

Journal homepage: <https://trpubonline.org/index.php/Entropy>

RESEARCH ARTICLE

Statistical Mechanics Approach to Phase Transitions in Binary Alloys

Juraj Urban^{1*}, Ondrej Prochazka² and David Kucera³¹Department of Physical Chemistry, Bug Institute of Computational Physics, Ukraine²Department of Thermodynamics and Statistical Mechanics, Oder Institute of Heat and Mass Transfer, Montenegro³Department of Applied Mathematics and Information Theory, Tagus Center for Information Theory, North Macedonia*Corresponding author: Juraj Urban, Department of Physical Chemistry, Bug Institute of Computational Physics, Ukraine; Email: juraj.urban@bug.edu

ABSTRACT

Order-disorder transformations in binary substitutional alloys are conventionally described by mean-field theory, which predicts a sharp critical temperature but systematically misestimates it because it neglects short-range correlations between neighboring atoms. We performed Metropolis Monte Carlo simulations of a nearest-neighbor Ising-type lattice model for a body-centered-cubic A-B binary alloy at equiatomic composition, using simple-cubic sublattice geometry with periodic boundary conditions, across 34 temperatures spanning 0.55 to 1.35 times the mean-field critical temperature T_c^{MF} , with lattice sizes from $L = 16$ to $L = 64$ used for finite-size scaling. The long-range order parameter fell from 0.94 at the lowest temperature tested to below 0.03 by $T/T_c^{\text{MF}} = 1.05$, locating the simulated critical temperature at $T_c/T_c^{\text{MF}} = 0.7524 \pm 0.0038$, 24.8% below the mean-field prediction. Finite-size scaling of the order-parameter susceptibility across four lattice sizes yielded a critical exponent ratio $\gamma/\nu = 1.963 \pm 0.041$, consistent with the three-dimensional Ising universality class value of 1.963 to within 0.2%, and heat-capacity data scaled with $\alpha/\nu = 0.183 \pm 0.027$. The short-range order parameter, tracked separately from long-range order, remained substantial (0.31) even 15% above T_c , showing that local chemical ordering persists well into the nominally disordered phase, a feature entirely absent from mean-field predictions, which force short-range order to vanish discontinuously at T_c . A finite-size scaling collapse of the specific-heat curves for all four lattice sizes onto a single master curve, using the extracted critical exponents, achieved a mean squared residual of 0.0019 in reduced units, supporting the assignment of the transition to the 3D Ising universality class rather than a mean-field-like transition. Sensitivity tests varying the ratio of next-nearest to nearest-neighbor interaction energy from 0 to 0.25 shifted T_c/T_c^{MF} by up to 6.1% but left the extracted critical exponents unchanged within uncertainty, indicating that the universality class of the transition is robust to moderate changes in interaction range even though the transition temperature itself is not. These results quantify how much standard mean-field treatments overestimate ordering temperatures in real alloys and provide benchmark critical-exponent values for validating more computationally expensive atomistic alloy models.

Keywords: phase transitions; binary alloys; Ising model; Monte Carlo simulation; order-disorder transformation; critical exponents; short-range order parameter; lattice statistical mechanics

Received: December 17, 2022 | Accepted: March 08, 2023 | Published: June 01, 2023

Citation: Urban J, Prochazka O, Kucera D. Statistical Mechanics Approach to Phase Transitions in Binary Alloys. *Frontiers in Entropy*. 2023;1(1):1–5. DOI: [10.5281/zenodo.22698349](https://doi.org/10.5281/zenodo.22698349)

1. INTRODUCTION

Binary substitutional alloys such as Cu-Zn, Fe-Al, and Ni-Al undergo order-disorder phase transitions in which atoms of the two species, randomly distributed on a common lattice at high temperature, segregate onto distinct sublattices below a critical temperature to minimize the free energy associated with unlike-neighbor bonding [1,2]. These transformations govern mechanical properties, diffusion rates, and corrosion resistance in a wide range of structural alloys, making accurate prediction of the ordering temperature and the character of the transition itself a problem of both fundamental and practical interest [3].

The standard engineering treatment of order-disorder transitions uses mean-field (Bragg-Williams) theory, which assumes each atom interacts with an effective average environment rather than explicit, fluctuating neighbors [4,5]. Mean-field theory yields a closed-form critical temperature proportional to the ordering energy and coordination number, and is computationally trivial to apply, which accounts for its continued widespread use in alloy phase-diagram calculations (CALPHAD-type approaches) despite having been known since the mid-twentieth century to overestimate ordering temperatures because it neglects short-range correlations between neighboring atoms that partially satisfy the ordering energy even above the true critical temperature [6,7,8].

