

Thermodynamic properties of Model CdTe/CdSe Mixtures.

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We report on the thermodynamic properties of binary compound mixtures of model group II-VI semiconductors. We use the a recently introduced Stillinger-Weber Hamiltonian to model binary mixtures of CdTe and CdSe. We use molecular dynamics simulations to calculate the volume and enthalpy of mixing as a function of molefraction. The lattice parameter of the mixture closely follows Vegard's Law: a linear relation. This implies that the excess volume is a cubic function of molefraction. A connection is made with hard sphere models of mixed fcc and zinblende structures. The potential energy exhibits a positive deviation of ideal soluton behavior; the excess enthalpy is nearly independent of temperatures studied (300K and 533K) and is well described by a simple cubic function of the molefraction. Using a regular solution approach (combining nonideal behavior for the enthalpy with ideal solution behavior for the entropy of mixing) we arrive at the Gibbs free energy of of the mixture. The Gibbs free energy results indicate that the CdTe and CdSe mixtures exhibit phase separation. The upper consolute temperature is found to be 335K. Finally, we provide the surface energy as a function of composition. It roughly follows ideal solution theory, but with a negative deviation (negative excess surface energy). This indicates that alloying increases the stability, even for nanoparticles.

2 Introduction

Ternary systems, such as mixtures of CdTe and CdSe, or $\text{CdTe}_{1-x}\text{Se}_x$ for short, are commonly used in the semi-conductor applications to help modify properties such as the lattice parameter and the size of the band gap. Our motivation for studying the thermodynamic properties of $\text{CdTe}_{1-x}\text{Se}_x$ stems from our interest in core/shell quantum dots (QD) such as CdTe/CdSe, a nanoparticle consisting of CdTe core surrounded by a shell of CdTe. It is well known that the considerable lattice mismatch (about 6%) between these two binaries can lead to defect formation that is believed to negatively impact the QD luminescence efficiency. A potential remedy may be found in alloying the interface (heterojunction) where the two phases meet. Without introducing other cations, one can consider the mixing of Te and Se, i.e., replacing some of the anions inside the CdTe phase with Se anions and vice versa in the CdSe phase. To assess the efficacy of such an alloying strategy one requires the thermodynamic mixing properties. In particular, one needs the lattice parameter, the free energy of mixing, and the surface energy over the entire range of composition.

Although there are some experimental results for the lattice parameter, the thermodynamic mixing properties are not readily available. It is natural then to use a molecular simulation approach to determine the basic thermodynamic properties of mixtures of binary II-VI compounds such as CdTe and CdSe. To facilitate this program we have recently developed an interaction model approach based on the Stillinger-Weber (SW) potential [1, 2]. This potential includes both two-body and three-body interactions. It is, of course, an empirical potential, originally developed for Si. However, it has been shown to possess a versatile functional form that lends itself to a generalization applicable to compounds as well.

In a recent paper we introduced a set of two-body and three-body potential SW parameters for any combination of the major II-VI elements Zn, Cd, Hg, S, Se, and Te [2]. The goal of reference [2] was to enable efficient atomistic simulations of defect mechanisms. The potential's fidelity was achieved by optimizing pertinent model parameters with respect to cohesive energy, lattice constants and bulk moduli of all binary compounds. We showed that our intermolecular potential correctly predicted crystalline growth of all binary compounds during molecular dynamics simulations of vapor deposition. We demonstrated that our potential is applicable to a variety of compound configurations involving all the six elements mentioned. We employed the potential to demonstrate a successful MD simulation of crystalline growth of alloyed compounds ($\text{Cd}_{0.28}\text{Zn}_{0.68}\text{Hg}_{0.04}$)($\text{Te}_{0.20}\text{Se}_{0.18}\text{S}_{0.62}$) onto a ZnS substrate. In addition, it was demonstrated that we could capture a variety of defects such as misfit dislocations, stacking faults, and sub-grain nucleation during a complex growth simulation of ZnS/CdSe/HgTe multilayers that contained all the six elements listed above.

We report on a modeling study of the mixing properties of $\text{CdTe}_{1-x}\text{Se}_x$. As a function of composition, x , we determine the lattice parameter, volume per particle, and the potential energy (enthalpy), Gibbs free energy as well as the surface energy. We compare the lattice parameter results with Vegard's Law, and make the connection with ideal solution theory.

Table 1: The Stillinger-Weber potential parameters for the ternary CdTe_{1-x}Se_x. See Zhou et al. [2]

	ϵ [eV]	σ [Å]	a	λ [eV]	γ	A	B
Cd-Cd	1.182358	2.663951	1.527956	32.5	1.2	7.9170	0.767446
Cd-Te	1.385284	2.352141	1.810919	32.5	1.2	7.0496	0.886125
Cd-Se	1.352371	2.045165	1.953387	32.5	1.2	7.0496	1.116149
Te-Te	1.849775	2.905254	1.594353	32.5	1.2	7.9170	0.73072
Te-Se	1.295053	2.231716	1.809645	32.5	1.2	7.0496	1.005396
Se-Se	2.400781	2.789002	1.544925	32.5	1.2	7.9170	0.76721

3 Simulation methods

We use molecular dynamics simulations to study the thermodynamic properties of binary mixtures. The natural choice is to perform these simulations at constant pressure, p , as this corresponds to the typical experimental conditions under which mixtures are most easily studied. Thus, we employ the constant pressure, constant temperature ensemble (i.e. NpT). We use a cubic simulation cell with periodic boundary conditions (pbc) applied in all three directions. Most simulations were performed with $N=1728$ atoms (Cd, Te, and Se) arranged in the cubic zincblende structure, which corresponds to $6 \times 6 \times 6 = 216$ cubic unit cells of 8 atoms (4 cations, 4 anions) each. Typically simulations started by generating a pure sample of either CdTe or CdSe. From these configurations of CdTe_{1-x}Se_x mixtures were generated by changing the identity of the anions randomly or otherwise.

