on rare-gas thermodynamics, rely on the Lennard-Jones potential to describe the pair interactions between atoms. The LJ potential is computationally efficient but somewhat empirical (in the original derivation by Lennard-Jones the r^{-6} and r^{-12} terms were derived purely empirically to obtain analytical expressions for the cohesive energies matching experimental solid-state results). It is then quite surprising that for the pressure versus temperature coexistence lines the LJ potential agrees with experimental measurements,[11] especially when one compares this to the results of more sophisticated calculations based on the Aziz[12,13] potential with added three-body corrections.[14] This is likely to be the signature of the parameterization of the LJ potential on high-temperature properties, although shortcomings in the simulations using the Aziz potential have also been suggested.[11] Using the LJ potential for clusters is even more questionable if quantitative accuracy is sought. Fortunately, the many-body expansion converges fast for the rare gases in the important region of the particle interactions at normal pressures and temperatures.[15,16] Indeed, the Cauchy equality $C_{12} = C_{44}$ holds reasonably well for the elastic constants of both neon and argon. Thus two-body, and if necessary three-body terms should be able to describe the interactions among rare-gas atoms quite correctly.

In this work we studied the thermal behavior of the rare-gas "magic number" clusters by Monte Carlo simulations in the canonical ensemble with the parallel tempering method.[17,18] In Figure 1 the heat capacities are shown for the clusters Ne_N and Ar_N with $N = 13$–923 as a function of temperature. The heat capacities indicating melting are found in the regions 10–22 K for Ne and 35–70 K for Ar, quite below the experimentally determined bulk melting points for these two elements (24.56 and 83.85 K). The melting peak becomes sharper with increasing cluster size. This trend is interrupted only by the onset of premelting phenomena, which are clearly visible for the larger clusters as additional peaks at lower temperatures. As a result of premelting, the entire $C_v(T)$ curves are much slower to converge in the simulation. Fortunately, as was also noted by Noya and Doye in their study of the LJ309 cluster[10] and by Mandelshtam and co-workers in the case of LJ75,[19] the slow convergence of premelting features does not significantly plague the convergence of the melting temperature. In our case, we have verified that the position of the main heat capacity peak is already well converged after 10 million cycles, allowing us to extract T_m to within 0.5 K.

As the fraction of surface atoms decreases with increasing cluster size, the melting peak is expected to converge towards the bulk value by increasing linearly with the surface/volume ratio, that is, with the inverse cluster radius $N^{-1/3}$.[20] This was demonstrated in early experiments by Buffat and Borel on deposited gold clusters[21] and is a result of melting being initiated on the surface. For the present icosahedral clusters, the fraction of surface atoms drops from 92% down to 39% between the smallest and largest clusters. The melting points inferred from simulations are represented in Figure 2 against $N^{-1/3}$.

As was expected from the above scaling arguments,[20] we find an almost linear behavior in $T_m(N^{-1/3})$ for both neon and argon clusters with $N \geq 147$. The values obtained for the smallest clusters, especially for $N = 13$, deviate noticeably from the linear fit, which we attribute to the more important, higher-order effects beyond the surface arising from the edges ($N^{-2/3}$ correction) and vertices (N^{-1} correction). Linear fitting the data of Figure 2 for the largest clusters and extrapolating to the bulk limit $N^{-1/3} \rightarrow 0$ yields $T_m = 26.9$ K for Ne and $T_m = 90.6$ K for Ar. These values are already in satisfactory agreement with the experimental data of 24.56 K for Ne and 83.85 K for Ar.[22]

