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First-principles determination of the solid-liquid-vapor triple point: The noble gases

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We report first-principles calculations of the triple point that allow us to predict the triple point temperature of atomic fluids to an accuracy that has not been previously possible. This is achieved by proposing a molecular simulation technique that can be used for solid-liquid equilibria at arbitrarily low pressures. It is demonstrated that the triple point is significantly influenced by the choice of two-body, three-body and quantum interactions. An improved theoretical understanding of triple points is important for both science in general, and metrology in particular, as it links the Boltzmann constant and the Kelvin temperature scale to fundamental constants.

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Apart from the notable exception of helium [1], pure elements and molecules are normally characterized by two distinct invariant properties, namely the critical and triple points, which occur at the extreme temperature range of vapor-liquid coexistence. At the upper temperature end, the critical point [2] signifies the end of vapor-liquid equilibria (VLE) and the transition to supercritical fluid behavior. The triple point [2], at the lower temperature end, is the only condition at which liquid, solid and vapor phases can coexist simultaneously.

There is an interesting dichotomy between the experimental measurements and theoretical understanding of these phenomena. The triple point temperature (T_{tp}) can be often measured [3] to mK accuracy, whereas there are very large uncertainties in critical point measurements. This is particularly the case for molten metals such as sodium that have estimated critical temperatures [4] in the thousands of K. However, since the pioneering work of van der Waals [5], the theoretical basis of the critical point has been studied extensively. The Ising-like behavior of the critical point is well-documented [6] and specialized molecular simulation techniques [7,8] have been developed that can be used to precisely estimate [9] the critical point of model systems. In contrast, there are no equivalent theoretical tools to aid the prediction of the triple point, which is typically estimated via either the extrapolation of high temperature (T) data or the intersection of curves obtained for the corresponding VLE and solid-liquid equilibria (SLE) data.

A good theoretical understanding of the triple point and the ability to accurately predict T_{tp} could have profound scientific implications. Until the very recent [10] adoption of a fixed value for the Boltzmann constant ($k = 1.380649 \times 10^{-23}$ J K^{-1}), the SI unit for temperature, K, was determined relative to a fixed T_{tp} of water of exactly 273.16 K. That is, the triple point was used to accurately determine one of the few fundamental constants in science. The T_{tp} of several elements remain essential for the integrity of the temperature scale [3] used in all scientific fields.

Molecular simulation [11] is arguably the theoretical method of choice for predicting triple points and other fluid behavior because models of interparticle interactions can be evaluated rigorously. The advent of improvements in computational chemistry [12] means that very accurate descriptions of at least two-body interaction of noble gases are available from first-principles. These data can be used to formulate [13,14] accurate *ab initio* potentials. Molecular simulation algorithms are available [15–17] for SLE, although their utility is confined to moderate to high pressures (p), whereas the triple point usually occurs very close to $p = 0$. There are two interdependent goals of this work. First, develop a general molecular simulation procedure capable of reliably predicting SLE at low p. Second, determine the T_{tp} of real systems as accurately as possible from first-principles.

Highly accurate first-principles data are available [18–24] for the two-body interactions of the stable noble gases. These first-principles data can be used to formulate a simplified *ab initio* atomic potential (SAAP) [25] that can be used in molecular simulation to determine both VLE [26,27] and SLE [28],

$$u_{2\text{B}}(r) = u_{\text{SAAP}}(r) = \frac{\left(\frac{a_0}{r}\right)\exp(a_1 r) + a_2\exp(a_3 r) + a_4}{1 + a_5 r^6}, \tag{1}$$

where $u(r)$ denotes the energy of interactions of particles at a given separation (r), and a_0, a_1, a_2, a_3, a_4, and a_5 are parameters [25] fitted to the first-principles energy-distance data. The high quality of the agreement has been extensively evaluated [25]. Although two-body interactions make the dominant contribution to intermolecular interaction, they are insufficient

