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Thermodynamically Consistent Nonrandom Mixing on a Bethe Lattice SCOTT MILNER, ExxonMobil — For over 40 years, engineering calculations of nonrandom mixing effects in lattice-based calculations of free energies of mixing in both small-molecule and polymeric solutions (e.g., the non-random two-liquid model, or NRTL) have been based on a strange approximation. By "strange", I mean that the approximation violates some commonsense sum rules in how the lattice is filled; namely, that "something is next to everything", and "everything is next to something". The resulting theories are thermodynamically inconsistent, and explicitly depend on combinations of interaction energies of which the exact mixing free energy is demonstrably independent. To remedy this, I have extended the exact solution of the Ising model on a Bethe lattice to an n-component mixture with arbitrary pairwise interactions. Explicit and practical expressions are obtained for the entropy and average energy per site, which incorporate nonrandom mixing in a thermodynamically consistent way. Although it still has mean-field exponents for the binary mixture critical point, the shape of the coexistence curve lies much closer to the exact results for the Ising model in $d = 3$ dimensions than do previous engineering-level theories. In addition, the model may be generalized easily to deal with mixtures of species occupying different numbers of sites on the lattice. Thus the model can be used to compute phase behavior for mixtures of molecules of different sizes, including polymeric solutions.

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