

The Kinetics of Mixing and the Fluctuation Theorem in Ideal Mixtures of Two-Component Fluids

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Using a simple combinatorial model we show that the fluctuation theorem holds for the nonequilibrium process of mixing in ideal mixtures of two-component fluids. For these systems, however, the validity of the theorem is only local, constrained to neighboring layers perpendicular to the direction of diffusion. After suggesting an approximate limit for the width of a layer, we present demonstrative calculations. We show that the fluctuation theorem is very closely connected to the phenomenological formalism of reaction kinetics, in particular, to unimolecular reactions which might be used for extracting data about transitional thermodynamics.