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to account for the properties of liquids. In particular, the effect of three-body interactions must be accounted for. Currently, three-body *ab initio* potentials [29] cannot be obtained to the same accuracy as two-body interactions. However, in many circumstances, it is well established [25,28–31] that the Axilrod-Teller-Muto (ATM) potential [32,33] is sufficient for the noble gases,

$$u_{3\mathrm{B}}(r) = u_{\mathrm{ATM}}(r) = \frac{\nu(1 + 3\cos\theta_i \cos\theta_j \cos\theta_k)}{(r_{ij} r_{ik} r_{jk})^3}, \quad (2)$$

where ν is the nonadditive coefficient [34,35]; θ_i, θ_j, and θ_k are inside angles of the triangle formed by three atoms denoted by i, j, and k; and r_{ij}, r_{ik}, and r_{jk} are the three side lengths of the triangle. In addition, the properties of neon and argon at low T are affected by quantum interactions, which can be evaluated by combining the first- and second-order Feynman-Hibbs (FH-1-2) terms [36]:

$$\begin{aligned} u_{\text{FH-1-2}} = {} & u_{2\mathrm{B}} + \frac{\beta\hbar^2}{12m}\left[u''_{2\mathrm{B}} + \frac{2u'_{2\mathrm{B}}}{r}\right] \\ & + \frac{\beta^2\hbar^4}{288m^2}\left[\frac{15u'_{2\mathrm{B}}}{r^3} + \frac{4u'''_{2\mathrm{B}}}{r} + u''''_{2\mathrm{B}}\right], \end{aligned} \quad (3)$$

In Eq. (3), the prime symbol denotes successive derivatives with respect to r, $\beta = 1/kT$, m is the mass of the individual particle, and $\hbar$ is Planck's constant divided by 2π. Using Eq. (1) to evaluate Eq. (3) means that first-principles data are also reflected in the quantum contribution.

The determination of the triple point requires a molecular simulation approach that determines SLE. The available algorithms [15–17] work reasonably well for moderate to high p but they are less accurate for very low p. This deficiency in existing methods is exemplified by the considerable variation in the triple point temperature reported in the literature [37,38] for the widely used Lennard-Jones (LJ) potential [39]. To obtain accurate values of the triple point, we developed an entropy correlation method. In this work, we will focus on the salient features, and the complete details will be given elsewhere [40].

During a canonical Monte Carlo (MC) simulation [11] the particles of the simulation ensemble are repeatedly displaced by random amounts, i.e., the location vector of particle i is changed according to $\mathbf{r}_i \leftarrow \mathbf{r}_i + \lambda\mathbf{u}$, where $\mathbf{u}$ is a unit vector with a random orientation. The displacement is rejected if it increases the internal energy of the ensemble too much, and accepted otherwise. λ is the maximum displacement width, which is typically adjusted during the simulation to achieve a fixed acceptance ratio α. Therefore, λ_α denotes the mean value of displacement parameter for α. The entropy correlation method for determining either SLE or more generally solid-fluid equilibria, is based on the observation [41] that the residual entropy for dense phases is a function of $1/\lambda_\alpha$. At low pressures this means [40],

$$S^{\mathrm{r}} \simeq -Nk\left(\frac{c_1}{\lambda_\alpha}(1 + c_3 e^{-c_2/\lambda_\alpha}) + c_0\right), \quad (4)$$

where N is the number of particles; c_0 c_1, c_2, and c_3 are coefficients that depend on the intermolecular potential, and c_0 also depends on α. It is easy to show [40] that the change in S^{r} along an isothermal compression from the molar density ρ_0 to ρ_1 can be obtained from

$$\begin{aligned} \Delta S^{\mathrm{r}}_{\mathrm{m}} &= S^{\mathrm{r}}_{\mathrm{m}}(\rho_1) - S^{\mathrm{r}}_{\mathrm{m}}(\rho_0) \\ &= \frac{H^{\mathrm{r}}_{\mathrm{m}}(\rho_1) - H^{\mathrm{r}}_{\mathrm{m}}(\rho_0)}{T} \\ &\quad - R\left(\int_{\rho_0}^{\rho_1} \frac{Z-1}{\rho} d\rho + Z(\rho_1) - Z(\rho_0)\right), \end{aligned} \quad (5)$$

where the m subscript denotes a molar quantity and H, Z, and R are the enthalpy, compressibility factor and universal gas constant, respectively. Using Eq. (4), the left-hand side of Eq. (5) is simply

$$\begin{aligned} \Delta S^{\mathrm{r}}_{\mathrm{m}} &= S^{\mathrm{r}}_{\mathrm{m}}(\rho_1) - S^{\mathrm{r}}_{\mathrm{m}}(\rho_0) \\ &= -Rc_1\left(\frac{1 + c_3 e^{-c_2/\lambda_\alpha(\rho_1)}}{\lambda_\alpha(\rho_1)} - \frac{1 + c_3 e^{-c_2/\lambda_\alpha(\rho_0)}}{\lambda_\alpha(\rho_0)}\right). \end{aligned} \quad (6)$$