To simulate group II-VI semiconductors, we employ the Stillinger-Weber hamiltonian to represent the the atomic interactions [1]. This is a versatile functional form, originally developed for Si, that includes both pair and three-body interactions, viz.,

$$\begin{aligned}
 V &= \sum_{i<j} v_2(r_{ij}) + \sum_{i<j<k} v_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \\
 &= \sum_{i<j} v_2(r_{ij}) + \sum_{i<j<k} h_{jik} + h_{ijk} + h_{ikj}
 \end{aligned} \tag{1}$$

and h_{jik} is shorthand for the energy contribution associated with angle θ_{jik} ,

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda g(r_{ij})g(r_{ik})(\cos\theta_{jik} - \cos\theta_0)^2 \tag{2}$$

Here, λ is a constant with units of energy, and θ_{jik} the angle subtended at particle i , formed by the ij bond and the ik bond. The cosine of θ_{jik} expressed in terms of distance vectors is,

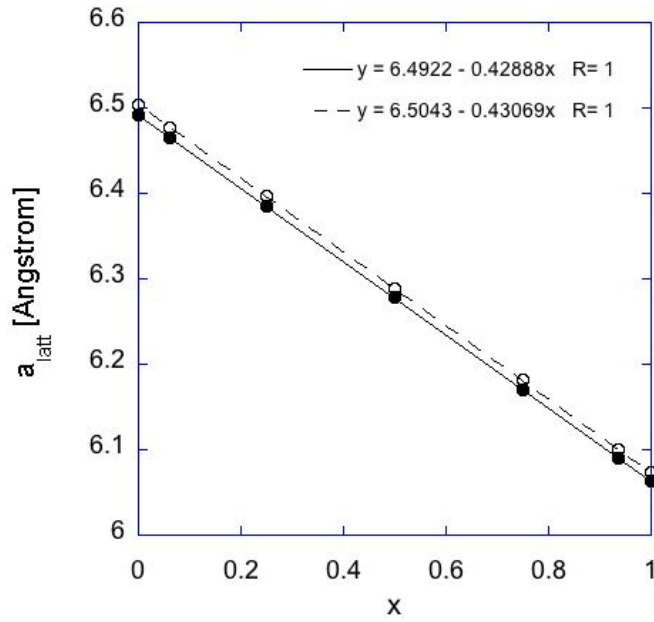


Figure 1: The lattice parameter as a function of composition (mole fraction of Se) for two temperatures: 300K(solid circles) and 533K (open circles). The lattice parameter for a mixture is calculated from the average volume as $a_{latt} = (\langle V \rangle / 216)^{1/3}$, for a system consisting of 216 unit cells. Also shown are the perfect linear fits to the data.

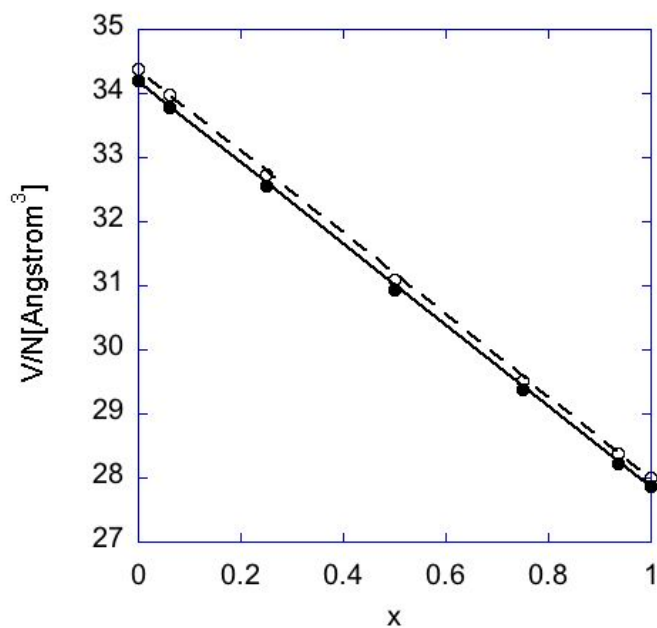


Figure 2: The volume per particle as a function of composition for two temperatures: 300K (solid circles) and 533K (open circles). The mole fraction of Se is denoted by x . The straight lines are the linear relationship that constitutes ideal solution behavior for the volume, i.e., $V^{id}(x) = xV_2 + (1-x)V_1$. For both temperatures, the simulation data indicate that there is a slight negative deviation from ideality, in accordance with the results of figure 1, see Appendix A.

$$\cos\theta_{jik} = \frac{\mathbf{r}_{ij}\mathbf{r}_{ik}}{r_{ij}r_{ik}} = \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ik} \quad (3)$$

$g(r)$ is a decay function with a cutoff between the first- and the second-neighbor shell. The decay function used by Stillinger and Weber is:

$$g(r) = \exp(\gamma/(r-a)) \quad (4)$$

Finally, the pair-potential contribution is strictly of finite range, a , and is of the form

$$v_2(r) = \epsilon A(Br^{-p} - r^{-q})e^{1/(r-a)}; \quad r \leq a \quad (5)$$

It has a depth of $-\epsilon$ at the minimum, and conveniently has a vanishing slope at $r = a$.

Earlier, we introduced a potential parameter set for a large range of group II-VI compounds and their mixtures (see Zhou et al.[2]). This set of parameters allows for an accurate representation of the semiconductor crystals and their alloys. We have collected the parameter values needed for $\text{CdTe}_{1-x}\text{Se}_x$ in Table 1.

4 Results

Our simulations are performed at (constant) zero pressure and at (constant) room temperature ($T = 300\text{K}$) and one elevated temperatures similar to what QDs would experience in applications (i.e., 260°C , or $T = 533\text{K}$). We start with the lattice parameters of zincblende crystals of the compound mixtures, $\text{CdTe}_{1-x}\text{Se}_x$, as a function of composition. To report the composition we will use the mole fraction of the Se anion, that is, $x \equiv N_{\text{Se}}/(N_{\text{Se}} + N_{\text{Te}})$.

We have collected the basic results for the *pure* components in table 2, where we list the lattice parameter, volume per particle, potential energy per particle and the surface energy per unit area. Below we provide the data for the mixed crystals in the form of excess functions of mole fraction x which, when combined with the tabulated data, allow for the calculation of all the quantities addressed in this paper.

Nearly a century ago Vegard[3] noticed that for several compounds, such as ionic salts, the lattice parameter is a near-linear function of x . This relationship is now known as Vegard's law, and it is a widely-used approximation for estimating the lattice parameter of various classes of compounds. Thus,

$$a_{12}(x) = xa_2 + (1-x)a_1 \quad (6)$$

where a_j denotes the lattice parameter of compound j . In figure 1 we plot the lattice parameter as a function of composition, x . For both temperatures we observe perfectly linear behavior. The

Table 2: Basic results for the the structure and energies of the pure compounds CdTe and CdSe, at two temperatures.