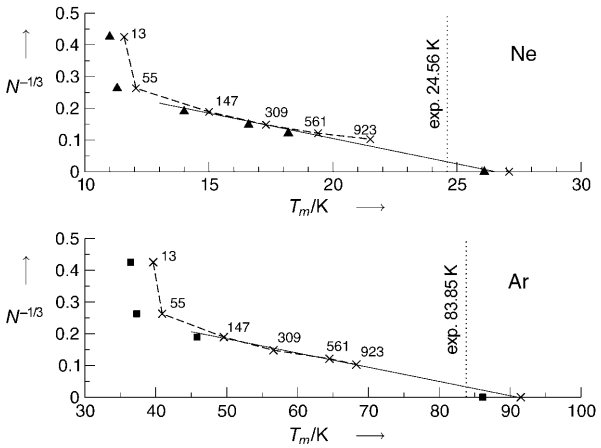

Figure 2. Dependence of melting temperature T_m on cluster size for neon (top panel) and argon (bottom panel), obtained using classical two-body ELJ interactions (crosses). The plots include the results obtained from bulk samples of 256 neon atoms and 108 argon atoms. For neon, quantum-corrected values are shown as triangles. For argon, three-body-corrected values are shown as squares. The experimental melting points of the bulk[22] are indicated as vertical dotted lines.

Melting of the infinite crystals of argon and neon has also been simulated directly using fcc samples with cubic periodic boundary conditions. Since the clusters studied are in the gas phase, the cell volume was allowed to vary under constant pressure for a more appropriate comparison. Typical $C_v(T)$ curves are shown in Figure 3 for the lattice sizes of 32 (Ar) and 108 and 256 (Ne) atoms. In contrast to the results with clusters, here finite size effects make the melting points converge to the infinite limit from higher temperatures. Even though we cannot yet extrapolate the melting points obtained from these bulk simulations to the macroscopic limit, the values for the 256-atom samples are consistent with the cluster extrapolation: we get 27.1 K for neon and 90.4 K for argon with the extended Lennard-Jones (ELJ) potential [see Eq. (2)]. The 108-atom samples lead to a further overestimation of about 0.7 K and 1.1 K for these two rare gases, respectively.

The smooth convergence of cluster melting points towards the simulated bulk limit is surprisingly good, considering that the clusters do not have the cubic crystal structure. We attribute this agreement to the same local coordination (12 atoms) in the two systems, even though the long-range order is lost in the icosahedral clusters.

Despite its high accuracy for the dimer potential curves, the extended Lennard-Jones potential overestimates the melting points of neon and argon, as determined either

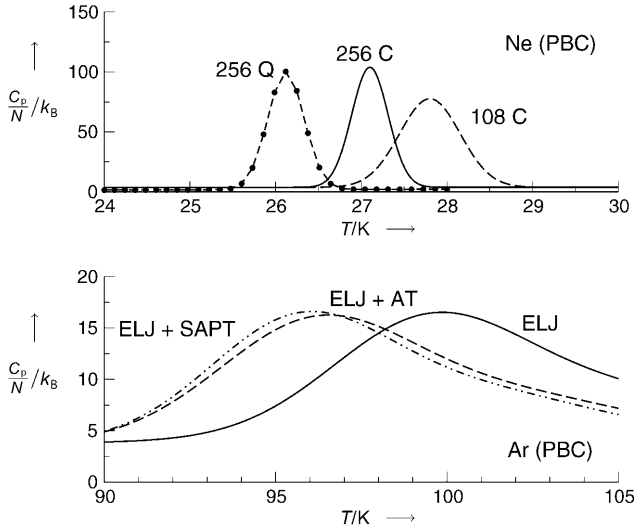

Figure 3. Equilibrium heat capacities of bulk samples with periodic boundary conditions and the initial fcc lattice at constant pressure ($p=0$). Top panel: Neon with $N=108$ or 256, without (C) and with (Q) quantum corrections. Botton panel: 32-atom argon cell with pure two-body (ELJ) interactions, with three-body Axilrod-Teller (ELJ + AT) corrections (– – –), and the three-body SAPT interactions (–•–•).

from clusters or from periodic samples. Inaccuracies of classical pair potentials are well known for the rare gases and were already discussed in the pioneering work by Barker and Klein,[23] among others. The other important effects include the many-body interactions for the heavier atoms and vibrational delocalization for the lighter atoms.