The difference in the residual chemical potentials between the fluid (f) and solid (s) phases is [40],

$$\Delta\mu^{\mathrm{r}} = H^{\mathrm{r,f}}_{\mathrm{m}} - H^{\mathrm{r,s}}_{\mathrm{m}} + RT\left[c_1\left(\frac{1 + c_3 e^{-c_2/\lambda^{\mathrm{f}}_\alpha}}{\lambda^{\mathrm{f}}_\alpha} - \frac{1 + c_3 e^{-c_2/\lambda^{\mathrm{s}}_\alpha}}{\lambda^{\mathrm{s}}_\alpha}\right) - \ln\left(\frac{V^{\mathrm{f}}}{V^{\mathrm{s}}}\right) - 1\right], \quad (7)$$

where V denotes the volume.

The calculation of solid-fluid equilibrium states with the entropy correlation method involved six steps:

(1) NpT MC simulations were performed for the temperature of interest and a series of p (in this work: 1–80 MPa). These simulations must be started from a gas or liquid state.

(2) The compression factors obtained from these simulations are interpolated with a polynomial to facilitate the integration. For this work we found a quadratic polynomial to be sufficient.

(3) Equation (6) was evaluated to obtain $\Delta S^{\mathrm{r}}_{\mathrm{m}}$. A plot of $\Delta S^{\mathrm{r}}_{\mathrm{m}}$ versus $1/\lambda_a$ should almost be a straight line.

(4) The residual enthalpies, molar volumes, and mean displacement parameters of the tentative solid phases were obtained from a series of NpT MC simulations at the same values of p but starting from face centered cubic lattices.

(5) The simulation results for the liquid and solid phases were used to obtain $\Delta\mu^{\mathrm{r}}$ from Eq. (7). We recommend fitting a second- or third-order polynomial to these differences as a function of p. The nearest root of this polynomial represents the equilibrium pressure at the given temperature.

TABLE I. Comparison of triple point temperatures (in K) obtained in this work with experimental values [3,43], other literature sources [44–46], and the LJ potential using revised [53] and conventional [52] ε values.

Atom	Expt	SAAP + ATM + FH-1-2[a]	SAAP[b]	ELJ + ATM + FH-1[c]	LJ[d]
Ne	24.541	25.09 (25.3)	27.94 (27.56)	26.9	24.25 (32.64)
Ar	83.798	83.90 (83.2)	93.41 (92.80)	90.6	83.57 (83.21)
Kr	115.775	115.09[e] (114.2[e])	129.94 (129.85)	110.94, 113.73	122.49 (113.91)
Xe	161.405	156.59[f]	179.09 (180.02)	156.07, 160.78	157.32 (154.33)

[a] Except for the case of Ne, which was reported in Ref. [28], values in brackets are our previously unpublished GDI estimates.
[b] Values in brackets are from Ref. [46].
[c] Ne and Ar values are from Ref. [44] and Kr and Xe values, which exclude FH-1 and use EATM, are from Ref. [45].
[d] Values in brackets are from the conventional ε data.
[e] Excludes FH-1-2, $N = 864$.
[f] Excludes FH-1-2, $N = 500$.

(6) Once the equilibrium p is known, the orthobaric molar volumes can be obtained by interpolating the simulation results for both the solid and the liquid phases.

The NpT MC simulations were conducted [42] in a cubic simulation box usually containing 1372 particles with a cutoff distance (r_c) of 5.5σ, where σ is the separation at which $u_2 = 0$. For calculations involving the SAAP, we did not observe [40] any statistically significant difference in the results for $N > 1372$. The conventional procedure [11] was used to obtain the long-range corrections for the two-body potentials. As discussed elsewhere [40], some care needs to be taken when applying long-range corrections for the solid because the condition that the radial distribution function is equal to one may not apply. For simulations involving the ATM potential, the contribution to the energy was obtained by summation over all triangles for which all side lengths $< r_c$ and the product of all side lengths $< r_c^3$. An approximate tail correction was added [40]. The contribution of the ATM potential was only computed after a change in volume because its contribution to the total energy does not depend strongly on the configuration. The simulations were allowed to equilibrate for 1×10^5 cycles, with a cycle consisting of N attempts to move a particle and one attempt to change the box size. After equilibration, the program forked into four production threads, each having 1.5×10^5 cycles.

