Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for: Structural and electronic changes in Ga-In and Ga-Sn alloys on melting

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Supporting figures and tables

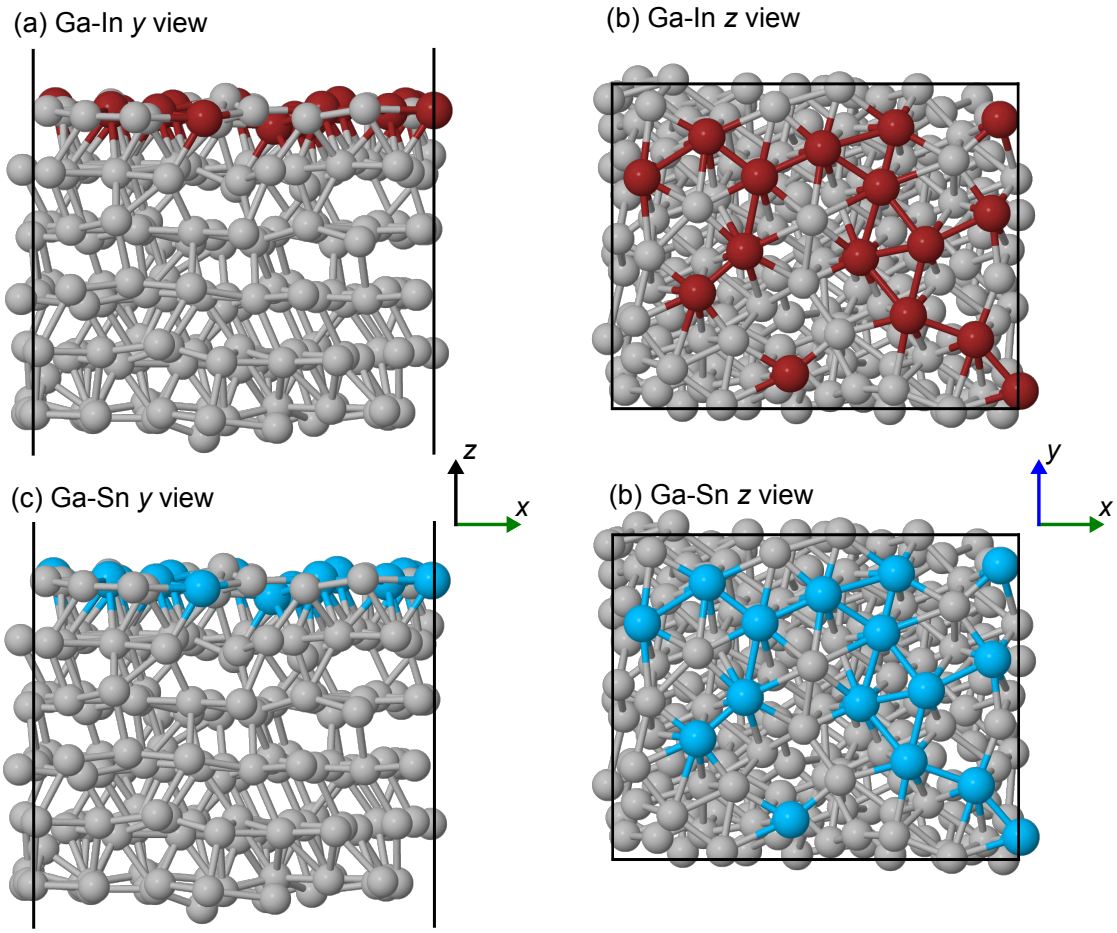

Figure S1: Structures of hexa-layer Ga doped with 7.8 at. % dopant only at the surface. For Ga-In the structures are viewed from (a) the y-direction and (b) the z-direction, and for Ga-Sn (also 7.8 at. %) and these views are shown in (c) and (d). In both cases the black lines mark the boundaries of the periodic cell. Key: Ga – grey, In – red, Sn – light blue.

Structure factor

The structure factor has been calculated as the discrete Fourier transform of the radial distribution function for both alloys at the three temperature brackets considered, and also for pure bulk Ga as a comparison (Figure S2). The plots for Ga-In are shown in Figure S3, and for Ga-Sn in Figure S4.

