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Solid–solid phase equilibria in the NaCl–KCl system

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ABSTRACT

Solid solutions, structurally ordered but compositionally disordered mixtures, can form for salts, metals, and even organic compounds. The NaCl–KCl system forms a solid solution at all compositions between 657 °C and 505 °C. Below a critical temperature of 505 °C, the system exhibits a miscibility gap with coexisting Na-rich and K-rich rocksalt phases. We calculate the phase diagram in this region using the semi-grand canonical Widom method, which averages over virtual particle transmutations. We verify our results by comparison with free energies calculated from thermodynamic integration and extrapolate the location of the critical point. Our calculations reproduce the experimental phase diagram remarkably well and illustrate how solid–solid equilibria and chemical potentials, including those at metastable conditions, can be computed for materials that form solid solutions.

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I. INTRODUCTION

Solid solutions are ubiquitous in metallurgy,\textsuperscript{1,2} geochemistry,\textsuperscript{3,4} biomineralization,\textsuperscript{5–7} and many other areas of modern materials science.\textsuperscript{8–13} The atoms in a solid solution reside at regular lattice positions, but the components are randomly intermixed on the lattice. At sufficiently low temperatures, many solid solutions separate into periodic phases with different compositions. Thus, solid solutions are nearly perfect realizations of the idealized lattice models that are widely used to study phase transitions in statistical mechanics.\textsuperscript{14,15} At low temperatures, some solid solutions form "coherent precipitates," i.e., solute-rich precipitates embedded in the surrounding solvent matrix, with both phases sharing one unbroken lattice. Furthermore, certain solid solutions can be quenched to form enormous populations of nanoscale coherent precipitates yielding materials with extraordinary mechanical, magnetic, and heat transfer properties. Examples include precipitate-hardened Ni–Ti–Al superalloys,\textsuperscript{16,17} Heusler or half-Heusler magnetic materials,\textsuperscript{18} and radiation resistant alloys for nuclear reactor claddings.\textsuperscript{19–21}

For these materials (also for solids in general), the earliest stages of crystallization, namely, nucleation and subsequent growth, are a major determinant of the structure and hence the properties of the resulting product. Consequently, fundamental studies of nucleation and growth are essential, but challenging both experimentally and theoretically.\textsuperscript{22–25} Notable studies of nucleation and growth in solid solutions have employed kinetic Monte Carlo simulations.\textsuperscript{24,25} However, rare events such as nucleation still pose challenges for kinetic Monte Carlo and molecular simulations. The available empirical potentials for multicomponent systems rarely make accurate property predictions, while \textit{ab initio} calculations are too costly to capture the statistical ensembles—a sampling issue.\textsuperscript{23}

Simple abstract model systems often yield the most useful and generalizable insights,\textsuperscript{20,22} but it is difficult to quantitatively test their predictions against the experiment. This paper investigates a simple but a real model system, a binary mixture of KCl and NaCl salts. Most molten salt mixtures exhibit a sharp eutectic point, without the rather wide and unusual solid solution region seen for NaCl–KCl. In the case of the NaCl–KCl solid solution, the chlorine atoms occupy...
every other site of a simple cubic lattice, just like in regular rocksalt. The sodium and potassium atoms, which occupy the other half of the rocksalt lattice, are randomly distributed. An illustration of the situation is shown in Fig. 1.

The full phase diagram of the NaCl–KCl system, obtained from the FTsalt database that combines multiple experimental results (along with the predicted data from the current simulation study) is shown in Fig. 2. The data displayed in the phase diagram were originally compiled by JANAF and have just recently been re-verified experimentally. Of particular interest to our study is the fact that for low temperatures, there exists a miscibility gap separating two compositionally different solid solutions, a Na-rich and a K-rich one.

Here, we have predicted the Na-rich/K-rich phase envelope in the solid part of the phase diagram using molecular simulation. The calculated phase diagram reproduces the experimental phase diagram remarkably well (Fig. 2). The calculations enable us to predict the difference in chemical potential for NaCl and KCl for any system composition, including the unstable region inside the two-phase envelope.

An important significance of this study is that having an accurate phase diagram now enables quantitative theoretical studies of nucleation to be carried out for this model, as the chemical potential is now accurately defined rather than assumed being equal to experimental data. Theoretical models invariably show divergence from experimental data, and the driving force or the chemical potential estimated from experimental data can be markedly different from that of the model, introducing significant uncertainty in the calculated nucleation rates.