	T [K]	a_{latt} [Å]	V/N [Å ³]	U_{pot}/N [eV]	U_s [eV/nm ²]
Cd-Te	300	6.491918	34.2002	-2.138597	4.211947
Cd-Te	533	6.503747	34.3875	-2.107696	4.207991
Cd-Se	300	6.063162	27.8617	-2.483526	5.758274
Cd-Se	533	6.073452	28.0038	-2.452310	5.745397

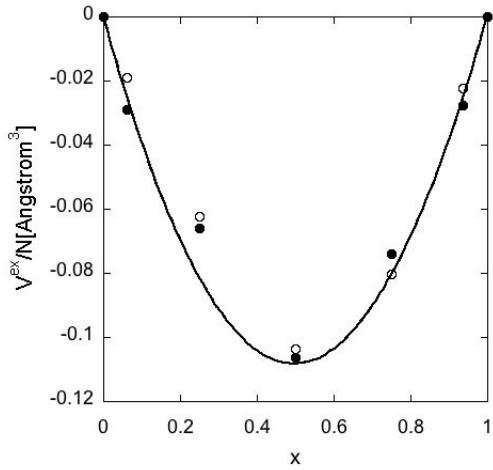


Figure 3: The lattice excess volume per particle, $v_{12}^{ex} \equiv v_{12} - v_{12}^d$, as a function of composition, for a compound mixture of CdTe_{1-x}Se_x. We show two temperatures, 300K(solid circles) and 533K (open circles). The black curve is expression 8, and is indistinguishable for the two temperatures. For more details, see the discussion in appendix A.

linear thermal expansion coefficients is small ($4.4 \times 10^{-5} \text{ \AA}/\text{K}$ at $x = 0$ and $5.1 \times 10^{-5} \text{ \AA}/\text{K}$ at $x = 1$), as the solid is nearly harmonic.

Ideal solution theory is an alternative mixture theory, with great application in fluid state theory [4]. It too is defined by a linear relationship for thermodynamic properties (e.g., enthalpy, free energy). For example, the volume per particle, $v = V/N$, for an ideal solution is given by

$$v_{12}^{id}(x) = xv_2 + (1-x)v_1 \quad (7)$$

The volume per particle is displayed in figure 2 together with relationship 7. Clearly, the volume per particle as measured for the compound mixture, is very close to the ideal solution. It shows only a very slight negative deviation.

The fact that the lattice parameter more closely follows linear behavior is significant [5]. One can easily convince oneself that perfect linear behavior of the lattice parameter (Vegard's law), and perfect linear behavior for the volume (ideal solution theory) can not both be satisfied at the same time (unless, trivially, $a_1 = a_2$ and hence $v_1 = v_2$). Moreover, we can show that Vegard's law implies a *negative* deviation from ideal behavior for the volume, which grows with the disparity of the lattice parameters of the pure crystals. This is demonstrated in Appendix A.

Thermodynamic properties, e.g., Y , of nonideal solutions are commonly expressed in terms of excess properties, i.e., $Y_{12}^{ex} \equiv Y_{12} - Y_{12}^{id}$, to facilitate the development of approximate thermodynamic models [4]. For the volume the ideal solution value is a linear combination of the pure component volumes, V_i , i.e., $V^{id} = \sum_i V_i$, and similarly for the energy and enthalpy. Further, the excess volume equals the volume change of mixing, ΔV , and similarly the excess enthalpy equals the enthalpy change of mixing, ΔH .

Given that $v_{12} = V_{12}/N = a_{12}^3/8$ for an 8-atom zincblende unit cell, it follows that

$$8v_{12}^{ex}(x) = [xa_2 + (1-x)a_1]^3 - xa_2^3 - (1-x)a_1^3 \quad (8)$$

From this we see that, apart from a trivial case cases (i.e., $a_2 = a_1$), $v_{12}^{ex} \neq 0$. In other words, Vegard's law implies nonideal behavior, and moreover, it leads to an expression for the excess volume that is a simple cubic function of x . The results for our compound mixtures, $\text{CdTe}_{1-x}\text{Se}_x$, are shown in figure 3, together with expression 8, with the coefficients determined by Vegard's law (see Appendix A). The latter expression provides an excellent approximation, reconfirming the accuracy of Vegard's law for this compound mixture.

There have been other reports in the literature regarding the lattice parameter as a function of composition. In particular, Denton and Ashcroft [6] studied binary mixtures of hard spheres (HS) of different diameter. They report an adherence to Vegard's law, but for thermodynamic states along the solid-fluid coexistence line, as opposed to keeping both p and T constant. In Appendix B we revisit those results and also introduce results for a HS system of *nonadditive* spheres that closely mimics our SW model.

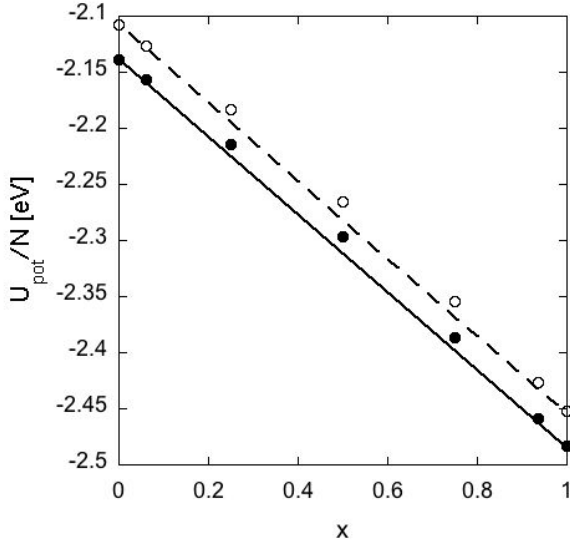


Figure 4: The potential energy per particle as a function of composition, for a compound mixture of $\text{CdTe}_{1-x}\text{Se}_x$. Two sets of data are shown: $T = 300\text{K}$ (solid circles, solid line), and $T = 533\text{K}$ (open circles, dashed line) The straight lines indicate ideal solution behavior. The data indicate a positive deviation from ideal solution behavior, see figure 5 below.

There appears to be only a limited number reports in the literature on measurements of the lattice parameter of ternary compounds, such as $\text{CdTe}_{1-x}\text{Se}_x$. In his review Williams [7] cites the work of Ben-dor and Yellin [8] and reports the lattice constant for $x=0.05$ (0.6462 nm) and $x=0.3$ (0.6353). Our values are 0.6470 and 0.6363 respectively, in excellent agreement.

