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Supplementary Information for

Nonequilibrium statistical thermodynamics of multicomponent interfaces

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This PDF file includes:

Supplementary text
Figs. S1 to S4
SI References

Supporting Information Text

Length Scales in the Diffuse Interface Model

As discussed in the main text, the diffuse interface model assumes that $|\nabla\psi| \ll b^{-1}$ where b is the length scale of the direct correlation function, $c(r)$, defined through the Ornstein-Zernike equation (1–3):

$$h(\boldsymbol{r}) = c(\boldsymbol{r}) + \rho \int c(\boldsymbol{r}')h(\boldsymbol{r}-\boldsymbol{r}')d\boldsymbol{r}' \quad [1]$$

where ρ is the particle number density and the total correlation function is defined $h(r) = g(r) - 1$ with $g(r)$ the radial distribution function. The direct correlation function represents the "inherent" correlation between two particles, which is dominated by the inter-particle pair potential. Thus, the length scale b is roughly the range of said potential. For the Lennard-Jones systems studied here, the range of $c(r)$ is approximately independent of temperature and density (as expected) and is on the order of $b \approx 2\sigma$ (4–7), consistent with the physical interpretation given above. Thus, for the diffuse interface model to describe the system appropriately, we must have $|\nabla\psi| \ll 1/2$ where the scalar ψ describes the transition from one phase to the other. For quantitative comparison with our simulation data, we identify ψ with the total mass density $\psi = \rho/\Delta\rho$, where we have normalized by the interfacial density jump so that $0 \leq \psi \leq 1$.

These data are shown in Fig. S1 for equilibrium systems at a variety of temperatures and chemical potential differences. Even for temperatures close to the critical point of the "gas-like" species, the normalized gradients reach values close to the 1/2 threshold identified earlier. Thus, the ranges of the direct correlation function and the interfacial gradients are comparable and the conditions for a thermodynamically consistent diffuse interface treatment are not satisfied. Gradients in other densities (species mass, energy) give similar results.

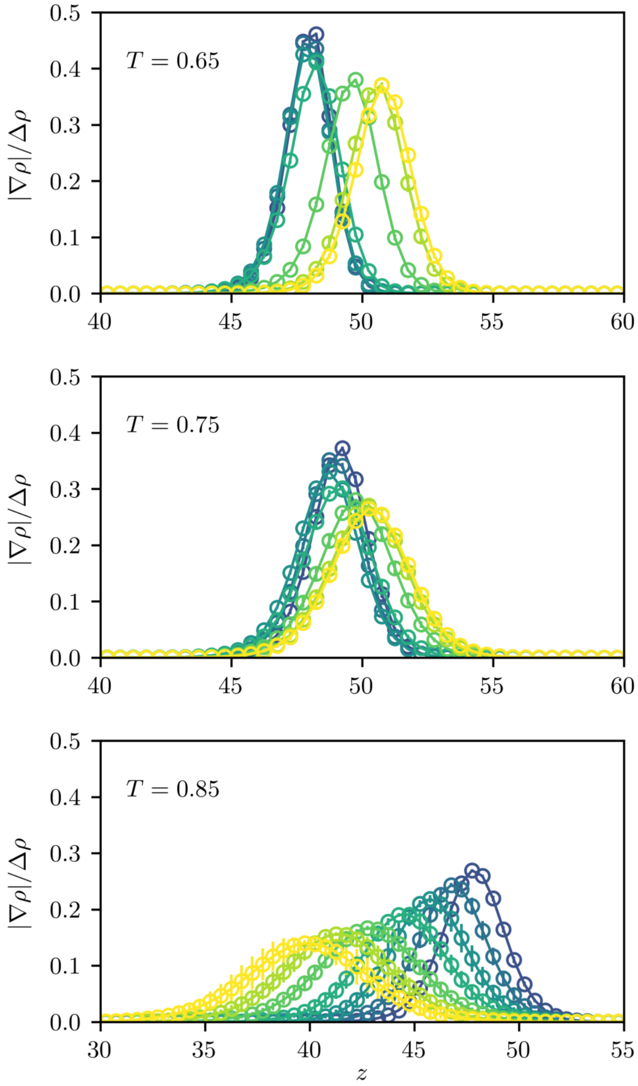

Fig. S1. Normalized mass density gradients for equilibrium binary systems. The colors represent different values of the chemical potential difference between components, ϕ with lower values shown more blue, and larger ones shown more yellow.