In predicting the phase diagram, we have employed two distinct approaches: (i) the semi-grand canonical approach with the dependent variable being composition as a function of set chemical potential difference and (ii) Widom’s semi-grand canonical approach involving virtual transmutation of one species to another to determine the chemical potential difference (the dependent variable in this case) as a function of set composition. While we have demonstrated that both approaches give consistent results, the Widom’s semi-grand approach has significant advantages and hence was our method of choice. We introduce the computational model in Sec. II A, outline the regular semi-grand canonical ensemble in Sec. II B, and compare it with semi-grand canonical Widom method.
in Sec. II C. Details of the coexistence calculations are presented in Secs. II D and II E. The results are presented and discussed in Sec. III followed by concluding remarks in Sec. IV.

II. MODEL AND METHODS

A. Force field

In order to model the NaCl–KCl system, we employ a Fumi–Tosi\textsuperscript{52} style force field. The full potential energy is given as a sum of pair terms,

\[ U = \sum_{i<j} u(r_{ij}), \]  

where

\[ u(r_{ij}) = A_{ij} \exp\left[B_{ij}(\sigma_{ij} - r_{ij})\right] - \frac{C_{ij}}{r_{ij}} - \frac{D_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}}, \]

and \( r_{ij} \) is the distance between particles \( i \) and \( j \). The parameters \( A_{ij}, B_{ij}, C_{ij}, D_{ij}, \) and \( \sigma_{ij} \) are specific for the combination of species \( i \) and \( j \), and hence, there are six sets of parameters for all the possible element pairings. These parameters, shown in Table I, are based on those given by Adams and MacDonald.\textsuperscript{50}

The final term in the force field is the electrostatic interaction, where the charges (in units of the elementary charge \( q \)) are +1 on Na and K and −1 on Cl. With the system of units employed in this study, \((4 \pi \varepsilon_0)^{-1} = 1389.35 \text{ kJ/mol Å}^2\), where \( \varepsilon_0 \) is the permittivity of free space.

Interestingly, in the parameter set tabulated by Adams and MacDonald,\textsuperscript{50} the Cl–Cl \( C \) parameter for Cl in NaCl (6985.70 \text{ Å}^6 \text{ kJ mol}^{-1}) is different from that for Cl in KCl (7497.60 \text{ Å}^6 \text{ kJ mol}^{-1}). Here, we have utilized the average of these two parameter values. The same is true for the Cl–Cl \( B \) and \( D \) parameters utilized in the present study. For the Na–K hetero-interaction, the \( \sigma \) parameter was taken as the arithmetic mean of the homo-interactions. For the \( C \) and \( D \) parameters, the commonly employed geometric mean mixing rule was found to be completely inappropriate: for instance, the Na–Cl \( C \) parameter obtained from the geometric mean of the Cl–Cl (in NaCl) and Na–Na \( C \) parameters yielded a value that was almost 25% larger than the specified Na–Cl \( C \) parameter tabulated by Adams and MacDonald.\textsuperscript{50} On searching the literature, we came across the alternative mixing rule proposed by Thakkar,\textsuperscript{38}

\[ C_{ij} = \frac{2\alpha_i \alpha_j C_i C_j}{\alpha_i^2 C_i + \alpha_j^2 C_j}, \]

where \( \alpha_i \) are (dimensionless) polarizabilities. Thakkar’s rule reproduced the Na–Cl \( C \) and \( D \) interaction parameters using polarizabilities taken from Mayer\textsuperscript{56} with no more than 4% deviation or better. Consequently, the Na–K \( C \) and \( D \) parameters were estimated with Thakkar’s mixing rule using the polarizabilities of \( \alpha_{Na} = 0.1820 \) and \( \alpha_K = 0.8443 \) from Mayer.\textsuperscript{50}

B. Semi-grand canonical ensemble simulation

Fluid–fluid phase equilibria require thermal, mechanical, and compositional equilibrium, i.e., \( T = T_1 = T_2, p = p_1 = p_2, \) and \( \mu(x_1, T, p) = \mu(x_2, T, p) \). If one can guess the approximate fluid densities and a composition between \( x_1 \) and \( x_2 \), then the equilibrium conditions can often be identified from a simple direct coexistence simulation. A system held at \( T, p \), and intermediate overall composition will spontaneously split into two phases, one at composition \( x_1 \) separated by an interface from the other at composition \( x_2 \). In a long thin simulation box with fixed cross section and pressure applied from the ends, the interface spontaneously forms perpendicular to the long axis such that surface tension exerts no pressure on the adjacent "bulk" phases. If the box is much longer than the interface thickness, the equilibrium compositions can then be estimated from the simulated concentration profiles.\textsuperscript{56,57} Similar direct coexistence simulations have been used to estimate solubilities of certain solids.\textsuperscript{55–57} An alternative collection of indirect Monte Carlo techniques, which have found widespread application, can identify phase coexistence conditions without ever simulating the interface between phases or guessing approximate densities and compositions. These include grand canonical ensemble simulations,\textsuperscript{56,57} the Gibbs ensemble simulations,\textsuperscript{50} Gibbs–Duhem integration,\textsuperscript{59,50} density of states methods,\textsuperscript{51,52} and osmotic ensemble Monte Carlo simulations.\textsuperscript{53}