The calculated structure factor for bulk liquid Ga is highly analogous to that which has

been previously reported, including the presence of a shoulder on the high-k side of the first peak.[S1,S2] The structure factor for the 2D In and Sn alloys has the same general shape as that of bulk Ga, irrespective of temperature, yet there are a few key differences. For one, there are a number of oscillatory sharp peaks at low-k, which are most likely the result of the model being finite in z-direction. Given that the structure factor was developed for, and is typically applied to, 3D extended systems, it is limited in describing the present 2D slab. However, there are still clear differences reflected in the structure factor between solid and liquid structures in the slab models. For instance, the structure factor is less smooth and contains more sharp signals for the solid materials. The largest peak at 2.5 Å^{-1} is also narrower and more intense for the solid structures than the liquid.

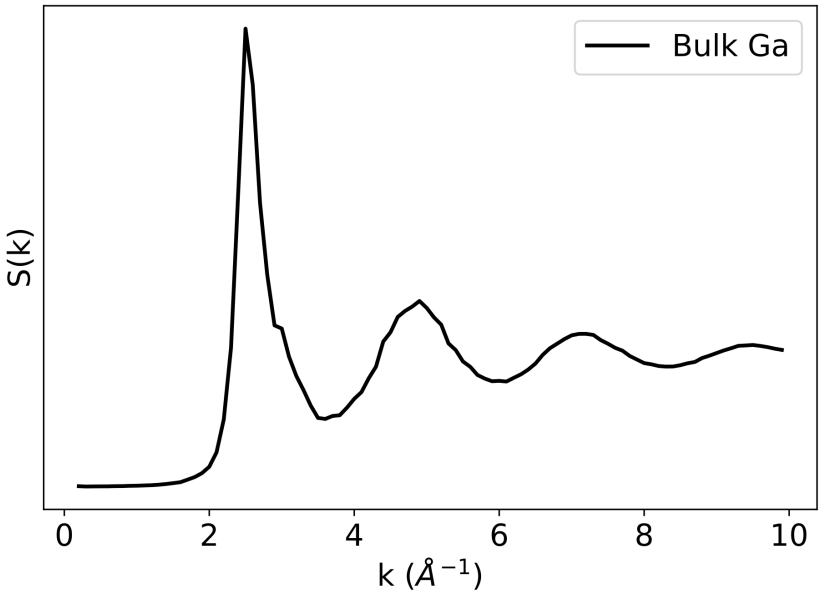

Figure S2: Structure factor calculated for bulk Ga with 384 atoms at 320 K as a comparison.

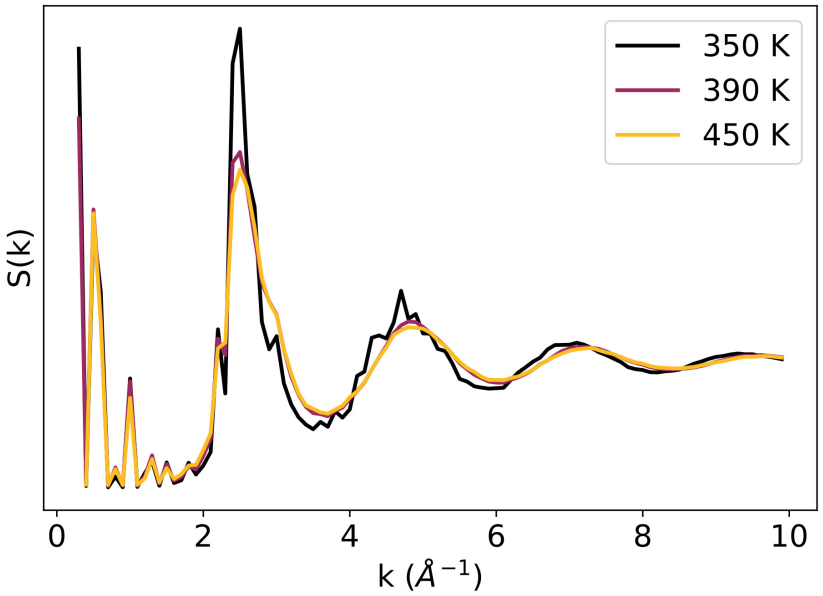

Figure S3: Structure factor calculated the 2D Ga-In slab structure at three different temperatures.