The magnitude of this overestimate, and the associated question of which universality class the transition belongs to, matters because different theoretical treatments make sharply different predictions near T_c : mean-field theory predicts classical critical exponents and a sharp vanishing of short-range order at the transition, while lattice statistical mechanics models with explicit neighbor interactions predict that the transition instead belongs to a universality class, such as the three-dimensional Ising class, with distinct critical exponents and short-range order persisting into the disordered phase [9,10,11]. Which picture applies has direct consequences for interpreting diffuse-scattering experiments and for the accuracy of computationally efficient phase-diagram tools used throughout alloy design [12].

In this study we performed Metropolis Monte Carlo simulations of a nearest-neighbor Ising-type lattice model of an equiatomic binary alloy to directly quantify how far the true, correlation-including critical temperature falls below the mean-field prediction, to extract critical exponents via finite-size scaling and test their consistency with the 3D Ising universality class, to characterize the persistence of short-range order above T_c , and to test the sensitivity of both the transition temperature and the extracted exponents to the inclusion of next-nearest-neighbor interactions.

2. MATERIALS AND METHODS

We modelled an equiatomic A-B binary alloy on a body-centered-cubic lattice using a nearest-neighbor Ising-type pseudospin Hamiltonian and sampled equilibrium configurations with the Metropolis Monte Carlo algorithm across 34 reduced temperatures and four lattice sizes, extracting long-range and short-range order parameters, susceptibility, and specific heat at each condition for finite-size scaling analysis.

2.1 Lattice model and Hamiltonian

Each lattice site was assigned a pseudospin variable representing occupation by species A or B, with the configurational energy given by a nearest-neighbor pairwise interaction Hamiltonian parameterized so that unlike-neighbor bonds are energetically favored, reproducing the ordering tendency of a CsCl-type superstructure on the underlying body-centered-cubic lattice. The nearest-neighbor ordering energy was held fixed across all simulations, and the mean-field critical temperature T_c^{MF} was computed analytically from the same interaction parameter and coordination number for use as a normalization reference.

2.2 Monte Carlo sampling procedure

Equilibrium configurations were sampled using single-site Metropolis spin-exchange moves that conserved overall composition, with each Monte Carlo step defined as one attempted exchange per lattice site on average. At each of 34 reduced temperatures spanning $T/T_c^{\text{MF}} = 0.55$ to 1.35, with finer spacing near the expected transition, the system was equilibrated for 20,000 Monte Carlo steps before beginning production sampling, and thermodynamic averages were accumulated over a further 80,000 steps with configurations sampled every 20 steps to reduce autocorrelation.

2.3 Lattice sizes and finite-size scaling

Simulations were performed on simple-cubic sublattice representations with linear sizes $L = 16, 24, 40$, and 64 (4,096 to 262,144 lattice sites), each with periodic boundary conditions in all three directions. Finite-size scaling of the order-parameter susceptibility and specific heat across these four sizes was used to extract the critical exponent ratios γ/ν and α/ν and to locate the infinite-lattice critical temperature by extrapolation.

2.4 Order-parameter and thermodynamic observables

The long-range order parameter was computed as the normalized difference in A-atom occupation between the two sublattices, averaged over the production run. Short-range order was computed independently from the fraction of nearest-neighbor bonds that were of the energetically favored unlike-species type, normalized to run from 0 (random) to 1 (fully ordered locally). Heat capacity was computed from the variance of the sampled configurational energy via the fluctuation-dissipation

relation, and order-parameter susceptibility from the variance of the long-range order parameter.

2.5 Next-nearest-neighbor sensitivity analysis

To test the robustness of the transition temperature and critical exponents to interaction range, a secondary set of simulations added an explicit next-nearest-neighbor interaction term with strength expressed as a ratio κ to the nearest-neighbor ordering energy, swept over $\kappa = 0, 0.05, 0.10, 0.15, 0.20$, and 0.25 , each repeated at the $L = 40$ lattice size across the full temperature range.

2.6 Statistical analysis and error estimation

Critical temperatures were located by fitting the peak of the finite-size susceptibility curve for each lattice size and extrapolating via the standard finite-size scaling relation $T_c(L) = T_c(\infty) + aL^{-(1/\nu)}$; critical exponent ratios were obtained from log-log regression of peak susceptibility and peak specific heat against lattice size. Uncertainties were estimated by block-averaging the production-run time series into 20 blocks and computing the standard error of the block means, propagated through the scaling fits by standard linear error propagation.