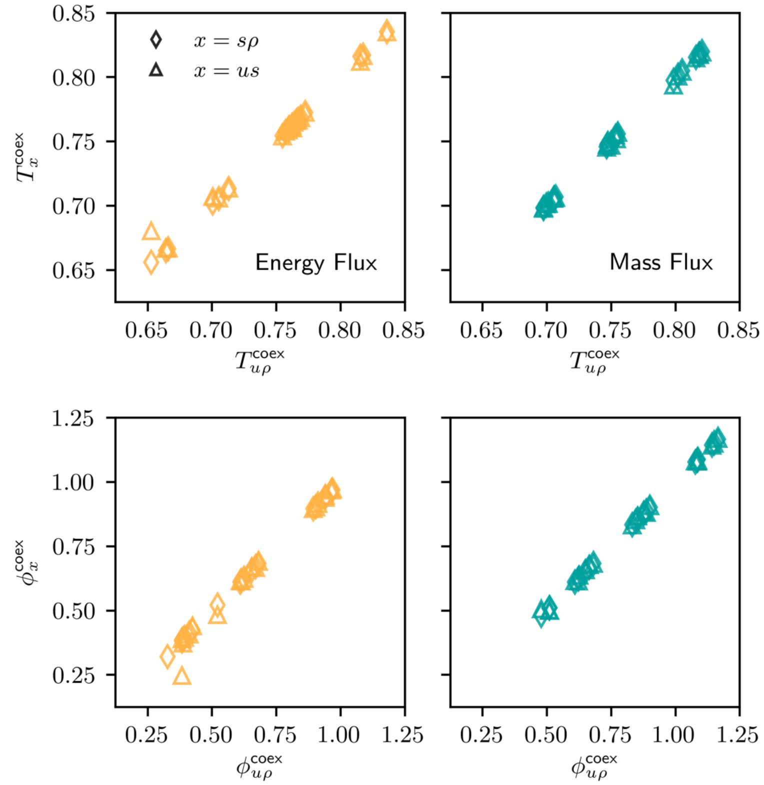

Fig. S2. Comparison between difference coexistence temperatures, whose values are determined by the various pairs of Eq. 4 that can be simultaneously solved: energy-mass (4a/c, denoted $u\rho$ and highlighted in the main text), entropy-mass (4a/b, denoted $s\rho$), and energy-entropy (4b/c, denoted us).

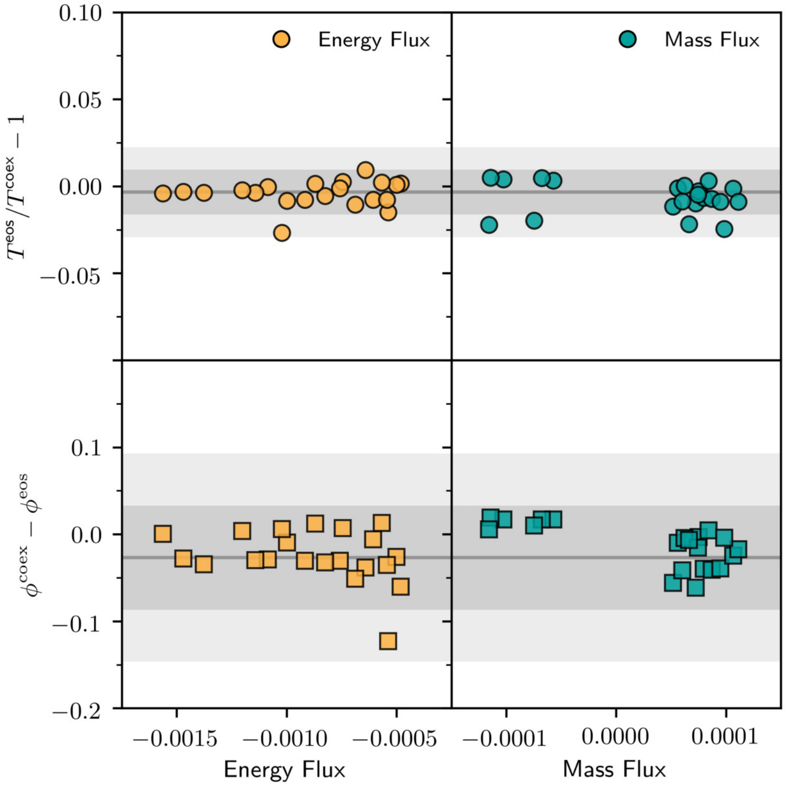

Fig. S3. Relative error between interfacial temperatures obtained from equilibrium equations of state, T^{eos}, and from Eqs. 4, T^{coex}, as a function of energy/mass flux.

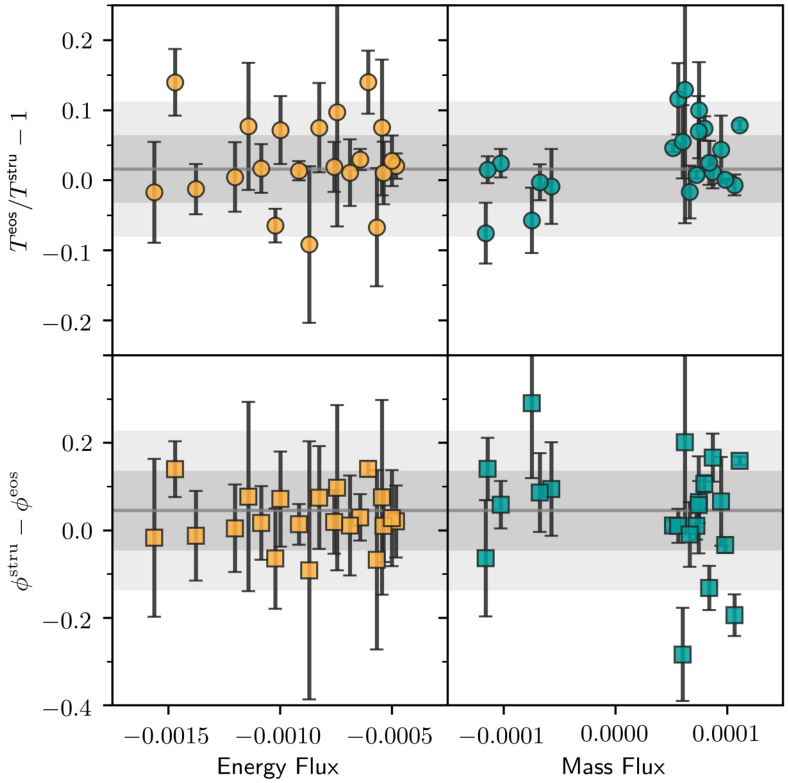

Fig. S4. Relative error between interfacial temperatures obtained from equilibrium equations of state, T^{eos}, and from Eqs. 5, T^{stru}, as a function of energy/mass flux.

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