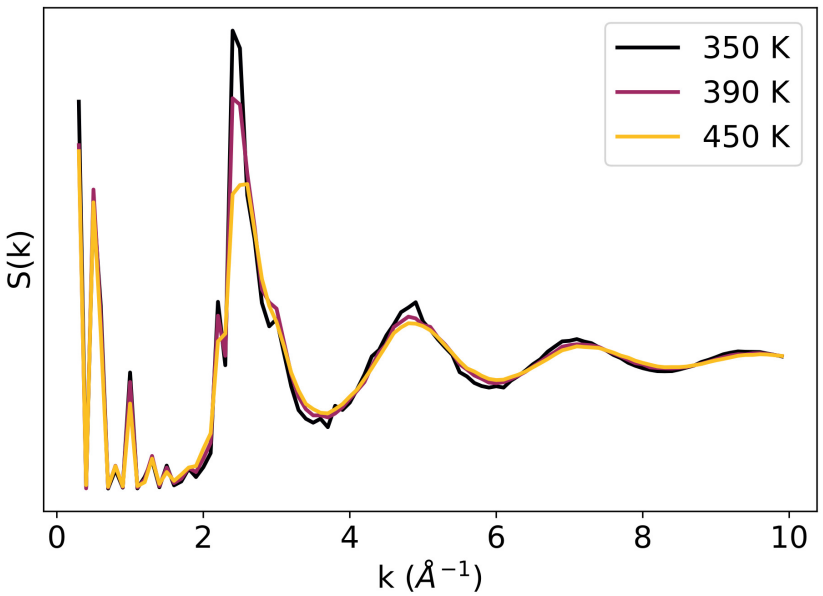

Figure S4: Structure factor calculated the 2D Ga-Sn slab structure at three different temperatures.

Mean squared displacement plots

In the Figures below the mean squared displacement has been calculated across structures at time points between 12 and 50 ps, using the structure at 12 ps as the reference. The slope of these plots yields the diffusion coefficient to be calculated over this range. Note that the plots have different y-axis scales.

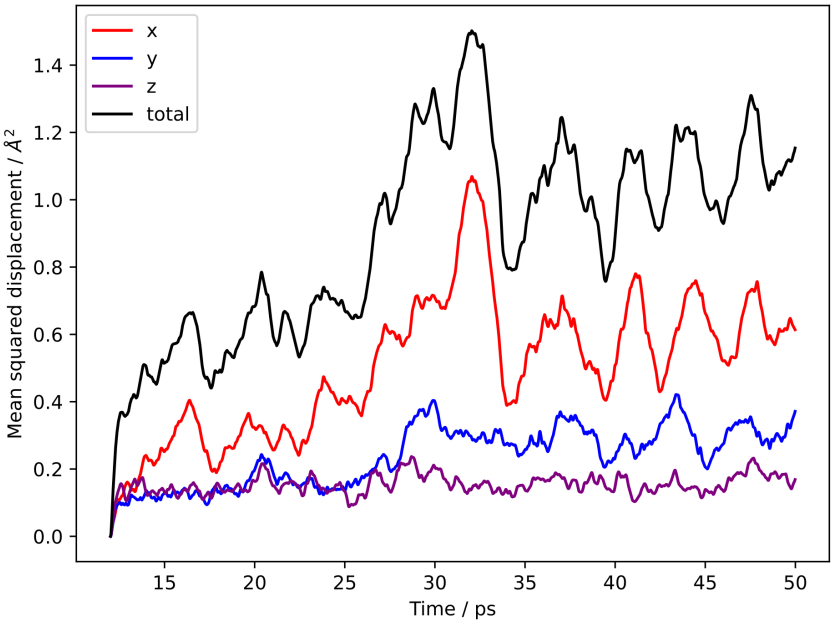

Figure S5: Mean squared displacement for Ga-In at 350 K, calculated between 12 and 50 ps with the 12 ps structure as a reference.