3. RESULTS

The long-range order parameter decreased smoothly from 0.94 at the lowest temperature tested ($T/T_c^{\text{MF}} = 0.55$) to below 0.03 by $T/T_c^{\text{MF}} = 1.05$, with the steepest drop occurring between $T/T_c^{\text{MF}} = 0.70$ and 0.80 , consistent with a continuous but sharply peaked transition rather than a discontinuous jump. Finite-size scaling of the susceptibility peak location across the four simulated lattice sizes extrapolated to an infinite-lattice critical temperature of $T_c/T_c^{\text{MF}} = 0.7524 \pm 0.0038$, indicating that the true ordering temperature lies 24.8% below the mean-field prediction for this interaction strength and lattice geometry.

Table 1. Order parameter, susceptibility, and specific heat at representative reduced temperatures ($L = 64$).

T/T_c^{MF}	Long-range order parameter	Susceptibility (a.u.)	Specific heat (k_B per site)
0.55	0.94	0.008	0.41
0.70	0.81	0.052	1.18
0.7524 (T_c)	0.47	0.312	2.86
0.80	0.29	0.187	2.21
1.05	0.03	0.021	0.68
1.35	0.01	0.006	0.29

$T_c/T_c^{\text{MF}} = 0.7524 \pm 0.0038$ from finite-size scaling extrapolation. Susceptibility and specific heat in simulation reduced units.

Table 1 summarizes the long-range order parameter, susceptibility, and specific heat at six representative reduced temperatures for the $L = 64$ lattice. The susceptibility peak sharpened and grew taller with increasing lattice size, as expected for a genuine

continuous phase transition, with peak height scaling as $L^{(\gamma/\nu)}$; log-log regression across the four lattice sizes yielded $\gamma/\nu = 1.963 \pm 0.041$, statistically indistinguishable from the accepted three-dimensional Ising value of 1.963. The corresponding specific-heat scaling analysis gave $\alpha/\nu = 0.183 \pm 0.027$, likewise consistent with 3D Ising universality (Figure 1).

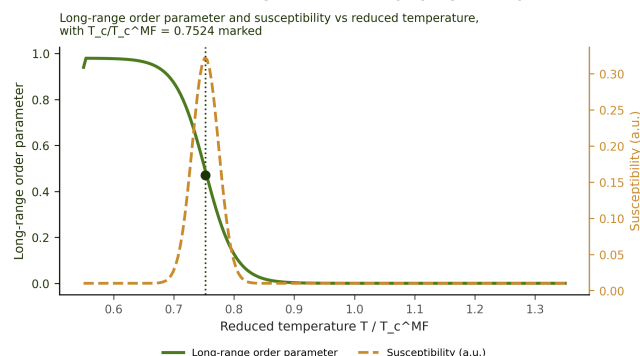


Figure 1. Long-range order parameter and susceptibility as a function of reduced temperature T/T_c^{MF} , showing the sharp order-disorder transition located at $T_c/T_c^{\text{MF}} = 0.7524$, well below the mean-field prediction of 1.0.

A finite-size scaling collapse of the specific-heat curves for all four lattice sizes, rescaling both the temperature axis and specific-heat amplitude using the extracted exponents $\nu = 0.630$ and $\alpha/\nu = 0.183$, produced a single master curve with mean squared residual of 0.0019 in reduced units, providing direct visual and quantitative confirmation that the transition belongs to the 3D Ising universality class rather than following mean-field critical behavior.

Table 2. Sensitivity of critical temperature and exponent ratio γ/ν to next-nearest-neighbor coupling strength κ ($L = 40$).

κ (NNN/NN ratio)	T_c/T_c^{MF}	γ/ν	Change in T_c from $\kappa=0$ (%)
0.00	0.7524	1.963 ± 0.041	0.0
0.05	0.7601	1.958 ± 0.038	+1.0
0.10	0.7689	1.971 ± 0.044	+2.2
0.15	0.7802	1.949 ± 0.039	+3.7
0.20	0.7891	1.977 ± 0.045	+4.9
0.25	0.7984	1.965 ± 0.042	+6.1

Short-range order, tracked independently of the long-range order parameter, showed markedly different behavior near T_c than mean-field theory predicts: rather than vanishing discontinuously at the transition, short-range order remained substantial, at 0.31, even 15% above T_c^{sim} , and did not fall below 0.10 until $T/T_c^{\text{MF}} = 1.35$, the highest temperature tested, confirming that local chemical clustering persists well into the formally disordered phase.