We now turn to the potential energy, U_{pot} as a function of x , which we note is related to enthalpy, H , by

$$H/N = \frac{3}{2}kT + U_{pot}/N + pv \quad (9)$$

where k is Boltzmann's constant. For our simulations at zero pressure, we find that H/N simply differs from U_{pot}/N by a constant equal to 1.5×0.025852 eV ($T = 300\text{K}$) or equal to 1.5×0.045930 eV ($T = 533\text{K}$). The results for U_{pot} are depicted in figure 4, showing a nearly linear relationship. More detail is shown in figure 5, where we subtracted the ideal solution behavior and plotted the excess value, $U_{pot}^{ex} = \Delta H$, where the latter quantity is the enthalpy of mixing. We notice that ΔU_{pot}^{ex} is a very weak function of T . Thus all the T -dependence of H comes from the ideal gas contribution. We will make use of this observation below, when we discuss phase behavior. As was the case in figure 3 for the excess volume, the excess potential energy can be represented accurately by a simple cubic function.

4.1 Phase behavior

To determine the free energy of mixing, $\Delta G = \Delta H - T\Delta S$, we require the entropy of mixing. In principle, one can calculate this quantity from a simulation using a variety of thermodynamic integration methods, see for instance reference [9]. Here, however, we will follow Hildebrand [10] and estimate the entropy of mixing by assuming ideal mixing, i.e.,

$$-\Delta S^{id}/Nk = x\ln x + (1-x)\ln(1-x) \quad (10)$$

and we obtain the Gibbs free energy of mixing as

$$\Delta G \approx \Delta H - T\Delta S^{id} \quad (11)$$

In 1927 Hildebrand [10] coined the phrase "regular solution" for a solution that combines nonideal behavior for the enthalpy with an ideal entropy of mixing. We show the results for the free energy of mixing in figure 6, where we plotted the dimensionless quantity $\Delta G/NkT$ for the two temperatures for interest. As we have seen above, the enthalpy of mixing (i.e., the excess potential energy, plotted in figure 5) is positive, but the entropy term is sufficiently large to make mixing favorable [11]. For the high temperature ($T = 533\text{K}$), a single mixed phase is always the stable phase and thus there exists complete miscibility over the entire range. However, the room temperature curve displays two points of inflection, and thus over the mole fraction range $0.298 < x < 0.815$, a linear combination of two phases is slightly lower in free energy. Thus in that range phase separation might occur. From figure 8 we see that the excess potential energy is nearly independent of T . If we assume U_{pot}^{ex} is indeed constant with temperature then it is straightforward to determine an upper consolute temperature of $T = 335\text{K}$ (or 62°C). The composition at the consolute point is $x = 0.575$. Within the analysis presented, the two phases coexisting below $T = 335\text{K}$ are both randomly substituted lattices. One phase is rich in Te, the other is rich in Se. Above $T = 335\text{K}$ there exists just a single randomly substituted phase. For a nano particle of $\text{CdTe}_{1-x}\text{Se}_x$, the phase separation we just identified might be suppressed, if the associated positive interfacial free energy contribution were to outweigh the free energy gain from a phase separation.

5 Simulations of Finite Samples

As stated, the results presented above concern simulations performed in the NpT ensemble, using periodic boundary conditions in all three directions. It is of interest to investigate the behavior of a finite block of material (see figure 7), surrounded by vapor (i.e., near vacuum given the low vapor pressure). One question to address concerns whether alloying (the replacement of Te atoms by Se atoms) can produce any noticeable effects due to site percolation. For example, in lattice models of conductivity populating a lattice with a certain fraction of filled sites can lead to a sudden onset of breakthrough conduction when a certain threshold of site occupancy is reached. For the

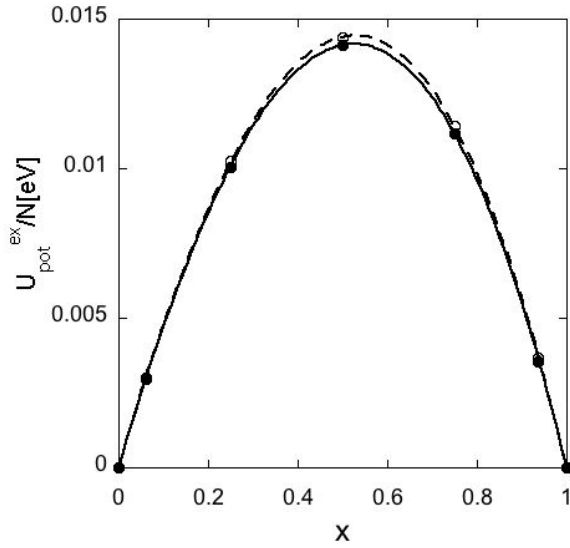


Figure 5: The excess potential energy per particle, or enthalpy of mixing ($\Delta H/N$), as a function of composition for a compound mixture of $\text{CdTe}_{1-x}\text{Se}_x$. We show two temperatures. $T = 300\text{K}$ results are shown by solid circles and a solid line, while $T = 533\text{K}$ are denoted by open circles and a dashed line. The curves are near perfect cubic fits (constrained to pass through $(0,0)$ and $(1,0)$) to the excess potential energy: the solid line is $0.050645x - 0.038916x^2 - 0.011729x^3$, the dashed line corresponds to $0.051111x - 0.038149x^2 - 0.012962x^3$