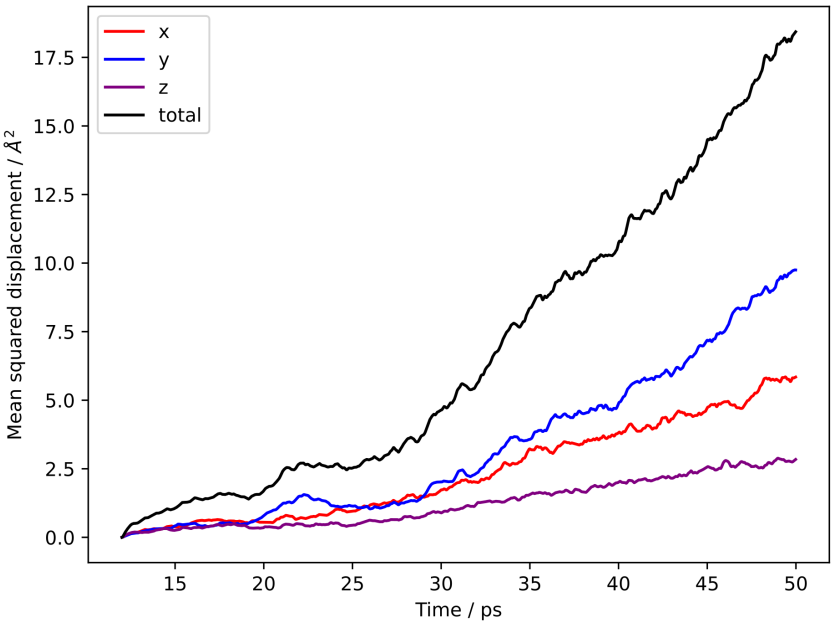

Figure S6: Mean squared displacement for Ga-In at 390 K, calculated between 12 and 50 ps with the 12 ps structure as a reference.

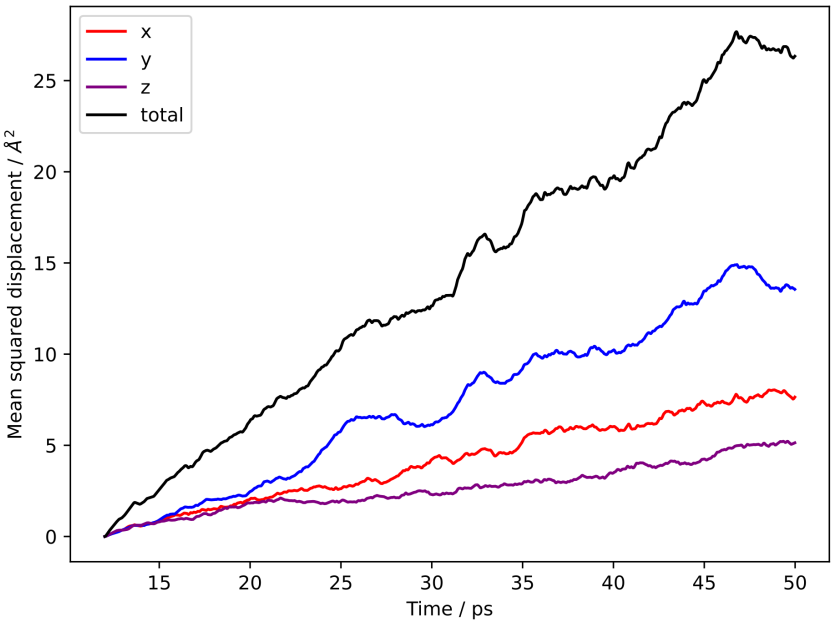

Figure S7: Mean squared displacement for Ga-In at 450 K, calculated between 12 and 50 ps with the 12 ps structure as a reference.