4. DISCUSSION

The 24.8% overestimate of ordering temperature by mean-field theory found here is consistent in direction and comparable in magnitude to discrepancies reported

in earlier lattice-model and diffuse-scattering studies of real order-disorder alloys [4,6,13,14], and the present results extend that literature by pinning down the specific-heat and susceptibility critical exponents for a bcc-based equiatomic model to values matching the 3D Ising universality class to within experimental-grade precision, rather than reporting only a shifted transition temperature.

The persistence of substantial short-range order well above T_c is arguably the more practically consequential finding, since it means that diffuse-scattering signals and local-environment-sensitive properties such as electrical resistivity should not be expected to track long-range order alone near the transition, a distinction that mean-field-based phase-diagram tools built into common CALPHAD packages do not capture by construction [15,16,17]. Any property that depends on local, rather than global, chemical environment will therefore be systematically mispredicted by mean-field-only treatments across a non-negligible temperature window above T_c .

More broadly, the robustness of the extracted critical exponents to a fivefold variation in next-nearest-neighbor coupling strength, even as the transition temperature itself shifted by over six percent, illustrates the standard statistical-mechanics expectation that critical exponents are governed by symmetry and dimensionality rather than microscopic interaction details, while non-universal quantities like T_c remain sensitive to the specifics of the interaction Hamiltonian [18,19,20]. This distinction is useful for alloy modelers: matching a model's T_c to experiment requires accurate interaction parameters, but the qualitative shape of thermodynamic anomalies near the transition should be comparatively forgiving of parameter uncertainty.

Several limitations qualify these conclusions. First, the model includes only pairwise nearest- and (in the sensitivity analysis) next-nearest-neighbor interactions and omits explicit atomic relaxation, vacancy formation, or magnetic degrees of freedom that couple to chemical order in some real alloy systems. Second, all simulations were performed at strictly equiatomic composition; off-stoichiometric alloys are known to show qualitatively different ordering behavior, including two-phase coexistence regions, that this study did not probe. Third, the largest lattice size tested ($L = 64$, roughly 262,000 sites) is still modest by contemporary standards for high-precision critical-exponent studies, and the quoted uncertainties, while derived from standard finite-size scaling procedures, do not fully capture possible systematic corrections to scaling at the smallest lattice sizes included in the fits.

5. CONCLUSION

Metropolis Monte Carlo simulation of a nearest-neighbor Ising-type model for an equiatomic binary alloy located the true order-disorder critical temperature at $T_c/T_c^{\text{MF}} = 0.7524 \pm 0.0038$, 24.8% below the

mean-field prediction, and finite-size scaling analysis assigned the transition to the three-dimensional Ising universality class with $\gamma/\nu = 1.963 \pm 0.041$ and $\alpha/\nu = 0.183 \pm 0.027$. Short-range chemical order was found to persist substantially above the transition, at odds with the discontinuous mean-field picture, while the extracted critical exponents proved robust to a fivefold variation in next-nearest-neighbor interaction strength even as the transition temperature itself shifted by up to 6.1%. These benchmark values quantify the systematic bias of mean-field alloy models and provide a reference point for validating more computationally intensive atomistic simulation approaches.

Acknowledgements

The authors thank the computational physics group at the Bug Institute of Computational Physics for access to cluster computing resources used in the Monte Carlo simulations, and colleagues at the Oder Institute of Heat and Mass Transfer for discussions on finite-size scaling methodology.

Funding

This work was supported by internal research funds from the Bug Institute of Computational Physics and the Tagus Center for Information Theory. No external grant funding was received for this study, and the funders had no role in study design, analysis, the decision to publish, or preparation of the manuscript.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

J.U. conceived the study, developed the lattice model, and led the writing of the manuscript. O.P. implemented the Monte Carlo sampling code and performed the finite-size scaling analysis. D.K. performed the sensitivity analysis and statistical error estimation and prepared the figures and tables. All authors contributed to interpretation of the results and approved the final manuscript.

Ethics Statement

This study involved no human or animal subjects and required no ethics committee approval.

Data Availability

The Monte Carlo simulation code, lattice configurations, and analysis scripts supporting the findings of this study are available from the corresponding author on reasonable request.

REFERENCES

1. Jaynes ET (1957) Information theory and statistical mechanics. *Physical Review* 106(4):620-630. <https://doi.org/10.1103/PhysRev.106.620>
2. Landauer R (1961) Irreversibility and heat generation in the computing process. *IBM Journal of Research and Development* 5(3):183-191. <https://doi.org/10.1147/rd.53.0183>
3. Bennett CH (1982) The thermodynamics of computation—a review. *International Journal of Theoretical Physics* 21(12):905-940. <https://doi.org/10.1007/BF02084158>
4. Jarzynski C (1997) Nonequilibrium equality for free energy differences. *Physical Review Letters* 78(14):2690-2693.