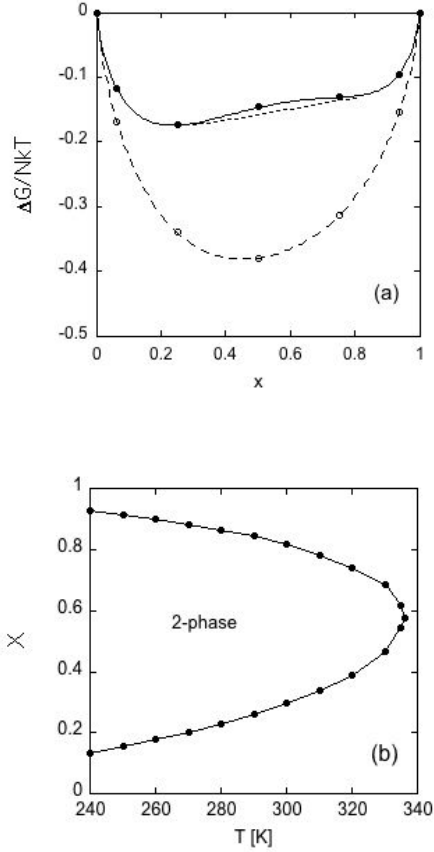


Figure 6: (a) The excess Gibbs free energy per particle as a function of composition, for a compound mixture of $\text{CdTe}_{1-x}\text{Se}_x$. We show two temperatures. $T = 300\text{K}$ results are shown by solid circles and a solid line, while $T = 533\text{K}$ are denoted by open circles and a dashed line. The curves represent regular solution theory: combining the excess enthalpy with the ideal entropy of mixing. For $T = 533\text{K}$ the system is miscible over the entire range. For $T = 300\text{K}$ the presence of the inflection points in ΔG suggest incomplete miscibility: two stable phases exist in the composition range $0.298 < x < 0.815$, as indicated by the dotted line, which represents the common tangent. Assuming a temperature independent excess potential energy (see figure 5) allows us to estimate the upper consolute temperature as $T = 335\text{K}$. (b) The coexistence composition envelope as a function of temperature. The coexisting phases consist of two randomly-substituted lattices, and are determined from the common tangent construction indicated in (a). One phase is rich in Te (small values of x), the other is rich in Se (large values of x). The consolute temperature is $T = 335\text{K}$ and at $x = 0.575$.

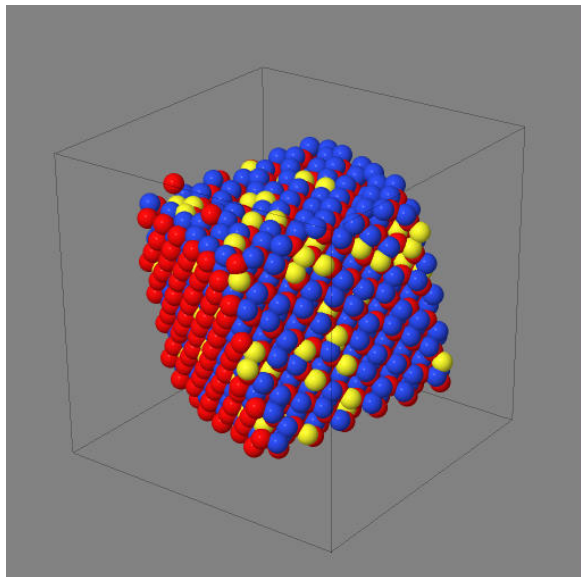


Figure 7: Image of the cubic nanoparticle of $\text{CdTe}_{1-x}\text{Se}_x$, $x = 0.2$ used in the MD simulation. The edge length is approximately 3.83 nm. Cd is shown in red, Te in blue and Se atoms are drawn in yellow. Three (100) faces are terminated by Cd while the opposing (100) faces are terminated by a mixture of Te and Se

diamond lattice this occurs when the occupancy fraction reaches threshold of 0.4299870. In an infinite lattice, above this occupancy threshold there is always at least one cluster that spans the entire system, providing conduction across the sample.

Replacing one Te atom by Se in a finite sample of CdTe reduces the bond lengths around the Se guest atom. Locally, there is a slight contraction of the lattice, that is resisted by the surrounding CdTe solid. It is conceivable that, as the concentration of Se is increased from zero, a critical mole fraction of Se is reached above which the lattice can no longer maintain the CdTe lattice spacing and a marked change in volume occurs. To investigate this effect we prepared a cube of CdTe (216 unit cells, 1728 atoms total) surrounded by a vacuum, running NVT simulations. Because the vapor pressure is negligible, these simulation correspond to simulations at a constant vapor pressure, which happens to be essentially zero. Strictly speaking, the volume for the finite-sized relaxed crystalline particle is not well defined, but a good objective measure of its size can be obtained from 1) the average next-nearest neighbor distance between Cd atoms, R_{CdCd} , or 2) from the radius of gyration, $R_G \equiv [N^{-1} \sum_i (\mathbf{r}_i - \mathbf{r}_{cm})^2]^{1/2}$ of the entire cube. Here $\mathbf{r}_{cm} \equiv N^{-1} \sum_i \mathbf{r}_i$ represents the center of mass position of the cube.

We present the results for R_{CdCd} in figure 8, and the radius of gyration results are shown in the inset to that figure. Both constitute linear measures of the structure of the compound mixture. The bond length shown is an average over all $CdCd$ pairs in the cube, which necessarily includes atoms that are close to the (100) surface where there is some relaxation of the bond lengths. Despite this effect the bond length follows a near perfect linear behavior. This is expected on the basis of Vegard's law, and indicates that there is no appreciable mechanical response that can be attributed to site-percolation. In a zincblende crystal the Cd-Cd distance is related to the lattice parameter, i.e., $R_{CdCd} = R_{TeTe} = \sqrt{2}a_{latt}$, and thus the slopes of figures 1 and 8 related by a factor of $\approx \sqrt{2}$

