Supplementary Information for "Coupling of isotropic and directional interactions and its effect on phase separation and self-assembly"

Debra J. Audus,[1, a)] Francis W. Starr,[2] and Jack F. Douglas[1, b)]
[1)] *Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*
[2)] *Physics Department, Wesleyan University, Middletown, CT 06459*

I. RENORMALIZED MEAN-FIELD THEORY

The second osmotic virial B_2 is plotted in Fig. 1 for the patchy model and MFT; renormalization dictates that B_2 for the RMFT matches the molecular model exactly.

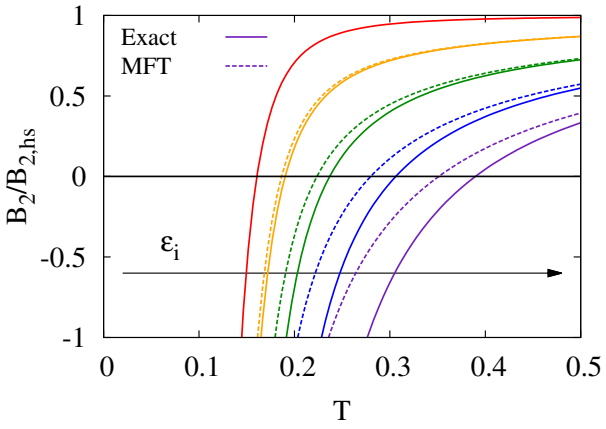

FIG. 1. Second osmotic virial for the patchy model and MFT.

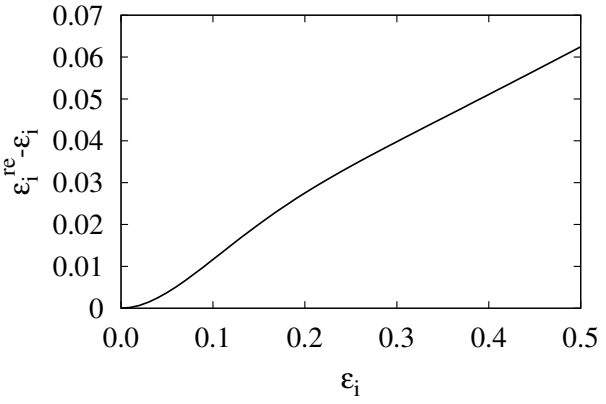

FIG. 2. Difference between the renormalized and unrenormalized isotropic interaction strength as a function of the unrenormalized value.

[a)] debra.audus@nist.gov
[b)] jack.douglas@nist.gov

A plot of the difference between the renormalized values of the isotropic interaction strength and the unrenormalized isotropic strength is shown in Fig. 2. Note that the percentage change becomes large for large ϵ_i.

II. ESTIMATING THE CRITICAL TEMPERATURE

Rather than using a scaling law combined with rectilinear diameters and simulation coexistence curves to estimate the location of the critical point,[1] we use a scaling analysis in the one phase region. Given our limited phase coexistence data, this method produces independent results, which are roughly consistent with the use of the scaling law. Specifically, we analyze the scaling of the correlation length determined from structure factor in the one phase region at densities that were close to the expected critical density. Since the presence of percolating clusters would effect our results, we limit ourselves to densities above the percolation transition; this means using $\rho = 0.2$ for $\epsilon_i = 0$, $\rho = 0.3$ for $\epsilon_i = 0.1$ and $\rho = 0.4$ otherwise.

The structure factor $S(k)$ was computed for a wide range of temperatures with the correlation length ξ determined using

$$S(k) = \frac{S(0)}{1 + k^2\xi^2}. \tag{1}$$

In particular, we plot $1/S(k)$ as a function of k^2 requiring at least four points for the fit and adding additional points until the root mean squared error was minimized. The resulting correlation lengths are plotted in Fig. 3b. These are then fitted using[2]

$$\xi = \xi_0 \left(\frac{T - T_c}{T_c} \right)^{-0.638} \tag{2}$$

where ξ_0 and T_c are fitting parameters dependent on ϵ_i. Physically, T_c is the critical temperature and the exponent of 0.638 is the Ising model correlation length exponent.[3] Unlike Ref. 2, we used T_c rather than T in the denominator, since our data is close to the critical point. These fits are plotted along with the data in Fig. 3a. The goodness of the fit can be seen when Eq. 2 is manipulated into power law form and plotted along with the data as can be seen in Fig. 3b. The critical density was determined using the critical temperature, the phase coexistence data and rectilinear diameters.