For multicomponent solid–solid equilibria, the same conditions apply at equilibrium. However, additional difficulties require methods beyond those used for fluid–fluid and fluid–solid equilibria. First, a dense crystalline solid with no vacancies has no free space for inserting or growing new particles, thus preventing the use of grand canonical simulations, osmotic ensemble simulations, and Gibbs-ensemble simulations with particle insertions. Second, a simulated periodic crystal has allowed volumes that are effectively fixed. The acceptance probability depends on the chemical potential difference between the species, rather than the individual chemical potentials. For the binary solid solution, the semigrand approach therefore yields the required composition ratio as the function of defined chemical potential difference \( \Delta \mu = \mu_B - \mu_A \).

TABLE I. Force field parameters for NaCl–KCl.

|       | \( A \) | \( B \) | \( C \) | \( D \) | \( \sigma \) |
|-------|--------|--------|--------|--------|--------|
|       | \text{kJ/mol} | \text{Å}^{-1} | \text{Å}^6 \text{ kJ/mol} | \text{Å}^8 \text{ kJ/mol} | \text{Å} |
| Na–Na | 25.444 | 3.155  | 101.17 | 48.18  | 2.340  |
| Na–Cl | 20.355 | 3.155  | 674.48 | 837.08 | 2.755  |
| Cl–Cl | 15.266 | 3.061  | 7241.65| 14 543.47| 3.170  |
| K–K   | 25.444 | 2.967  | 1463.38| 1 445.31| 2.926  |
| K–Na  | 25.444 | 3.061  | 377.31 | 260.28 | 2.633  |
| K–Cl  | 20.355 | 2.967  | 2890.63| 4 396.16| 3.048  |
We utilized the semi-grand ensemble for the NaCl–KCl solid solution to determine co-existence compositions at a number of temperatures but found that strategy cumbersome and inefficient compared with the Widom’s semi-grand approach detailed in Sec. II C.

C. Semi-grand canonical Widom simulation

The test particle method originally introduced by Widom\textsuperscript{57} directly probes the excess chemical potential of a substance in a simulation. In the case of a system of $N$ identical particles of mass $m$ at pressure $p$ and temperature $T$, the isothermal-isobaric partition function is

$$Z_{NpT} = \frac{\beta p}{N!} \int_0^\infty dV e^{-\beta pV} \int d^3p N e^{\beta H(r, p)},$$

where $H(r, p)$ is the system’s Hamiltonian, $\beta = 1/k_B T$, $k_B$ is the Boltzmann constant, and $h$ is Planck’s constant. The chemical potential $\mu$ can be calculated from

$$\beta \mu = \frac{\partial}{\partial N} \left[ -\ln Z_{NpT} \right].$$

The Hamiltonian is

$$H(r, p) = \sum_{i=1}^N \frac{p_i^2}{2m} + U(r),$$

so we can split $\mu$ into an ideal and excess part,

$$\mu = \mu^{id} + \mu^{ex}.$$  

The ideal part is given by setting $U(r) = 0$, explicitly performing the momentum integrals, and then applying Eq. (5),

$$e^{-\beta \mu^{id}} = \frac{1}{\beta p \Lambda^3},$$

where $\Lambda = \sqrt{\beta h^2/2\pi m}$ is the thermal de Broglie wavelength.

For large $N$, the derivative in Eq. (5) can be substituted by a finite difference $\Delta N = 1$, and the logarithm turns a difference into a ratio of partition functions. One can then show that in the thermodynamic limit, we have, for the excess part,

$$e^{-\beta \mu^{ex}} = \frac{\beta p \left( V e^{-\beta \Delta U(r_1, \ldots, r_N)} \right)}{N + 1}.$$  

The average is taken over a uniformly distributed test particle (index 0) in a regular $NpT$ simulation box, and the factor in the exponential is the energy change associated with the virtual insertion of this test particle. In the case of an $NVT$ ensemble, Widom’s formula reduces to

$$e^{-\beta \mu} = \left( e^{-\beta \Delta U(r_1, \ldots, r_N)} \right)^N.$$  

While, in principle, exact Widom’s method in practice suffers from poor convergence in dense systems or crystals.