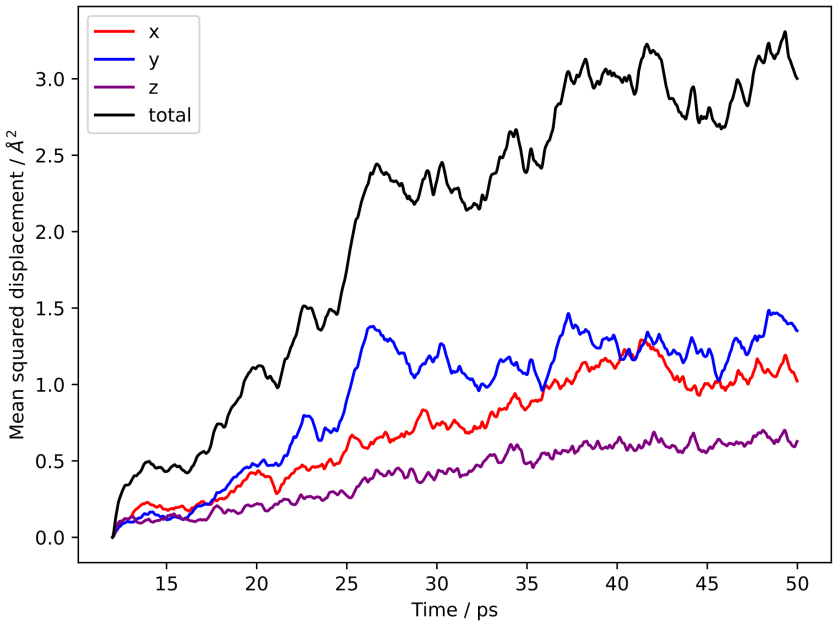

Figure S8: Mean squared displacement for Ga-Sn at 270 K, calculated between 12 and 50 ps with the 12 ps structure as a reference.

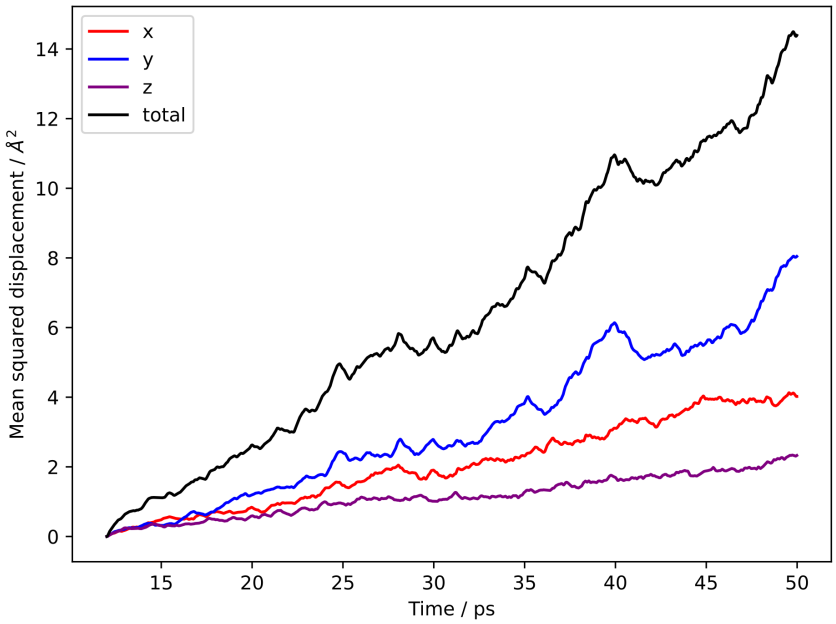

Figure S9: Mean squared displacement for Ga-Sn at 350 K, calculated between 12 and 50 ps with the 12 ps structure as a reference.