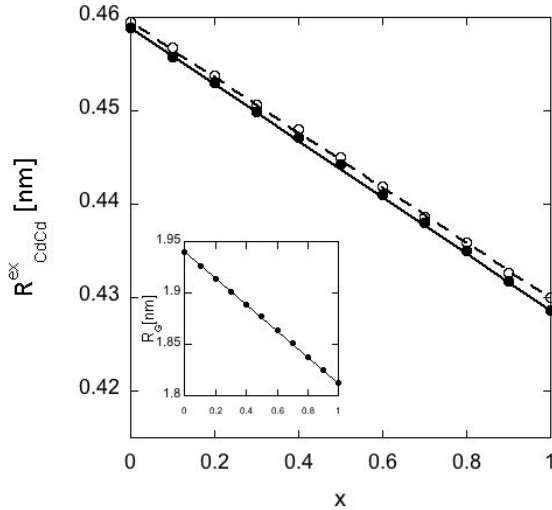


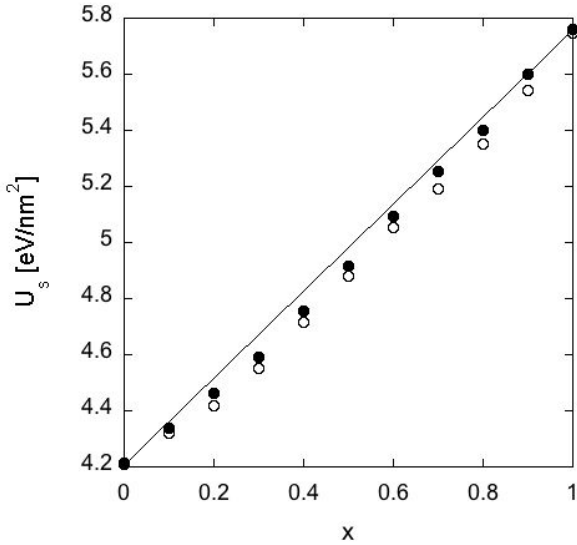
Figure 8: The bond length R_{CdCd} as a function of composition (i.e., mole fraction of Se). Two temperatures are shown: $T = 300\text{K}$ (solid circles, solid line) and $T = 533\text{K}$ (open circles, dashed line). The straight lines corresponds to ideal solution behavior for the bond length, i.e., a linear combination of R_{CdCd} in pure CdTe and pure CdSe. The inset shows the radius of gyration, R_G as a function of composition for $T = 300\text{K}$. The straight line corresponds to ideal solution behavior for the radius of gyration, i.e., a linear combination of R_G of a cube of pure CdTe and pure CdSe.

also. The radius of gyration, R_G , of a cube of length L is equal to $L/2$. Our cube contains 6 unit cells on the side thus the slope in the inset to figure 8 is approximately $6/\sqrt{2}$ times that of figure 8. This is indeed the case, c.f. 0.1269 nm vs 0.1284 nm.

We have determined the deviation from linear behavior of the bond length with composition by calculating $R^{ex} \equiv R - R^{id}$. The dimensionless ratio, R^{ex}/R^{id} exhibits a maximum deviation from zero $\approx 0.1\%$ and occurs near $x = 0.5$.

5.1 Surface energy

The results of the previous two sections, the bulk and a finite cubical particle, allow us to make an estimate of the surface energy as a function of composition. The cubical particle has six (100) faces. Three of these are terminated by Cd atoms, while the remaining three are terminated by the anion (Te or Se). The surface energy, U_s , is defined as



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Figure 9: The surface energy versus the mole fraction of Se for a cube of edge length ≈ 0.63 nm. We show the results for two temperatures: $T = 300\text{K}$ (solid circles, solid line) and $T = 533\text{K}$ (open circles, dashed line). The straight line indicates ideal solution behavior for the surface energy.

$$U_s = \frac{N_p}{A_p}(U_p/N - U_b/N) \quad (12)$$

where the subscript "p" denotes a property of the finite particle (e.g., cube), while the subscript "b" denotes a bulk property. $A_p = A_p(x)$ denotes the total surface area of the particle. We note that U_s is not a pure surface quantity, as the particles edges and vertices must also make a contribution that is included in the difference on the right hand side. In principle, by studying particles of different sizes one could potentially extract the edge and vertex contributions,. The first scales as $(A_p)^{1/2}$ and the other is constant.

The results for U_s , as a function of composition are shown in figure 9, which shows that the surface energy is positive and is mostly a linear function of the mole fraction. Following the discussion above, it is natural to apply ideal solution theory and define a surface excess energy as the deviation from ideal behavior, viz.,

$$U_s^{ex} = U_s - U_s^{id} \quad (13)$$

The results for the excess surface energy are shown in figure 10 for $T = 300\text{K}$ and $T = 533\text{K}$, together with a cubic fit. We see that the excess surface energy is negative over the entire range, and appears to be slightly asymmetric. The negative sign indicates that mixing inside a nanoparticle helps to lower the energy per unit area, and hence the surface free energy per unit area. That implies that for $\text{CdTe}_{1-x}\text{Se}_x$ the mixed state is stabilized by the presence of free surfaces.

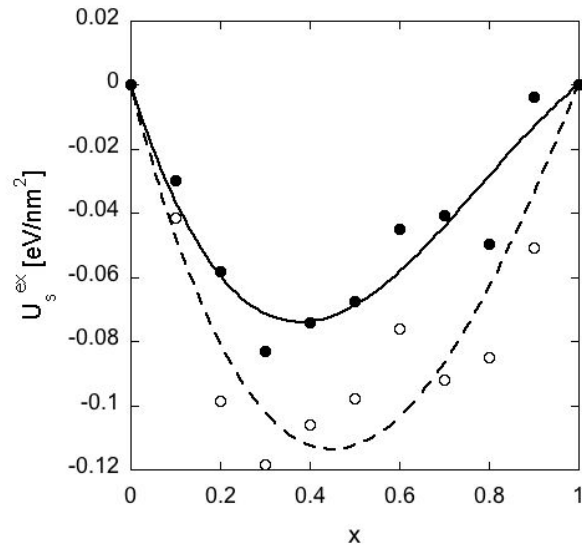


Figure 10: The excess surface energy versus the mole fraction of Se for a cube of edge length ≈ 0.63 nm. We show the results for two temperatures: $T = 300\text{K}$ (solid circles, solid line) and $T = 533\text{K}$ (open circles, dashed line). The data show a negative deviation from ideal solution behavior that increases with temperature. The curves are simple cubic fits, constrained to go through $(0,0)$ and $(1,0)$, to the excess surface energy: the solid line is $-0.43606x + 0.75778x^2 - 0.321720x^3$, the dashed line corresponds to $-0.54056x + 0.72157x^2 - 0.181010x^3$

6 Discussion and conclusions

We have investigated the behavior of mixed crystals of CdTe and CdSe, type II-IV compounds. In particular, we have studied $\text{CdTe}_{1-x}\text{Se}_x$ over the entire range of x , using molecular simulation. We employed our recently developed set of Stillinger-Weber potentials [2, 1], which provide an accurate intermolecular model for this kind of study.

Crystals of $\text{CdTe}_{1-x}\text{Se}_x$ obey Vegard's law perfectly. For the two temperatures studied, room temperature (300K), and an elevated temperature (260°C, 533K) that QDs might experience during operations, combined with zero pressure, the lattice parameter is a perfect linear function of mole-fraction. This behavior was first observed for salt crystals by Vegard. We showed that perfect linear behavior implies a cubic function of x for the excess volume. We compared the observed behavior with that of two simple geometric models, binary hard spheres mixtures and a nonadditive hard sphere model of a zincblende mixture. Both these models show deviations of Vegard's law, indicating that simple geometric models cannot explain all the behavior we observe.

We also examined the thermodynamic properties of $\text{CdTe}_{1-x}\text{Se}_x$. In particular, we obtain the potential energy (enthalpy) and compare with ideal solution theory. There is a positive excess enthalpy that is essentially independent of T over the temperature range studied. By combining a cubic excess enthalpy with an ideal solution entropy of mixing we calculated the Gibbs free energy of mixing. We find that for room temperature there is a phase separation into two phases, each randomly mixed. For $T = 533\text{K}$ there is complete miscibility.