For multi-component systems, an alternative approach to virtual particle insertions is to average over virtual particle transmutations, as shown by Sindzingre et al.\textsuperscript{64} This makes the method applicable to crystals, enabling the determination of the chemical potential difference for the transmutation of one chemical species to another in the lattice. Consider a two-component system (comprised of components $A$ and $B$) at temperature $T$ and pressure $p$. The total particle number is $N = N_A + N_B$. Now, the partition function is

$$Z_{N_A, N_B, T} = \int_0^\infty dV e^{\beta \mu V} Z_{N_A, N_B, V, T},$$

where

$$Z_{N_A, N_B, V, T} = \frac{N!}{N_A!N_B!} \frac{1}{\Lambda_A} \frac{1}{\Lambda_B}$$

and the ideal part is given by

$$Z_{N_A, N_B, T}^{id} = \frac{N!}{N_A!N_B!} \left( \frac{1}{\Lambda_A} \right)^{N_A} \left( \frac{1}{\Lambda_B} \right)^{N_B},$$

where $\Lambda_A = \sqrt{\beta h^2/2m_{A}}$ is the thermal de Broglie wavelength for species $A$ with mass $m_A$ and $\Lambda_B$ is defined accordingly. The chemical potential for species $A$ is the derivative

$$\beta \mu_A = -\frac{\partial}{\partial N_A} \ln Z_{N_A, N_B, T} = \beta (\mu^{id}_A + \mu^{ex}_A),$$

with $\mu_B$ defined accordingly.

Consider the difference in chemical potential,

$$\Delta \mu \equiv \mu_B - \mu_A.$$  

The ideal component of the chemical potential difference can be calculated analytically,

$$\Delta \mu^{id} \equiv \mu^{id}_B - \mu^{id}_A = -\frac{1}{\beta} \left[ \frac{3}{2} \ln \left( \frac{m_B}{m_A} \right) + \ln \left( \frac{N_A}{N_B} \right) \right].$$  

For the excess chemical potential difference, we consider the case when a particle of type $A$ is converted into type $B$ or vice versa. The difference in excess chemical potential is then directly related to the exponential average of the energy change for the transmutation,

$$\Delta \mu^{ex} \equiv \mu^{ex}_B - \mu^{ex}_A = -\frac{1}{\beta} \ln \left( e^{-\beta \Delta U(A^+, B^-)} \right)_{N_A, N_B},$$  

$$= -\frac{1}{\beta} \ln \left( e^{-\beta \Delta U(A^-, B^+)} \right)_{N_A, N_B}.$$  

This quantity can be probed using virtual Monte Carlo transmutation moves in an otherwise standard $NpT$ simulation, which itself can be either Monte Carlo or molecular dynamics. It is worth noting that here, the system composition is fixed at $(N_A, N_B)$, while the excess chemical potential difference is the dependent variable. This is in stark contrast to a simulation in the semi-grand canonical ensemble, where one fixes the chemical potential difference and obtains the composition as a result. Note that Widom’s semi-grand method was used in an earlier study to predict the phase diagram of MgO–MnO solid solution,\textsuperscript{7} but that work refers to the method as a semi-grand canonical simulation.
D. Gibbs free energy from the chemical potential difference

In a binary mixture of species A and B, the full Gibbs free energy per particle is given as

\begin{equation}
\hat{G}(N_A, N_B, p, T) = x_A \mu_A + x_B \mu_B,
\end{equation}

where \( x_i = N_i / N \) is the mole fraction of species \( i \) and \( \hat{G} = G / N \). Since \( x_B = 1 - x_A \), we have

\begin{equation}
\frac{\partial \hat{G}}{\partial x_B} = \mu_B - \mu_A = \Delta \mu,
\end{equation}

which relates the Gibbs free energy to the chemical potential difference that we obtain from simulations. Using the simplified notation \( x = x_B \), one has

\begin{equation}
\hat{G}(x) = \hat{G}_A + \int_0^x dx' \Delta \mu(x').
\end{equation}

In other words, but for the reference value \( \hat{G}_A \) (the Gibbs free energy of a pure A system), the calculation of \( \Delta \mu \) as a function of system composition is sufficient to construct its Gibbs free energy as a function of composition, enabling the determination of co-existence points and hence the binary phase diagram.