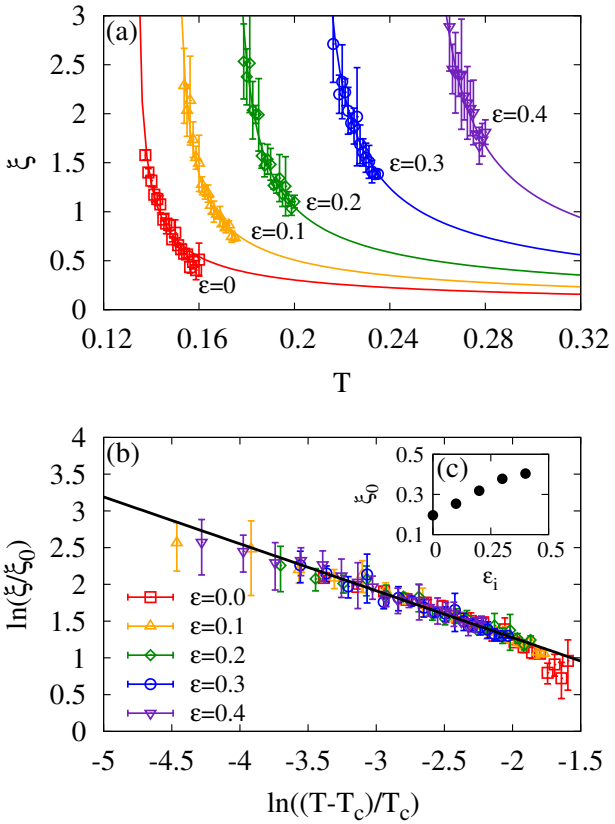

FIG. 3. (a) The correlation length ξ as a function of temperature for various relative interaction strengths. (b) The fit of the correlation length ξ for all data after manipulation into power law form. (c) The fitting parameter ξ_0 as a function of ϵ_i. Uncertainties correspond to 95 % confidence intervals.

III. PHASE COEXISTENCE AND TRANSITION LINES: AN ISOTROPIC REFERENCE

The general trends such as the size of the clustering region, are invariant to the reference used for the temperature. For completeness Fig. 4, which contains the RMFT phase separation curves and the $T_{\Phi=1/2}$ transition lines, uses an isotropic reference for the temperature. As can be seen, the region in which clustering occurs is still much larger for $\epsilon_i = 0.1$ (orange) than $\epsilon_i = 0.4$ (purple).

IV. TESTING THE FLORY-STOCKMAYER PREDICTION FOR $\langle M \rangle$

The relationship between $\langle M \rangle$ and X using Flory-Stockmayer theory is

$$\langle M \rangle = \frac{2}{5X - 3} \tag{3}$$

with X determined from $\Phi = 1 - X^5$. In the manuscript, we combine these relations and show that they held for the expected range. However, a linear relationship can be

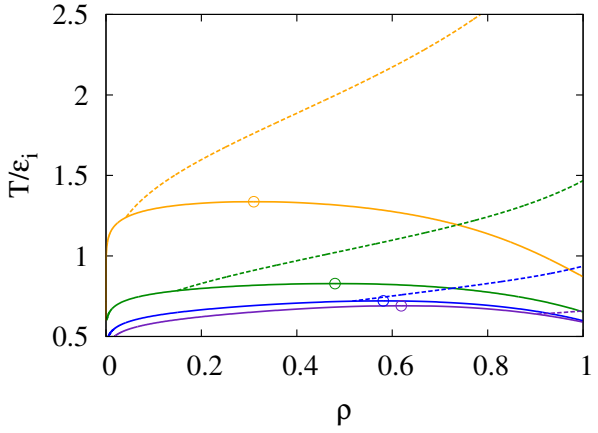

FIG. 4. Phase separation curves (solid) and the clustering transition lines (dashed) for $T_{\Phi=1/2}$ for mean-field theory. The curves correspond to ϵ_i = 0.1, 0.2, 0.3, and 0.4 from top to bottom.

deduced by plotting $1/\langle M \rangle$ as a function of X from the simulations. This linear relationship is plotted in Fig. 5.

