Critical Properties of Aluminum

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Aluminum is one of the most ubiquitous elements on Earth. Since its isolation in 1825, aluminum has found many technological uses, but its physical properties are well-known only at low reduced temperature. In this work, Gibbs ensemble Monte Carlo calculations are performed using a validated embedded-atom potential to obtain the vapor—liquid coexistence curve and the critical properties for elemental aluminum. This demonstrates the ability of modern simulations to predict fundamental physical properties that are extremely difficult to measure directly.

Due to their strong cohesive interactions, the critical properties of most metals are not amenable to conventional experiments, and only the critical temperatures, $T_c$, of mercury and alkalis have been measured directly. Estimates of $T_c$ for other metals are based upon relationships between $T_c$ and other measured thermodynamic properties. For Al, an analysis of isobaric expansion experiments yields a value of 5726 K. Another estimate, based upon the assumption that the entropies of vaporization of different metals are equal at the same reduced temperature, yields a value of 8550 K. Renaudin et al. compared new experimental data for pressure versus internal energy to two equations of state that extrapolate to the lower end of experiment-based estimates for $T_c$ of $\sim 12 100$ and $\sim 6400$ K and obtained better agreement with the latter. Young and Alder and Likalter developed scaling laws based, respectively, on the van der Waals model and on the plasma-like behavior of metallic near-critical fluids and, respectively, estimated 7151 and 8860 K for $T_c$ of Al.

Aluminum is of technological importance not only as a lightweight, rust-resistant structural material but also as an ingredient for high-energy fuels and, potentially, as a hydrogen storage device. For many applications, such as the controlled growth of Al nanoparticles, precise knowledge of Al’s saturated vapor pressure and heat of vaporization up to the critical point is pivotal. Al are known with such poor precision. In cases where an experimental determination of the critical properties is difficult, molecular simulations using accurate potential energy functions offer a practical alternative. However, the application of this technique to metals is usually impeded by insufficient knowledge of the potential energy function.

Recently, some of us and co-workers have presented the first validated potential energy function for a nanophase metal, in particular, nanoaluminum. That is, an analytic embedded-atom potential (called NP-B) was parametrized to reproduce accurate DFT energies for clusters and nanoparticles of various sizes, a strategy made possible only by the development of reliable density functionals that yield these data.

In the present report, we use the NP-B potential and, for comparison, a different embedded-atom potential to obtain the vapor—liquid coexistence curve and critical properties of Al from Gibbs ensemble Monte Carlo simulations. Because of the large dimer binding energies of metal particles, aggregation-volume-bias Monte Carlo strategies are used to efficiently sample cluster formation/breakage in the vapor phase and to establish the correct equilibrium distribution of clusters of different sizes. Configurational-bias Monte Carlo techniques are used to enhance the acceptance rate for particle swaps between the two phases. Further details of the simulations are provided in the Supporting Information.

Figure 1 shows the temperature—density projection for the vapor—liquid coexistence curve of Al computed using the NP-B and MDEA potentials with the experimental liquid density at 1173 K plotted for comparison. Most striking is the difference in the critical temperatures for NP-B ($T_c = 6299 \pm 48$ K) and MDEA ($T_c = 3381 \pm 13$ K). The latter estimate falls substantially below the lower end of experiment-based estimates for $T_c$. The corresponding values for the critical densities and pressures are $\rho_c = 707 \pm 60$ kg/m$^3$ and $p_c = 884 \pm 19$ atm for NP-B, and $\rho_c = 675 \pm 36$ kg/m$^3$ and $p_c = 435 \pm 20$ atm for MDEA. The error ranges given for calculated quantities arise from the sampling statistics (two standard deviations) and the extrapolation procedure used to determine the critical constants (see Supporting Information). This shows that the accuracy of the potential function and not the simulation protocol is the limiting factor in the reliability of these calculations.

Figure 2 shows a Clausius—Clapeyron plot of the logarithm of the saturated vapor pressure versus the inverse temperature. At low temperature, the saturated vapor pressure for the MDEA potential falls substantially above the experimental estimate (which is based on measurement of the saturated vapor pressure, heat of vaporization, and heat capacity of the liquid phase at the triple point), whereas the NP-B potential slightly under-

![Figure 1](image-url)
A cluster analysis for the vapor phase shows that at 1500 K for the NP-B potential, less than 0.2% of the atoms are involved in the formation of clusters, and the NP-B vapor deviates significantly from an ideal gas only at higher temperatures. In contrast, the MDEA vapor phase is very nonideal even at temperatures close to the experimental triple point; the vapor at 1500 K contains only 0.1% monomers.

In conclusion, an embedded-atom potential parametrized to accurate energies of nanoclusters is used to calculate the vapor—liquid equilibrium properties of Al. The results are satisfactory at low temperatures where experimental data are available. Al’s saturated vapor phase behaves ideally for $T < 2000$ K, beyond which clustering in the vapor phase becomes appreciable—knowledge that is needed for the controlled growth of nanoparticles from the vapor phase. The critical temperature predicted by using this potential is close to 6300 K, near the lower end of the range of values (5700–12 100 K) extrapolated from experimental data. In this way, advances in computational material science are resolving fundamental questions about the physical properties of the elements that have remained too difficult for direct experimental measurement even 180 years after the isolation of the element.

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Supporting Information Available: A detailed description of the potential models, the simulation parameters, and analysis procedures, numerical results, and a plot of the compressibility factor. This material is available free of charge via the Internet at http://pubs.acs.org.

References