The T_{tp} determined at $p = 0$ for neon, argon, krypton, and xenon are summarized in Table I, which also provides a comparison with both experimental data [3,43] and previous theoretical evaluations [44–46] in the literature. The experimental data used in the comparison are accurate to 1 mK and are used as reference values for the temperature scale [43]. Our calculations of the triple point temperature are accurate to $\pm$ 0.1 K. Alternative measurements [47,48] are within a very narrow range of the reference values. The actual triple point p is greater than 0 but its value is so low that the error introduced by this approximation is merely a few mK.

The calculations for neon, argon, krypton, and xenon involved various combinations of SAAP, ATM, and FH-1-2 contributions. Results for xenon are included to complete the analysis of the stable noble gases. However, as discussed below, the best available [24] first-principles data for xenon are not of the same high quality probably due to significant relativistic effects. This means it is currently unrealistic to expect results of similar quality for xenon as for neon, argon, and krypton. In Table I, the calculations involving the SAAP, ATM and FH-1-2 potentials are genuine predictions from theory without any input from either empirical parameters or other attempts to optimize the agreement with experiment.

For neon, argon and krypton, the T_{tp} determined using only the SAAP is at best 10% higher than the experimental value (Table I). In view of the accuracy of the SAAP in reproducing two-body interactions, this confirms the important contributions of other interactions. A comparison is also given with T_{tp} for SAAP reported previously by Singh *et al.* [46]. Although there is good agreement between the two sets of values, the relatively small discrepancies nonetheless highlight the influence of different simulation methods. The entropy correlation method reported here was specifically designed to be reliable for low p.

Previous work [28] for the VLE and SLE properties of neon indicated that both ATM and FH-1-2 interactions are important. It is apparent from the comparison given in Table I that the combination of SAAP + ATM + FH-1-2 interactions allows the determination of the T_{tp} of neon to ≈ 0.5 K of the experimental value. In contrast, the discrepancy using only SAAP is ≈ 3 K. Pahl *et al.* [44] reported calculations for neon using two-body interactions modeled by an extended Lennard-Jones (ELJ potential) with both the ATM potential and first order (FH-1) interactions. Their value of $T_{tp} = 26.9$ K is closer to the SAAP only value (27.94 K) than the SAAP + ATM + FH-1-2 (25.09 K) value. This can probably be attributed to the inaccuracy of the ELJ potential, which affects the contributions of both two-body and FH-1 interactions. The absence of a second-order Feynman-Hibbs term also contributes to the reduced accuracy reported by Pahl *et al.* [44].

The T_{tp} of argon occurs at temperatures at with quantum influences are still likely to be significant. Therefore, we performed simulations involving SAAP + ATM + FH-1-2 interactions, which resulted (Table I) in a predicted T_{tp} that is only ≈ 0.1 K higher than the experimental value. This high level of accuracy, which is very close to the best available experimental data, reflects the reduced uncertainty due to quantum influences; the accuracy of the potential; and the accuracy of the simulation method. In contrast, the value using ELJ + ATM + FH-1 interactions for argon reported by Pahl *et al.* [44] (Table I) is ≈ 7 K above the experimental value. In common with their neon results, it is closer (≈ 3 K below) to the SAAP only value than to the experimental value. The reasons for this inaccuracy are the same as identified above for neon.

Quantum influences were omitted from our calculations for both krypton and xenon, as they are likely to be negligible. The T_{tp} for krypton calculated using SAAP + ATM interactions underestimates the experimental value by ≈ 0.7 K. This is a slightly larger discrepancy than observed for either neon or argon, which reflects the challenges in accurately modeling the properties of larger atoms. We note that some inconsistencies in the thermodynamic behavior of krypton have been reported [49] previously. These challenges are also reflected in the estimated T_{tp} reported by Smits *et al.* [45] who reported two significantly different values (110.94 K and 113.73 K) when using the ELJ + extended ATM (EATM) [50] potentials, which are both less accurate than our calculations. The differences in the values reported by Smits *et al.* [45] are the outcome of using two different calculation methods. This again highlights the importance of the careful choice of calculation methods at low p.

