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Title

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Comment on “Elucidating the Mechanism of Nucleation near the Gas–Liquid Spinodal”

In a recent Letter [1], Bhimalapuram, Chakrabarty and Bagchi (BCB) study the phase transformation mechanism of the Lennard–Jones fluid and the non-conserved Ising model. They compute the free energy as a function of the size of the largest droplet of the stable phase. In apparent contradiction to classical nucleation theory (CNT), they find that in both systems the free energy develops a minimum at subcritical cluster sizes. In this Comment we argue that this minimum is specific to the chosen order parameter, and that the observed behavior is in fact consistent with CNT.

CNT states that the free energy $F(N)$ of a *single* cluster of size N is a concave function with a maximum at the critical nucleus size N_c . BCB, on the other hand, calculate the probability distribution of N^* , the size of the largest cluster in the system, and compute the free energy $\beta F^*(N^*) = -\ln P(N^*)$, where $\beta = 1/k_B T$. This order parameter does not measure the size of a single cluster. Instead, when sampling small values of N^* , one measures the statistical weight of configurations in which *all* clusters are at most N^* in size. Hence a free energy penalty is incurred when one constrains N^* to values smaller than the largest average cluster in the simulation volume V . It is this penalty that causes the sudden increase of F^* as $N^* \rightarrow 0$ and the minimum at intermediate values of N^* .

We now illustrate how $F(N)$ can be calculated from simulations. Our argument is intuitive but not exact, a formal derivation that yields an equivalent result can be found in Ref. 2. We choose the Ising model for concreteness. We aim to compute the probability that a given cluster has size N , where we imagine the center of the cluster to be fixed at site i . To simplify the calculation we consider clusters that overlap with site i , and correct for the N -fold translational degeneracy in a second step.

Let $s_i \in \{-1, 1\}$ be the state of site i . Let C_i be the size of the cluster that site i belongs to if $s_i = 1$, and $C_i = 0$ otherwise. The number of clusters of size $N \geq 1$ is then $M_N = \sum_i \delta_{C_i, N} / N$, where δ is the Kronecker Delta. The mean number density of such clusters is $\rho_N = \langle M_N \rangle / V = \langle \delta_{C_i, N} \rangle / N$. Given that there is a cluster that overlaps with site i , the probability that it has size N is $P(C_i = N | s_i = 1) = N \rho_N / \langle \delta_{s_i, 1} \rangle$. To correct for the translational degeneracy mentioned previously we define $\beta F(N) = -\ln P(C_i = N | s_i = 1) + \ln N$ as the free energy of a single cluster. Hence, up to a constant independent of N , $\beta F(N) = -\ln \rho_N$.

We have not yet specified the ensemble average, denoted by $\langle \cdot \rangle$. For quenches that are not too deep it is convenient to use a biasing potential that couples to

N^* to keep the system in the metastable state. This method was used in Refs. 2 and 3 to compute $F(N)$ for the Lennard–Jones fluid and the Ising model.

Fig. 1 shows results for one of the quench conditions considered by BCB. We find that $F(N)$ is monotonically

FIG. 1: (Color online) Free energies of cluster growth in the non-conserved Ising model for a quench to $h/J = 0.6$ at $T/T_c = 0.6$, computed in the ensemble where $N^* \leq 120$.

increasing up to N_c and independent of system size, in agreement with CNT. $F^*(N^*)$ exhibits the minimum discovered by BCB, but its location depends strongly on V . For sufficiently large system sizes the activation barrier in $F^*(N^*)$ vanishes entirely. This behavior is a consequence of the extremal character of the order parameter N^* and is unrelated to the stability of an individual droplet.

The asymptotic behavior of $F^*(N^*)$ can be understood by noting that $P(N^*) = P(M_{N^*} \geq 1, M_N = 0 \text{ for } N > N^*)$. For large N^* this probability is dominated by $P(M_{N^*} \geq 1) \approx \langle M_{N^*} \rangle$, which yields $\beta F^*(N^*) \approx \beta F(N^*) - \ln V$. For small N^* the second term dominates. Assuming the M_N to be independent Poissonian random variables, we obtain the estimate $\beta F^*(N^*) = -\sum_{N > N^*} \ln P(M_N = 0) = \sum_{N > N^*} \langle M_N \rangle$, which qualitatively captures the increase of F^* as $N^* \rightarrow 0$.

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