In the context of mixtures, the Gibbs free energy is often written in a slightly different form as

\begin{equation}
\hat{G} = \hat{G}^I + \hat{G}^E.
\end{equation}

Again, \( \hat{G} \) is split into an ideal and excess part, but “ideal” and “excess” in this case have a different meaning. The ideal Gibbs energy is now given as

\begin{equation}
\frac{\hat{G}^I(x)}{k_B T} = (1 - x) \frac{\hat{G}_A}{k_B T} + x \frac{\hat{G}_B}{k_B T} + (1 - x) \ln(1 - x) + x \ln x,
\end{equation}

where \( \hat{G}_A \) and \( \hat{G}_B \) describe the pure end states (including all non-idealities in the sense of Sec. II C). The ideal Gibbs energy of the mixture is a composition-weighted linear combination of the pure states plus two mixing entropy terms. This result is consistent with explicitly integrating the ideal gas case, i.e., using Eq. (16) in Eq. (21), and noting that in the special case of two ideal gases that only differ in particle mass, we have

\begin{equation}
\frac{\hat{G}_B}{k_B T} = \frac{\hat{G}_A}{k_B T} - \frac{3}{2} \ln \frac{m_B}{m_A}.
\end{equation}

Naturally, for any system with non-zero interactions (such as NaCl–KCl), this simple relation between \( \hat{G}_A \) and \( \hat{G}_B \) does not hold true.

The change of notation is intended here as we want to emphasize that we will, in the following, assume some functional form for the excess part and fit it to the simulation results. The simplest choice for \( \hat{G}^E \) is called the regular solution model, and is usually written in the form

\begin{equation}
\frac{\hat{G}^E}{k_B T (1 - x)x} = \Omega.
\end{equation}

The regular solution model is symmetric with respect to \( A-B \) interactions, i.e., \( A \) in a \( B \) solvent has the same \( \hat{G}^E \) as \( B \) in an \( A \) solvent. The single parameter \( \Omega \) measures the difference in interaction between the two species. More explicitly,

\begin{equation}
\Omega = N_b \left( \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right),
\end{equation}

where \( N_b \) is the number of bonds per particle and \( \epsilon_i \) is the interaction energy of a bond between species \( i \) and \( j \). Our results show that a regular solution model is not sufficient for the NaCl–KCl mixture. Asymmetry can be introduced with the two-parameter Margules model,

\begin{equation}
\frac{\hat{G}^E}{k_B T (1 - x)x} = W_1 (1 - x) + W_2 x,
\end{equation}

which we used to fit our simulation data. Specifically, we combine Eqs. (22), (23) and (27) to get the full Gibbs free energy and then take the derivative with respect to \( x \) in order to obtain \( \Delta \mu \), Eq. (20). The final functional form we use to fit \( \Delta \mu(x) \) is hence

\begin{equation}
\frac{\Delta \mu}{k_B T} = W_0 + \ln \left( \frac{x}{1 - x} \right) + W_1 (1 - x)(1 - 3x) - W_2 x(1 - 3(1 - x)),
\end{equation}

where the parameter \( W_0 = (\hat{G}_B - \hat{G}_A) / k_B T \) can be identified as the chemical potential difference of the pure phases. The corresponding Gibbs free energy per particle is

\begin{equation}
\frac{\hat{G}(x)}{k_B T} = xW_0 + (1 - x) \ln(1 - x) + x \ln x
\end{equation}

\begin{equation}
+ x(1 - x) \left[ W_1 (1 - x) + W_2 x \right].
\end{equation}

Here, we have used the normalization \( \hat{G}_A = 0 \). As we will see momentarily, knowledge of the absolute value is not important for the construction of the phase diagram. However, should the Gibbs free energies \( \hat{G}_A \) and \( \hat{G}_B \) of the pure end states be known, the fitted value of \( W_0 \) can serve as a consistency check.

E. Construction of the phase diagram

Consider the Gibbs free energy as a function of system composition as shown in Fig. 3 (blue curve). Two-phase coexistence occurs if this function has a concave region. A homogeneous system with a concentration \( x_0 < x < x_1 \) is not thermodynamically stable, and the two coexistence concentrations \( x_0 \) and \( x_1 \) are found with a double tangent construction in the diagram. There, a homogeneous system can lower its free energy by going down to the orange line, the double tangent. Physically, the linear function corresponds to a system that consists of two separated phases of composition \( x_0 \) (A-rich) and \( x_1 \) (B-rich), ignoring any interface terms. The double tangent to a function \( f(x) \) is found by solving a system of two equations with two unknowns,

\begin{equation}
f'(x_0) = f'(x_1),
\end{equation}

\begin{equation}
f(x_0) + f'(x_0)(x_1 - x_0) = f(x_1).
\end{equation}

An important thing to note is that one can replace \( f(x) \) by \( g(x) = f(x) + kx \), i.e., add an arbitrary linear term, without changing
F. Simulation details