Table I includes a comparison of T_{tp} obtained from SAAP + ATM + FH-1-2 using the current method with simulations extrapolating Gibbs-Duhem integration (GDI) [16] as reported elsewhere [28]. The accuracy of GDI simulation relies heavily on obtaining accurate starting points as the integration procedure quickly propagates initial errors. For neon, an isochoric melting method (which is good at high pressures only) was used to generate an initial state, which allowed subsequent calculations to much lower p and a reasonable extrapolation to the triple point. In contrast, GDI simulations for both argon and krypton could not be reliably extended to very low p, which affected the accuracy of the extrapolated T_{tp}. It is apparent from the comparison in Table I that the method reported here improves the accuracy of T_{tp} in all cases.

In contrast to the very good results obtained for the other noble gas atoms, T_{tp} of xenon is underestimated by approximately 5 K. The primary reason for this discrepancy is that the best available first-principles two-body potentials for xenon underestimate the attractive contributions. This is clearly evident from a comparison with experiment for the second virial coefficient (B_2), which is a genuine two-body property. For example, using the procedure detailed elsewhere [27], at 200 K the xenon two-body potential yields $B_2 = -274.5\ \text{cm}^3\ \text{mol}^{-1}$, which is substantially above the experimental value [51] of $-279.7 \pm 3\ \text{cm}^3\ \text{mol}^{-1}$. In contrast, the first-principles two-body potentials of the other noble gases yield near-perfect agreement with experimental B_2 values. Smits *et al.* [45] reported two very different values of T_{tp}, which in common with their different values for krypton, reflect uncertainties in their calculation procedures.

Table I also provides a comparison with the widely used LJ potential [39]. Recently, Schultz and Kofke [37] provided a very precise estimate of the triple point temperature of the LJ potential that differed significantly from earlier estimates [38], i.e., $T_{\text{tp}} = 0.69455\ \varepsilon/k$. Calculating the LJ T_{tp} for real fluids requires empirically determined values of ε. In Table I, we compare T_{tp} using both the commonly accepted literature [52] values ($\varepsilon_{\text{Ne}}/k = 47.0$ K, $\varepsilon_{\text{Ar}}/k = 119.8$ K, $\varepsilon_{\text{Kr}}/k = 164.0$ K, $\varepsilon_{\text{Xe}}/k = 222.2$ K) and recently revised [53] values ($\varepsilon_{\text{Ne}}/k = 34.91$ K, $\varepsilon_{\text{Ar}}/k = 120.32$ K, $\varepsilon_{\text{Kr}}/k = 176.34$ K, $\varepsilon_{\text{Xe}}/k = 226.51$ K). It is apparent from Table I that the revised ε values yield the best agreement with experiment for neon, argon, and xenon whereas the conventional ε value is better for the T_{tp} of krypton. However, if the lower LJ estimates ($T_{\text{tp}} = 0.661\ \varepsilon/k$ to $0.698\ \varepsilon/k$) summarized elsewhere [38] were used, T_{tp} would be mostly well below the experimental values. An exception is that accuracy of the T_{tp} for krypton would be improved when using the revised ε value. The quality of the agreement obtained with the LJ potential depends entirely on the fortuitous choice of ε rather than any theoretically based insights.

The correlation procedure between MC displacement and S_{r}, which is at the heart of our method reported here, is not confined to atoms. In particular, it has been demonstrated to work for both rigid two- and three-centered molecules [41] and mixtures of molecules [54]. Therefore, in principle, the method could be used to obtain T_{tp} for both molecular systems and mixtures. In contrast, alternative SLE simulation methods are: not easily extended to molecules [15,55]; rely on the accuracy of the evaluation [15] of chemical potentials that may result in unreliable melting pressures; involve undesirable surface effects [46]; and cannot be feasibly used [15,37] for either *ab initio* or nonadditive potentials because of the increased computational cost.

In summary, first-principles calculations are narrowing the gap on the accurate determination of T_{tp} for real fluids. The T_{tp} is affected by two-body, three-body, and quantum influences. Apart from the phenomenological insights this provides for SLE, this is significant because knowledge T_{tp} affects both the temperature scale and determination of the Boltzmann constant that are of fundamental importance in science. To achieve this enhanced level of accuracy, improved molecular simulation techniques, such as the entropy correlation simulation technique reported here, are required for low values of p.

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