The phase segregation behavior is expected to be even more pronounced when CdTe is combined with CdS. This is indicated by an inspection of potential parameters for II-VI elements Zn-Cd-Hg-S-Se-Te [2]. This shows that for a Cd compound the largest difference in lattice parameter as well as the potential energy occurs between CdTe and CdS. This most likely will produce a larger deviation in nonideality for the enthalpy and a higher consolute temperature, predicting stronger phase segregation. Similarly, when CdSe is combined with CdS, one has the smallest differences in lattice parameter and potential energy, and consequently one would expect that mixture to show most mixing and be most like an ideal solution.

Finally, by performing simulations of finite samples, cubic nanoparticles, we obtained an estimate for the surface energy as a function of composition. The excess surface energy is negative, indicating that a finite particle is stabilized by a mixed phase.

7 Acknowledgements

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8 Appendix A

Expanding equation 8 for the excess volume, we obtain a cubic equation in x , viz.,

$$8v_{12}^{ex}(x) = c_0 + c_1x + c_2x^2 + c_3x^3 \quad (14)$$

where the coefficients c_i in terms of a_1 and a_2 are given by

$$\begin{aligned} c_0 &= 0 \\ c_1 &= 3a_1^2a_2 - 2a_1^3 - a_2^3 \\ c_2 &= 3a_1a_2^2 - 6a_1^2a_2 + 3a_1^3 \\ c_3 &= 3a_1^2a_2 - 3a_1a_2^2 + a_2^3 - a_1^3 \end{aligned} \quad (15)$$

We can simplify this further upon verifying that $c_3 = -(c_1 + c_2)$, since by definition, $v_{12}^{ex}(x)$ must vanish for $x = 1$. Thus,

$$\begin{aligned} 8v_{12}^{ex}(x) &= c_1x + c_2x^2 - (c_1 + c_2)x^3 \\ &= c_1x\left(1 + \frac{c_2}{c_1}x - \left(1 + \frac{c_2}{c_1}\right)x^2\right) \end{aligned} \quad (16)$$

where the last line is included to show that $v_{12}^{ex}(x)$ is reduced to the familiar form $Ax(1-x)$ under conditions where $c_2 \approx -c_1$. That is, the excess volume of the mixture has a symmetric parabolic form, with an extremum at $x = 1/2$. This form is often encountered in the description of nonideal liquid mixtures [4].

We can also show that $v_{12}^{ex}(x)$ is negative (or zero) for all compositions. Thus, Vegard's law implies that the volume of the mixture exhibits negative deviations from ideality. To demonstrate this, note that

$$c_1 = a_1^3\left[3\frac{a_2}{a_1} - 2 - \left(\frac{a_2}{a_1}\right)^3\right] \leq 0 \quad \text{for } a_1, a_2 \geq 0 \quad (17)$$

Specializing to the case of $\text{CdTe}_{1-x}\text{Se}_x$ at $T = 300\text{K}$ for which $a_1 = 6.49192 \text{ \AA}$ and $a_2 = 6.06316 \text{ \AA}$ at $T = 300\text{K}$, we find that $c_1 = -0.437680 \text{ \AA}^3$, $c_2 = 0.447533 \text{ \AA}^3$ and $c_3 = -9.8524 \times 10^{-3} \text{ \AA}^3$. For $T = 533\text{K}$ the values are very similar, $a_1 = 6.50375 \text{ \AA}$ and $a_2 = 6.07345 \text{ \AA}$, which gives $c_1 = -0.441614 \text{ \AA}^3$, $c_2 = 0.451573 \text{ \AA}^3$ and $c_3 = -9.9588 \times 10^{-3} \text{ \AA}^3$.

For both temperatures we conclude that $c_2 \approx -c_1$, we see that the excess volume is indeed nearly a symmetric parabola,

$$8v_{12}^{ex}(x) \approx c_1x(1-x) \quad (18)$$

as is confirmed in figure 3.

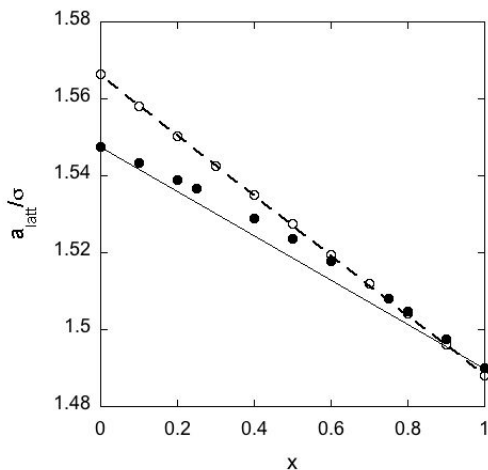


Figure 11: The lattice parameter as a function of mole fraction for a substitutional fcc crystal of binary additive HS mixture, with $\sigma_2/\sigma_1 = 0.95$ (c.f., [9, 6]). The abscissa, x , denotes the mole fraction of species 2, that is, $x \equiv N_2/(N_1 + N_2)$. We consider two cases, the first measures the lattice parameter at constant p and T (solid circles). We observe significant (positive) deviations from Vegard’s law (represented by the straight line). A similar conclusion applies to the volume per particle (not shown), thus the excess volume is positive. The second case, following Denton and Ashcroft [6], the open circles show the lattice parameter along the solid–fluid coexistence line, using the coexistence data of Kranendonk and Frenkel [9] to determine the pressures and compositions. Remarkably, the coexistence data display perfectly linear behavior of the lattice parameter.

9 Appendix B

In this appendix we explore Vegard’s law for binary and ternary hard sphere systems, applying both additive and nonadditive collision rules. Some years ago, Denton and Ashcroft [6] reported on the applicability of Vegard’s law for hard sphere systems. In particular, they used density functional theory (DFT) to study substitutional fcc crystals of binary hard sphere mixtures. They were motivated to determine if simple geometric effects, e.g., the size difference between hard spheres, could play a significant role in determining the crystalline structures of alloys, expanding on previous studies of solids of binary hard sphere mixtures [9, 12]. The authors chose to make the comparison by looking at systems under conditions of solid–fluid coexistence, and concluded that for a size ratio $\sigma_2/\sigma_1 = 0.95$, close to unity, Vegard’s law is a good prediction. Significant deviations were observed for size ratios σ_2/σ_1 deviating more from unity.