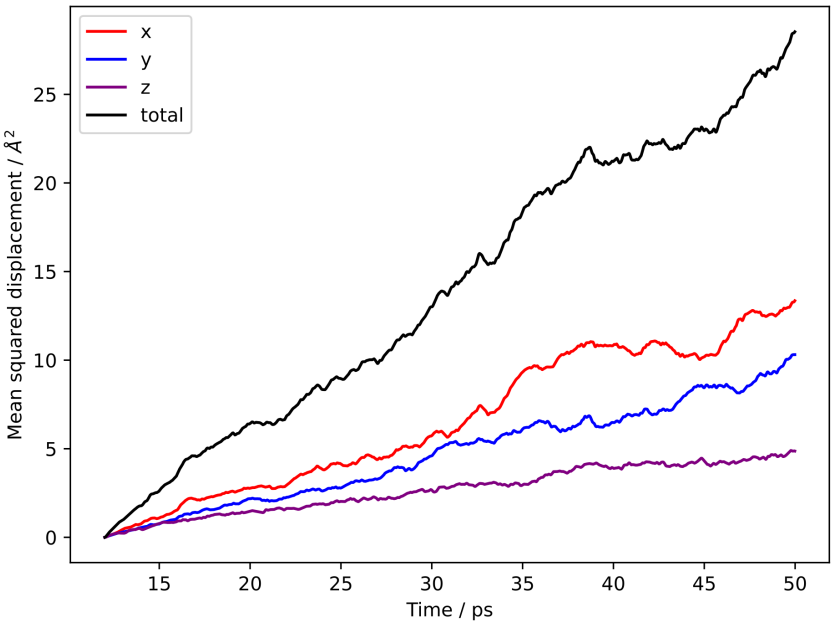

Figure S10: Mean squared displacement for Ga-Sn at 450 K, calculated between 12 and 50 ps with the 12 ps structure as a reference.

Charge density and electron localisation function analyses

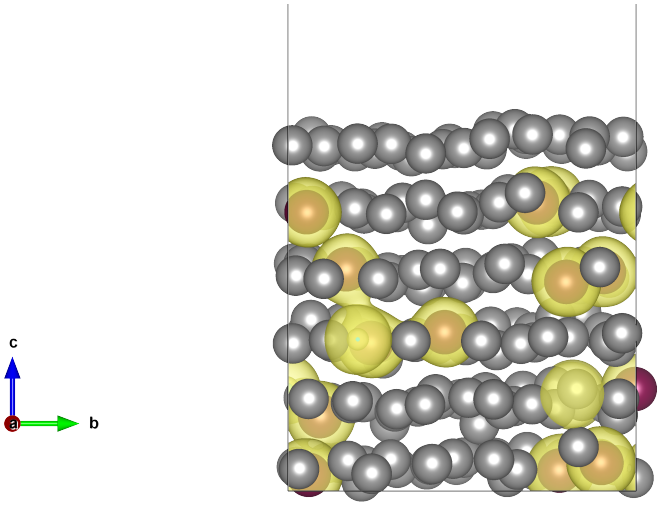

Figure S11: Charge density difference between Ga-Sn and Ga-In starting seed structures in the *ab initio* molecular dynamics run. The yellow isosurface (level = 0.005 $e^-/\mathring{A}^3$) shows the extra electron density associated with Sn doping as opposed to In, which may be disruptive to the layered Ga structure. Key: Ga - grey, dopant - red.

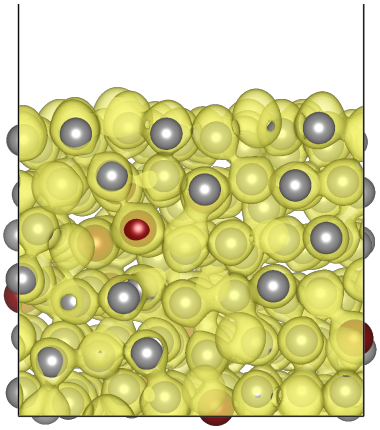

Figure S12: Electron localisation function analysis of a Ga-In snapshot, taken 12 ps into the *ab initio* molecular dynamics simulation (i.e. after equilibration). The electronic structure appears metallic, and there is no evidence of distinct covalent bonds (isosurface level= 0.6). Key: Ga - grey, In - red.

Comparison of ADF and RDF at different time windows

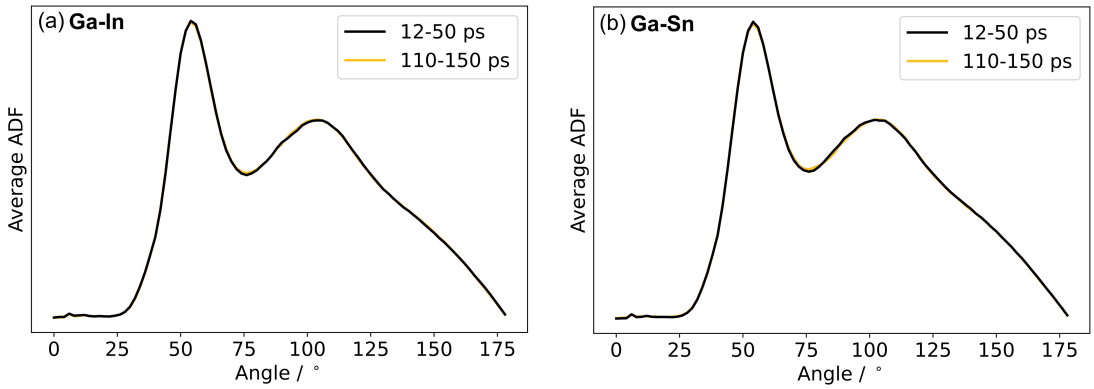

Figure S13: A comparison of the ADF for the 450 K temperature bracket at different time windows. (a) Shows the Ga-In alloy, and (b) Ga-Sn. It is clear that the migration of dopant, which occurs over the course of the *ab initio* molecular dynamics simulation, does not significantly change the ADF.