The primary simulations to obtain the phase diagram were carried out using an in-house code, ATOMH. We also used LAMMPS and DL_POLY for auxiliary calculations. If not otherwise stated, the system size was $N = 256$ ion pairs, or 512 particles, and the pressure $p = 1$ bar. The cutoff for the non-bonded van der Waals and real-space Coulombic interactions was 0.9 nm. Long range van der Waals corrections were applied to the energy and the virial. The long-range part of the Coulomb interaction was calculated using Ewald summation, with the relative accuracy parameter set to $10^{-6}$. For MD simulations, the time step was $\Delta t = 2$ fs. For MC simulations, one sweep corresponded to 512 single-particle moves and on average 50 exchange moves (Na and K swaps) and ten volume moves. The quantity of interest, the chemical potential difference $\Delta \mu$, was sampled every 50 sweeps by performing a virtual transmutation of every Na atom of one type and updating the corresponding average [Eqs. (17) and (18)].

III. RESULTS AND DISCUSSION

A. Force field checks

For a first check of the force field accuracy, we performed simulations of the pure NaCl and KCl crystalline phases, respectively. The average lattice energies at $T = 298$ K were $U(\text{NaCl}) = -769.95 \pm 0.01$ kJ mol$^{-1}$ per ion-pair, and $U(\text{KCl}) = -700.43 \pm 0.01$ kJ mol$^{-1}$ per ion-pair, which are in excellent agreement with experimentally determined lattice energies, $U_{\text{expt}}(\text{NaCl}) = -770.3$ kJ mol$^{-1}$ per ion-pair, and $U_{\text{expt}}(\text{KCl}) = -701.2$ kJ mol$^{-1}$ per ion-pair.\(^4\)

The results for the lattice constants at $T = 298$ K are given in Fig. 4. Accounting for the estimated uncertainty, there is good agreement between both the MC and MD results and different simulation packages. There are eight atoms per unit cell, so the lattice constant and (number) density are related by $\rho = 8/a^3$. The densities are $\rho(\text{NaCl}) = 0.043595 \pm 0.000007$ Å$^{-3}$ and $\rho(\text{KCl}) = 0.032008 \pm 0.000004$ Å$^{-3}$. The corresponding mass densities are $\rho_m(\text{NaCl}) = 2.1154 \pm 0.0004$ g/cm$^3$ and $\rho_m(\text{KCl}) = 1.9812 \pm 0.0002$ g/cm$^3$. Densities of the mixture as a function of composition for a few other selected temperatures are shown in Fig. 5. In the range of temperatures investigated, there is an approximately linear relationship similar to Vegard’s law\(^5\) between the lattice constant, composition, and temperature,

\[
a = c_x x + c_T T + a_0. \tag{33}
\]

The fitted parameter values are $c_x = 0.62796$ Å, $c_T = 3.1485 \times 10^{-4}$ Å/K, and $a_0 = 5.5911$ Å.

B. Free energies of the pure end states

We calculated the (Helmholtz) free energies of pure NaCl ($x = 0$) and pure KCl ($x = 1$) using the Einstein crystal approach via thermodynamic integration (TI). These calculations closely followed those in a previous work of Anwar, Frenkel, and Noro,\(^7\) so only a brief overview is given here. The simulations were carried out at a fixed volume corresponding to a pressure of $p = 1$ bar. We used the Gauss–Legendre quadrature with $n = 16 \lambda$ nodes for the numerical integration of the free energy derivative $\partial F/\partial \lambda$. The following temperature $T$ and pressure $p$ of the system,$\lambda$ and $\Omega$ are related by $\Omega = 4\pi^{3/2} \lambda^3$.

\[
F(x) = U(x) + T S(x) - \mu(x),
\]

where $U(x), S(x)$ and $\mu(x)$ are the internal energy, entropy, and chemical potential of the mixture, respectively.