Notice that, by choosing to follow the coexistence line, one does *not* follow a constant T and p path. Although a valid choice, it is not clear that this is the appropriate condition to use if we seek to make contact with our semi-conductor compounds. Therefore, in figure 11 we deviate from Denton and Ashcroft [6], and return to the common approach and show the lattice parameter for constant T and p . We see that the data appear fairly linear, but clearly exhibit a positive deviation from Vegard’s law, to be contrasted with the conclusions of Denton and Ashcroft. The same conclusion

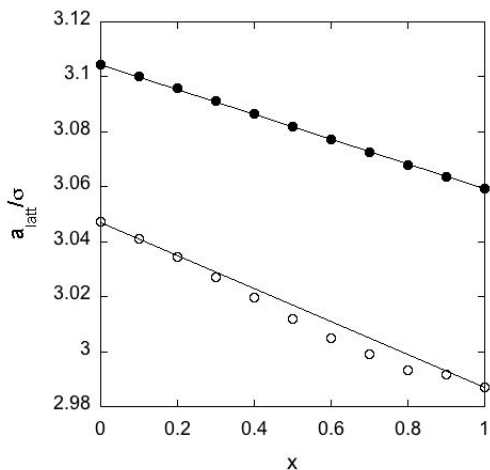


Figure 12: The lattice parameter as a function of mole fraction for a substitutional zincblende crystal of a nonadditive HS mixture where species 2, with $\sigma_2/\sigma_1 = 1$ is replaced by species 3. The abscissa x denotes the mole fraction of species 3, i.e., $x \equiv N_3/(N_2 + N_3)$. We show the results for two size ratios. The solid circles correspond to a nonadditive mixture where $\sigma_3/\sigma_1 = 0.95$, and $\beta p \sigma_1^3 = 3.0977$, while open circles are the results for $\sigma_3/\sigma_1 = 0.90$, and $\beta p \sigma_1^3 = 4.0481$. We observe that for the size ratio closer to unity Vegard's law is obeyed, while for $\sigma_3/\sigma_1 = 0.90$ there are significant (negative) deviations.

applies to the volume per particle (not shown), which also exhibits a positive deviation from ideal solution behavior.

As mentioned above, Denton and Ashcroft [6] used DFT to determine fluid-solid coexistence. Unfortunately, the DFT coexistence results are markedly different from the molecular simulation prediction of Kranendonk and Frenkel [9] (c.f., figures 1 of reference [6] and [9]). Since the latter authors do not supply the lattice parameter, we ran our own molecular dynamics simulations to determine the lattice parameter of the solid phase. To this end we extracted [13] the coexistence mole fractions and pressure data of figure 1 of [9], and ran molecular dynamics calculations for these conditions. The resulting coexistence lattice parameter versus x is shown in figure 12. It clearly follows Vegard's law. Somewhat surprisingly, our simulation lattice parameter coincides with the DFT lattice parameter of Denton and Ashcroft [6]. This implies that the DFT and simulation agree on the packing fraction and mole fraction relationship of the solid phase at coexistence, despite large discrepancies in the $p - x$ coexistence diagram.

The compound lattices discussed for $\text{CdTe}_{1-x}\text{Se}_x$ differ from the binary HS mixtures in that the zincblende structure of $\text{CdTe}_{1-x}\text{Se}_x$, the arrangement of the Cd atoms is a constant feature. That is, one of the two fcc sub-lattices that make up the zincblende structure is not subject to alloying, only the anion fcc sub-lattice is. To investigate whether geometric considerations alone could explain the $\text{CdTe}_{1-x}\text{Se}_x$ compound adherence to Vegard's law, we investigate a ternary mixture of non additive hard spheres. A nonadditive HS system is defined by specifying the cross collision

diameter for spheres of species i colliding with spheres of species j as

$$\sigma_{ij} = \alpha_{ij}(\sigma_i + \sigma_j)/2 \quad (19)$$

From this definition we see that the traditional additive HS mixture is recovered by setting $\alpha_{ij} = \alpha_{ji} = 1$ for all $\{i, j\}$ pairs .

We know that a binary system with $\alpha_{ij} = 1$ if $i \neq j$, and $\alpha_{ij} = 2$ if $i = j$ will result in a zincblende structure when the packing fraction is sufficiently big (e.g., for a packing fraction [14] $\eta > 0.135$, say). This is a direct result of the "charge ordering" that is induced by this particular choice of parameters. That is, species 1 prefers to be surrounded by species 2, and each species prefers to increase the distance between like partners. For other parameter combinations, the NaCl or CsCl structures are found to be the stable crystal structures. Thus, even though the nonadditive HS model is purely repulsive and short-ranged, it shares the charge ordering and crystal structures with the ionic systems.

To facilitate the comparison with our $\text{CdTe}_{1-x}\text{Se}_x$ simulations we extended the binary nonadditive HS mixture to a ternary mixture, and performed molecular dynamics simulations for a mixture where $\sigma_2/\sigma_1 = 1$; $\sigma_3/\sigma_1 = 0.95$ or 0.9 . This choice of parameter values was combined with the following nonadditivity parameters: $\alpha_{12} = \alpha_{13} = 1$; $\alpha_{ij} = 2$ for $i = j$; and $\alpha_{23} = 2$. The latter choice ensures that species 2 and 3 repel each other as other like species. We can think of this model as equivalent to a ternary ionic salt such as $\text{KCl}_{1-x}\text{Br}_x$, which is one of the salts originally studied by Vegard [3].

Results for the lattice parameter of the nonadditive ternary model are compiled in figure 12, where we plot the results for two size ratios, i.e., $\sigma_3/\sigma_1 = 0.95$ and 0.9 . We observe that for a size ratio of 0.95 the ternary nonadditive HS model follows the linear Vegard prediction, just as it does for $\text{CdTe}_{1-x}\text{Se}_x$. However, there is a very slight negative deviation for the larger molefractions. This system also closely follows ideal solution behavior. In contrast, for a size ratio of 0.9 there is a noticeable (*negative*) deviation from Vegard's law, as there is from ideal solution behavior. The results presented in this appendix illustrate that Vegard's law is not generally obeyed and, moreover, simple geometric models such as binary HS, or ternary nonadditive HS are not more likely to exhibit linear behavior for the variation lattice parameter with mole fraction.

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- [14] The packing fraction is given by $\eta = (\pi/6) \sum_i N_i \sigma_i^3 / V$.