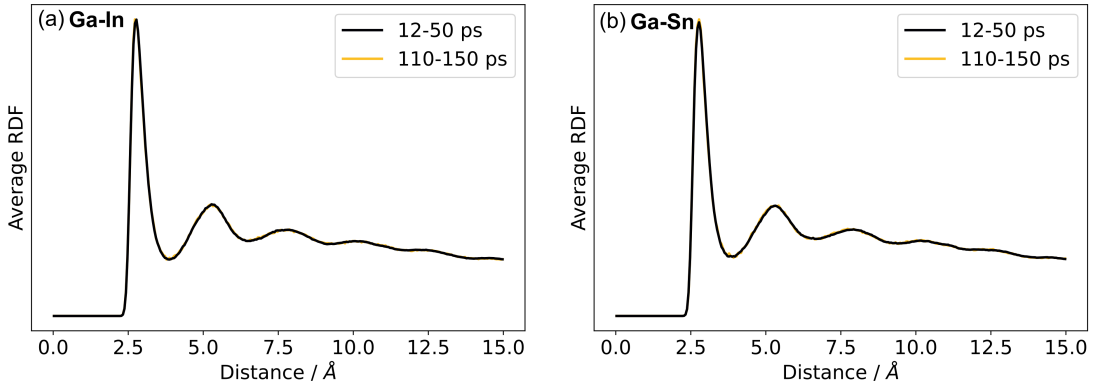

Figure S14: A comparison of the RDF for the 450 K temperature bracket at different time windows. (a) Shows the Ga-In alloy, and (b) Ga-Sn. It is clear that the migration of dopant, which occurs over the course of the *ab initio* molecular dynamics simulation, does not significantly change the RDF.

Surface migration additional plots

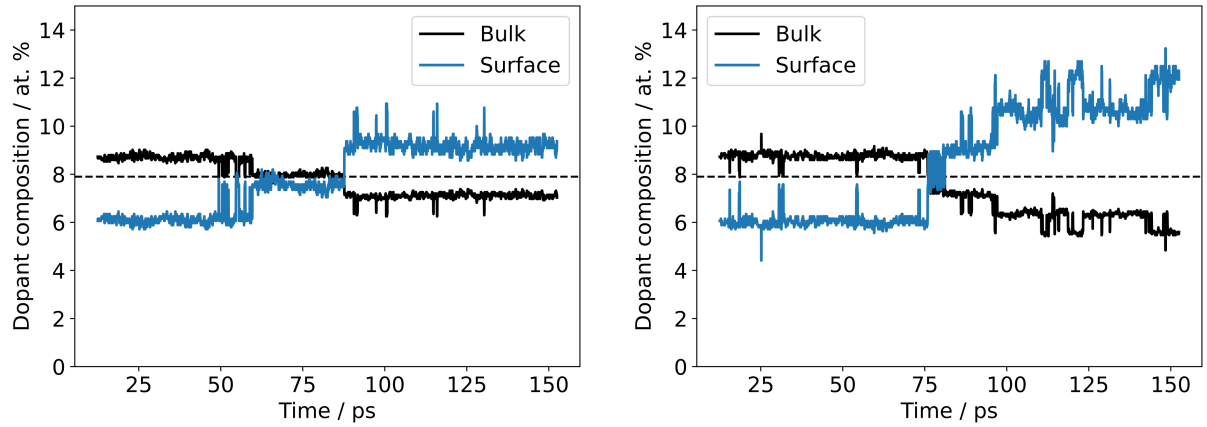

Figure S15: Plots showing the composition (in atomic %) of the surface and the bulk of Ga-In (left) and Ga-Sn (right) over 150 ps of *ab initio* MD simulation when starting seed structure was in a different random configuration of dopant to that in the main text. Both analyses were conducted at temperatures above the melting point, where the alloy is a liquid.