The double tangent construction yields the coexistence concentrations $x_0$ and $x_1$.

\[
\ln \frac{x}{1-x} = \Omega (2x - 1) \tag{32}
\]

does not have an algebraic solution.

\[
G(x) = \int_{x_0}^{x} \frac{F(x')}{x'} dx' + \frac{\mu(x)}{x} + RT \ln x - \mu_{\text{expt}} 
\]

FIG. 3. (Blue) Gibbs free energy as a function of composition when there is two-phase coexistence. The data shown are for the NaCl–KCl system at a temperature of 500 K, with $x$ denoting the mole fraction of KCl. Note that the linear part of the Gibbs energy has been subtracted, as this will not affect the final result. (Orange) The double tangent construction yields the coexistence concentrations $x_0$ and $x_1$. These equations and hence the result for $(x_0, x_1)$. In practice, almost always the equations have to be solved numerically. To give an example, even in the simple case of a regular solution model, the resulting equation

\[
\ln \frac{x}{1-x} = \Omega (2x - 1) \tag{32}
\]

does not have an algebraic solution.

\[
G(x) = \int_{x_0}^{x} \frac{F(x')}{x'} dx' + \frac{\mu(x)}{x} + RT \ln x - \mu_{\text{expt}} 
\]
equations are provided in the supplementary material. In the Einstein crystal part of the calculation, the thermal de Broglie wavelength $\Lambda$ was set to 1 Å for all species. For the conditions investigated here, the $pV$ term to convert the Helmholtz free energy into a Gibbs free energy is very small and hence deemed unimportant. For example, for $\text{NaCl}$ at 298 K, the correction is $pV_{\text{NaCl}}/Nk_B T = 0.001$, much smaller than even the probably slightly underestimated uncertainty in the Helmholtz free energy. The results are summarized in Table II.

For $\text{NaCl}$ at 298 K, our result is $\hat{F}_{\text{NaCl}}/k_B T = -306.525 \pm 0.005$. The result compares well with that of Aragones et al., which is $-306.22 \pm 0.005$. Note that these authors reported the value per particle, while in our study, all values are given per ion pair, which accounts for the factor two difference to the raw result reported in Table II of the reference. As discussed in Sec. II A, the $\text{Cl}\text{-Cl}$ B, C, and $D$ potential parameters utilized in the present study differ from the $\text{Cl}\text{-Cl}$ parameters of pure $\text{NaCl}$ in the study by Aragones, Sanz, and Vega. Our $B$, $C$, and $D$ parameters are averages from the $\text{Cl}\text{-Cl}$ parameters for pure $\text{NaCl}$ and $\text{KCl}$ systems, possibly contributing to the 0.3 $k_B T$ difference between our $\text{NaCl}$ free energies and theirs.

### C. Phase diagram calculation

The miscibility gap is theoretically unstable and inaccessible to regular semigrand canonical simulations, an issue which was noted by Sadigh et al.. Given a fixed $\Delta \mu$, the semigrand canonical simulations always find a composition on either side of the miscibility gap and stay there. Without a good initial guess for the value of $\Delta \mu$ at coexistence, one needs to find it in a tedious, iterative procedure. For example, one can run semigrand simulations with a coarse grid of $\Delta \mu$ values and then iteratively improve the resolution of $\Delta \mu$ at coexistence. Results from this procedure at $T = 600$ K are shown in blue in Fig. 6. This procedure must be repeated for each temperature below the critical point.

Figure 6 also shows results from Widom’s semi-grand method. While both methods agree on the overall curve, only Widom’s semi-grand method is able to probe the miscibility gap. Furthermore, for the Widom method, the total number of simulations necessary to run is much lower, as the whole curve can be obtained in a single parameter sweep varying the $\text{KCl}$ mole fraction from 0 to 1 in equal increments.

For the Widom method, a $\text{NaCl}-\text{KCl}$ solid solution of any arbitrary composition is unable to undergo phase separation into the two co-existing phases due to interfacial energy barriers, enabling its chemical potential to be monitored. This opportunity of being able to sample the chemical potential of unstable and metastable structures is essential to the application of the double tangent method. Hence, it appears that the same interfacial barriers that limit the study of phase transition phenomena by brute force simulation serve here to make the miscibility gap accessible. To confirm that the system does not phase-separate into an Na-rich and a K-rich domain over the full length of our simulations, we carried out spatial and temporal correlation analysis. The analysis and associated results are detailed in the supplementary material and indeed confirm the systems remain homogeneous. For larger systems that do phase-separate, one would need to employ alternative sampling techniques to probe the miscibility gap, such as the generalized replica exchange method developed by Kim et al..