The leading order three-body correction $V^{(3)}$ is the triple-dipole Axilrod–Teller (AT) interaction,[24] which is usually sufficient under small pressures. More accurate forms have been derived by Lotrich and Szalewicz using symmetry-adapted perturbation theory (SAPT).[25] We repeated the simulation on the 32-atom argon bulk sample using both the AT and SAPT potentials. For these calculations a cutoff of 5.8 Å was used in the evaluation of three-body interactions. The plots of the heat capacities, represented in the bottom panel of Figure 3, show comparable variations when the three-body forces are included: the melting point is shifted by about 3.8–4 K to lower temperatures. The similar caloric curves obtained with the AT and SAPT potentials indicate that the AT interaction is sufficiently accurate for the present problem. This can be explained by the known partial cancellation between the higher-order nonpair interactions.[26]

Additional simulations for the smallest argon clusters containing up to 147 atoms and for the 108-atom bulk sample were carried out using the AT potential (Figure 2). Computational cost did not allow us to get sufficient convergence for the bulk 256-atom sample. For clusters, we found the lowering in the melting point to be 3.2, 3.6, and 3.8 K for Ar_{13}, Ar_{55}, and Ar_{147}, respectively, which extrapolates linearly to $|\Delta T_m| = -4.3$ K in the macroscopic limit, or to $T_m = 86.3$ K. For the bulk simulation, the depression in the melting temperature is found to be approximately 4.1 K, leading to $T_m = 87.4$ K, which is also in much better agreement with experiment.

Three-body interactions are not expected to be so crucial for the less polarizable neon. Calculations on Ne_{13} and Ne_{55} with the AT contribution show only a very modest change in the melting temperature ($|\Delta T_m| < 0.05$ K), which is also expected for the larger clusters. However, the light mass of neon makes it more prone to vibrational delocalization. From the equilibrium distance r_{eq} and the well depth ε of the dimer energy curve, the de Boer parameter $\Lambda = \hbar/r_{eq}\sqrt{m\varepsilon}$ provides a good estimation of the magnitude of quantum effects. Its value for neon ($\Lambda_{Ne} = 0.078$) suggests a quasiclassical character, whereas argon can be confidently treated as classical ($\Lambda_{Ar} = 0.025$).

Besides the rigorous path-integral Monte Carlo approach[27,28] or the more approximate variational method of Mandelshtam and Frantsuzov[29] based on Gaussian wavepackets, the simple quantum-corrected potentials are convenient under moderate temperatures and for large systems. In this work the Feynman–Hibbs quasiclassical potential $\tilde{V}_{ELJ}(r) = V_{ELJ}(r) + \hbar^2 \Delta V_{ELJ}(r)/24\, m k_B T$, where ΔV_{ELJ} is the Laplacian of the ELJ potential, was considered as it gives a very satisfactory agreement with more sophisticated quantum Monte Carlo methods for small clusters.[30] Note that this effective potential is temperature dependent, which prevents the use of the histogram reweighting method for the continuous determination of caloric curves.

The importance of quantum effects is illustrated in the upper panel of Figure 3, where the heat capacities for the bulk sample of 256 atoms are shown in the classical and quantum-corrected cases. The latter calculations show a decrease in the melting point of about 1 K. The results of simulations of neon clusters, included in Figure 2, generally exhibit a similar shift of 0.7–1 K; this is in agreement with the conclusions reached by other authors who used the Lennard-Jones potential for cluster sizes below 39 atoms.[31,28,32] Considering that the thermal de Broglie wavelength should not depend too much on cluster size, we can confidently attribute a shift of about $\Delta T_m = -1$ K as a result of vibrational delocalization in neon, leading to $T_m = 25.9$ K from cluster extrapolation. For argon we expect quantum effects to be smaller than the uncertainty in our extrapolation procedure.