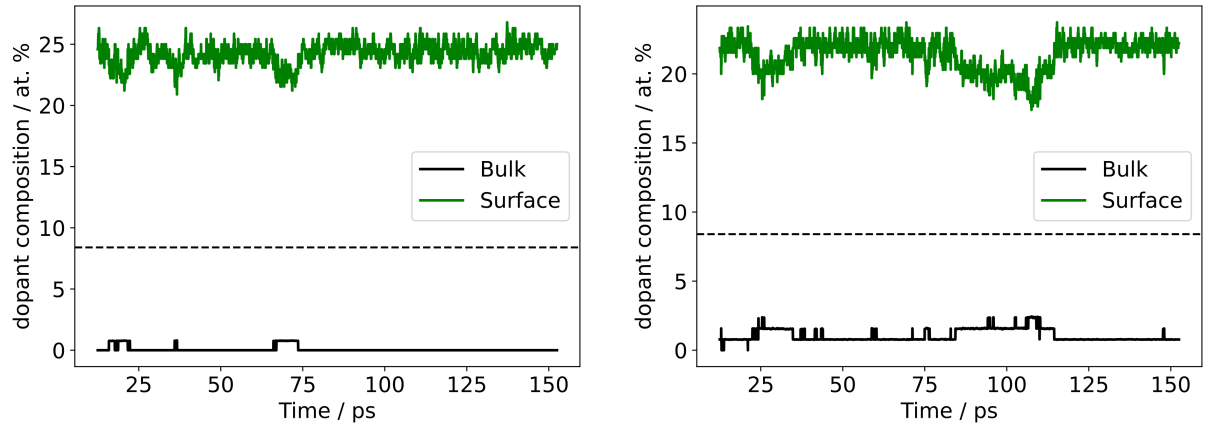

Figure S16: Plots showing the composition (in atomic %) of the surface and the bulk of Ga-In (left) and Ga-Sn (right) over 150 ps of *ab initio* MD simulation when starting seed structure had all the dopant atoms at a single surface. The simulations were conducted at 450 K in both cases, where the alloy is a liquid.

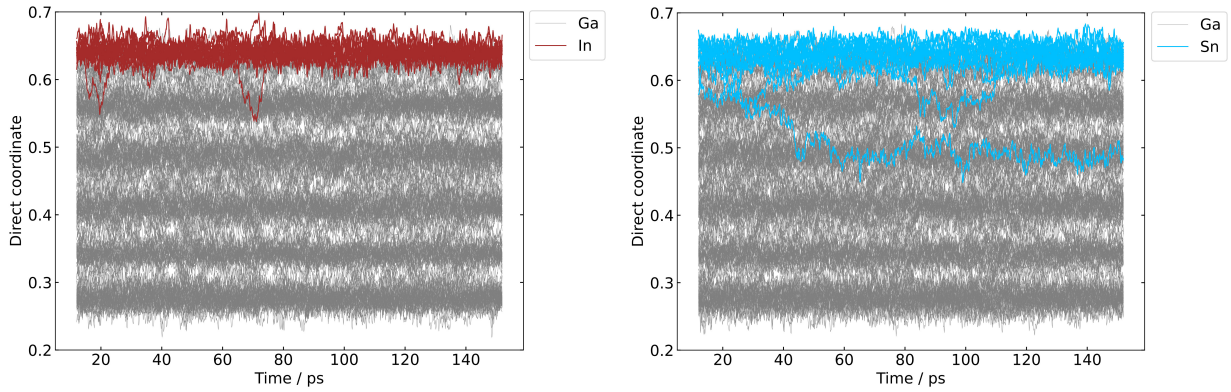

Figure S17: Plots showing the atomic trajectories in the z-dimension for atoms in Ga-In (left) and Ga-Sn (right) alloys when the seed structure is one with all dopants at the surface of the model.

References

(S1) Wu, T.-M. *AIP Conference Proceedings* **2013**, *1518*, 411–418.

(S2) Tsai, K. H.; Wu, T.-M.; Tsay, S.-F. *The Journal of Chemical Physics* **2010**, *132*, 034502.