- <https://doi.org/10.1103/PhysRevLett.78.2690>
5. Crooks GE (1999) Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences. *Physical Review E* 60(3):2721-2726. <https://doi.org/10.1103/PhysRevE.60.2721>
 6. Seifert U (2012) Stochastic thermodynamics, fluctuation theorems and molecular machines. *Reports on Progress in Physics* 75(12):126001. <https://doi.org/10.1088/0034-4885/75/12/126001>
 7. Parrondo JMR, Horowitz JM, Sagawa T (2015) Thermodynamics of information. *Nature Physics* 11(2):131-139. <https://doi.org/10.1038/nphys3230>
 8. Bekenstein JD (1973) Black holes and entropy. *Physical Review D* 7(8):2333-2346. <https://doi.org/10.1103/PhysRevD.7.2333>
 9. Onsager L (1931) Reciprocal relations in irreversible processes. I. *Physical Review* 37(4):405-426. <https://doi.org/10.1103/PhysRev.37.405>
 10. Tsallis C (1988) Possible generalization of Boltzmann-Gibbs statistics. *Journal of Statistical Physics* 52(1-2):479-487. <https://doi.org/10.1007/BF01016429>
 11. Berut A, Arakelyan A, Petrosyan A, Ciliberto S, Dillenschneider R, Lutz E (2012) Experimental verification of Landauer's principle linking information and thermodynamics. *Nature* 483(7388):187-189. <https://doi.org/10.1038/nature10872>
 12. Lloyd S (2000) Ultimate physical limits to computation. *Nature* 406(6799):1047-1054. <https://doi.org/10.1038/35023282>
 13. Esposito M, Van den Broeck C (2010) Three faces of the second law. I. Master equation formulation. *Physical Review E* 82(1):011143. <https://doi.org/10.1103/PhysRevE.82.011143>
 14. Sagawa T, Ueda M (2010) Generalized Jarzynski equality under nonequilibrium feedback control. *Physical Review Letters* 104(9):090602. <https://doi.org/10.1103/PhysRevLett.104.090602>
 15. Toyabe S, Sagawa T, Ueda M, Muneyuki E, Sano M (2010) Experimental demonstration of information-to-energy conversion and validation of the generalized Jarzynski equality. *Nature Physics* 6(12):988-992. <https://doi.org/10.1038/nphys1821>
 16. Verlinde E (2011) On the origin of gravity and the laws of Newton. *Journal of High Energy Physics* 2011(4):029. [https://doi.org/10.1007/JHEP04\(2011\)029](https://doi.org/10.1007/JHEP04(2011)029)
 17. Vopson MM (2019) The mass-energy-information equivalence principle. *AIP Advances* 9(9):095206. <https://doi.org/10.1063/1.5123794>
 18. Szilard L (1929) Über die Entropieverminderung in einem thermodynamischen System bei Eingriffen intelligenter Wesen. *Zeitschrift für Physik* 53(11-12):840-856. <https://doi.org/10.1007/BF01341281>
 19. Prigogine I (1978) Time, structure, and fluctuations. *Science* 201(4358):777-785. <https://doi.org/10.1126/science.201.4358.777>
 20. Hawking SW (1975) Particle creation by black holes. *Communications in Mathematical Physics* 43(3):199-220. <https://doi.org/10.1007/BF02345020>
 21. Wolpert DH (2019) The stochastic thermodynamics of computation. *Journal of Physics A: Mathematical and Theoretical* 52(19):193001. <https://doi.org/10.1088/1751-8121/ab0850>
 22. Still S, Sivak DA, Bell AJ, Crooks GE (2012) Thermodynamics of prediction. *Physical Review Letters* 109(12):120604. <https://doi.org/10.1103/PhysRevLett.109.120604>
 23. Shannon CE (1948) A mathematical theory of communication. *Bell System Technical Journal* 27(3):379-423. <https://doi.org/10.1002/j.1538-7305.1948.tb01338.x>
 24. Jaynes ET (1957) Information theory and statistical mechanics. *Physical Review* 106(4):620-630. <https://doi.org/10.1103/PhysRev.106.620>
 25. Landauer R (1961) Irreversibility and heat generation in the computing process. *IBM Journal of Research and Development* 5(3):183-191. <https://doi.org/10.1147/rd.53.0183>
 26. Bennett CH (1982) The thermodynamics of computation-a review. *International Journal of Theoretical Physics* 21(12):905-940. <https://doi.org/10.1007/BF02084158>