In summary, we have calculated the melting temperatures of neon and argon without any experimental input, using ab initio potentials by extrapolating the values obtained from clusters or by direct simulation from periodic boxes. Good agreement between the two approaches was found in both cases. After including quantum corrections for neon and three-body interactions for argon, our calculated melting temperatures are 25.9–26.0 K for Ne and 86.3–87.0 K for Ar, in good accordance with experimental data of 24.56 K and 83.85 K, respectively.[22] The remaining discrepancies include residual inaccuracies in our potential, excessively small systems (for both clusters and bulk calculations), and the extrapolation procedure itself, which we estimate to be accurate to about 1 K.

Methods

Within our exchange Monte Carlo scheme,[17,18] 32 trajectories covering the range of melting temperatures were propagated

simultaneously and an exchange between neighboring trajectories was attempted with a 10% probability after each MC cycle. All cluster calculations were initialized with the corresponding ground-state Mackay icosahedral structure. Evaporation or fragmentation of the clusters was inhibited by keeping the cluster inside a hard sphere of radius $R_N + r_e$, where R_N is the radius of the ground-state N-atom cluster and r_e is the equilibrium distance of the dimer.

Additional simulations of bulk samples were performed with 32, 108, and 256 atoms using periodic boundary conditions in the minimum image convention. The atoms were initially distributed on a fcc lattice, and the cell was allowed to change volume under constant pressure ($p = 0$). The interactions were cut at half the box size and long-range corrections were included as customary.[2]

We thoroughly investigated the convergence of our results with the number of MC cycles, and all calculations were performed with an additional 20% equilibration cycles, and extended if necessary. The melting temperatures were determined from the equilibrium heat capacity $C_v(T)$, which shows a maximum at the phase transition rounded by size effects. The heat capacities were obtained as a continuous function of temperature from the simulation data using the histogram reweighting technique.[9]

We used a truncated expansion of the many-body interaction potential energy derived from accurate ab initio theory for a cluster of size N [Eq. (1)].

$$V_{\mathrm{int}}(N) = \sum_{n} V^{(n)}(N) = \sum_{i<j}^{N} V^{(2)}(r_{ij}) + \sum_{i<j<k}^{N} V^{(3)}(r_{ij}, r_{ik}, r_{jk}) + \cdots \tag{1}$$

The two-body interaction potentials chosen here were obtained by fitting accurate ab initio data points of the neon and argon dimers obtained at the CCSD(T) level (underlying extended aug-cc-pV5Z basis set).[33] They are written as a function of the pair distance r as a simple, extended Lennard-Jones (ELJ) form, where c_k are the fitting parameters [Eq. (2)].[15]

$$V^{(2)}_{\mathrm{ELJ}}(r) = \sum_{k=3}^{8} c_{2k}\, r^{-2k} \tag{2}$$

Details are found in Ref. [15]. The ELJ potential is as accurate as the Aziz form,[12,13] including the short- and long-range regions, but its computational efficiency is comparable to that of the simple LJ interaction.[34] This allowed us to perform MC simulations on relatively large cluster sizes.

Received: June 10, 2008
Published online: September 26, 2008

Keywords: melting processes · Monte Carlo simulations · noble gases · quantum effects