Our experience of Widom’s semi-grand approach suggests that this methodology would readily carry over to more complex solid solution systems. There appears to be a remarkable coupling of this method with solid solution phase stability. Convergence of this method requires appreciable overlap of the energy

### TABLE II. Helmholtz free energies for pure crystalline phases of $\text{NaCl}$ and $\text{KCl}$ from thermodynamic integration with the thermal de Broglie wavelength set to 1 Å for all species to enable easier comparison with published values of Aragones et al.

| $T$ (K) | $\hat{F}_{\text{NaCl}}/k_B T$ | $\hat{F}_{\text{KCl}}/k_B T$ |
|---------|-----------------|-----------------|
| 298     | $-306.525 \pm 0.005$ | $-279.119 \pm 0.004$ |
| 600     | $-150.766 \pm 0.005$ | $-137.474 \pm 0.005$ |

FIG. 6. Comparison between a regular semi-grand canonical simulation and the Widom-like virtual transmutation method for NaCl-KCl at $T = 800$ K. It is not possible to access the miscibility gap region with the regular semi-grand method.
distributions of the original system and that of the virtual perturbed state (when a molecule has been transmutated). This translates to the transmutation energy differences not being excessively large. Phase stability of a solid solution relies on exactly the same energy criteria—the substitution energy difference again must not be too large. The implication is that any system that forms a solid solution is likely to be accessible to Widom’s semi-grand sampling, which would include flexible molecular systems too.

We have performed simulations covering the full range of compositions for multiple temperatures (Fig. 7). The obtained fit parameters $W_1$ and $W_2$ are used to find the corresponding coexistence concentrations $x_0$ and $x_1$ via a double tangent construction. The highest temperature, 800 K, is above the critical point. This is already obvious from the functional form of $\Delta \mu(x)$, which is strictly monotonic. Consequently, the corresponding Gibbs free energy is convex, and no phase coexistence occurs. The results for $(x_0, x_1)$ are shown in Fig. 2 and plotted on top of the experimental phase diagram from the literature. Note that in this figure, the x-axis denotes the mole fraction of NaCl. The accuracy of the prediction is remarkable, highlighting the quality of the NaCl–KCl forcefield, validating Thakkar’s mixing rule, and the power of Widom’s semi-grand simulation protocol. The largest deviations between the experimental results and the ones computed in this study appear at higher temperatures near the critical point. Presumably, this is due to larger fluctuations in the vicinity of the critical point, which make it harder for the computational results to converge.

To verify the consistency of our simulations, we show the results for the Gibbs free energy difference between the two pure phases ($\hat{G}_{\text{KCl}} - \hat{G}_{\text{NaCl}}$) as a function of temperature in Fig. 8. The data shown here are derived from both the independently determined free energies of the pure end states and from the semi-grand canonical Widom simulations. For the Widom simulations, the free energy difference corresponds directly to the value of the fit parameter $W_0$. The free energies of the pure KCl and NaCl are those calculated using thermodynamic integration starting from an Einstein crystal at $T = 298$ K and $T = 600$ K. As seen in the figure, we have almost perfect agreement between the two methods. Note that the semi-grand canonical Widom results for $T = 298$ K are not shown in Fig. 7, and we use them only for the consistency check.

D. Critical point extrapolation

We use Guggenheim’s empirical formula to extrapolate the critical point. The original formula is for the critical point in a gas-liquid transition of argon, and it gives the gas ($\rho_g$) and liquid ($\rho_l$) densities as a function of temperature,
The critical point is \((T_c, \rho_c)\). In the present application, mole fraction \(x\) is substituted for the density. We allow both the critical point and the numerical parameters 0.75 and 1.75 to change in order to give the best fit to our data. The result is shown in Fig. 9.

IV. CONCLUDING REMARKS

We have demonstrated that the semi-grand canonical Widom method can accurately and efficiently compute the phase diagram for a multicomponent solid as a function of temperature and composition. Specifically, we have computed the binodal for solid solutions of Tosi–Fumi NaCl and KCl below the critical temperature. We used the semi-grand Widom framework to compute the chemical potential difference between NaCl and KCl components as a function of composition. The chemical potential data were converted to ideal and excess free energies, fitted to a Margules model, and then used to determine coexistence compositions by common tangent constructions.

Our results are in remarkable agreement with the phase diagram based on experimental data, a testament to the Fumi–Tosi diagram based on experimental data, a testament to the Fumi–Tosi

SUPPLEMENTARY MATERIAL

See the supplementary material for details on the thermodynamic integration procedure to calculate the free energies of the pure salts and absolute free energy results using the true thermal de Broglie wavelengths, comparison of our version of the Cl–Cl interaction with the one used in earlier studies and the lattice parameter of the mixture for different temperatures, and a spatial and temporal correlation analysis to ensure compositional homogeneity throughout the unstable zone of the phase diagram.

AUTHOR’S CONTRIBUTION

J.A. and C.L. contributed equally to this work.

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