[1] C. Caleman, D. van der Spoel, *Angew. Chem.* **2008**, *120*, 1439; *Angew. Chem. Int. Ed.* **2008**, *47*, 1417.
[2] D. Frenkel, B. Smit, *Understanding Molecular Simulation*, 2nd ed., Academic Press, San Diego, **2002**.
[3] D. A. Kofke, *Mol. Phys.* **1993**, *78*, 1331.
[4] A. Ladd, L. Woodcock, *Chem. Phys. Lett.* **1977**, *51*, 155.
[5] J. R. Errington, *J. Chem. Phys.* **2004**, *120*, 3130.
[6] K. Russel, T. P. Martin, *Phys. Rep.* **1996**, *273*, 199.
[7] O. Echt, K. Sattler, E. Recknagel, *Phys. Rev. Lett.* **1981**, *47*, 1121.
[8] I. A. Harris, R. S. Kidwell, J. A. Northby, *Phys. Rev. Lett.* **1984**, *53*, 2390.
[9] P. Labastie, R. L. Whetten, *Phys. Rev. Lett.* **1990**, *65*, 1567.
[10] E. G. Noya, J. P. K. Doye, *J. Chem. Phys.* **2006**, *124*, 104503.
[11] M. A. van der Hoef, *J. Chem. Phys.* **2000**, *113*, 8142.
[12] R. A. Aziz, M. J. Slaman, *Chem. Phys.* **1989**, *130*, 187.
[13] R. A. Aziz, M. J. Slaman, *Mol. Phys.* **1986**, *58*, 679.
[14] J. H. Kim, T. Ree, F. H. Ree, *J. Chem. Phys.* **1989**, *91*, 3133.
[15] P. Schwerdtfeger, N. Gaston, R. P. Krawczyk, R. Tonner, G. E. Moyano, *Phys. Rev. B* **2006**, *73*, 064112.
[16] A. Hermann, R. P. Krawczyk, M. Lein, P. Schwerdtfeger, I. P. Hamilton, J. J. P. Stewart, *Phys. Rev. A* **2006**, *73*, 064112.
[17] R. H. Swendsen, J.-S. Wang, *Phys. Rev. Lett.* **1986**, *57*, 2607.
[18] G. Geyer in *Computing Science and Statistics: Proceedings of the 23rd Symposium on the Interface* (Ed.: E. K. Keramidas), Interface Foundation, Fairfax Station, **1991**, p. 156.
[19] V. A. Mandelshtam, P. A. Frantsuzov, F. Calvo, *J. Phys. Chem. A* **2006**, *110*, 5326.
[20] T. L. Hill, *Thermodynamics of small systems*, Parts I and II, Dover, New York, **1994**.
[21] P. Buffat, J.-P. Borel, *Phys. Rev. A* **1976**, *13*, 2287.
[22] *CRC Handbook of Chemistry and Physics*, 85th ed., CRC, Boca Raton, FL, **2005**.
[23] J. A. Barker, M. L. Klein, *Phys. Rev. B* **1973**, *7*, 4707.
[24] B. M. Axilrod, E. Teller, *J. Chem. Phys.* **1943**, *11*, 299.
[25] V. Lotrich, K. Szalewicz, *J. Chem. Phys.* **1997**, *106*, 9688.
[26] R. Bukowski, K. Szalewicz, *J. Chem. Phys.* **2001**, *114*, 9518.
[27] C. Predescu, P. A. Frantsuzov, V. A. Mandelshtam, *J. Chem. Phys.* **2005**, *122*, 154305.
[28] J. P. Neirotti, D. L. Freeman, D. L. Doll, *J. Chem. Phys.* **2000**, *112*, 3990.
[29] P. Frantsuzov, V. A. Mandelshtam, *J. Chem. Phys.* **2004**, *121*, 9247.
[30] F. Calvo, J. P. K. Doye, D. J. Wales, *J. Chem. Phys.* **2001**, *114*, 7312.
[31] C. Chakravarty, *J. Chem. Phys.* **2005**, *122*, 956.
[32] P. A. Frantsuzov, D. Meluzzi, V. A. Mandelshtam, *Phys. Rev. Lett.* **2006**, *96*, 113401.
[33] S. M. Cybulski, R. R. Toczylowski, *J. Chem. Phys.* **1999**, *111*, 10520.
[34] G. E. Moyano, P. Schwerdtfeger, K. Rosciszewski, *Phys. Rev. B* **2007**, *75*, 024101.