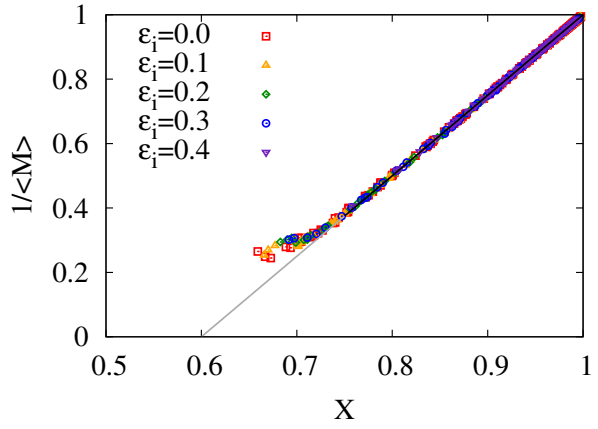

FIG. 5. The linear relationship between $1/\langle M \rangle$ and X with solid line given by $5/2X - 3/2$. The line in gray denotes an extension of the line beyond its range of validity.

V. QUANTIFICATION OF FINITE SIZE EFFECTS

In order to quantify the magnitude of the finite size effects on our calculations involving self-assembly, we determine both the order parameter Φ and the probability of percolation p_{perc} for a box whose length is halved in every direction, *i.e.*, a box length of 5 instead of 10. These results are compared with those from the paper in Fig. 6. As can be seen in Fig. 6a, the simulation data for the smaller box perfectly overlaps with the fits from the larger box. Thus, the effect of finite size effects on the

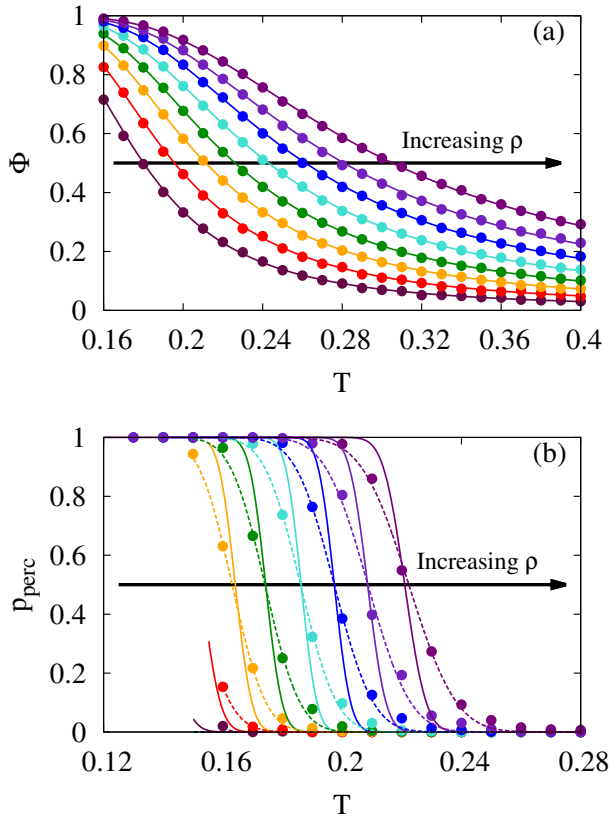

FIG. 6. (a) The order parameter for a box length of 5 superimposed with fits to data generated using a box length of 10. (b) The percolation probability with a box size of 5 (points) with fits (dashed lines) along with fits from data generated with a box length of 10.

order parameter is negligible. The probability of percolation is more sensitive, as can be seen in Fig. 6b. The fits from the smaller box clearly do not overlap with those from the larger box; however, the temperature at which the probability of percolation is one half is only minimally effected. From percolation theory,[4] the probability is known to be a Heaviside function in the thermodynamic limit, with rounding observed as finite size effects become more predominant. Together, this suggests that the location of the cluster transition line generated using the probability of percolation is only slightly affected by finite size effects. Phase coexistence curves are likely more sensitive to finite size effects. However, predictions of the difference between mean-field theory and simulation data suggest the critical temperature should not be significantly effected. Therefore, the same box size is used for both self-assembly and phase separation.

[1]D. Frenkel and B. Smit, *Understanding Molecular Simulation From Algorithms to Applications* (Academic Press, 2002).
[2]K. Mortensen, "Structural studies of polymer systems using small-angle neutron scattering," in *Advanced functional molecules and polymers. Vol. 2. processing and spectroscopy*, edited by H. Nalwa (Overseas Publishers Association, 2001) pp. 223–269.
[3]J. Sengers, "Universality of critical phenomena in classical fluids," in *Phase Transitions Cargèse 1980*, edited by M. Lévy, J.-C. Le Guillou, and J. Zinn-Justin (Springer US, 1982) pp. 95–135.
[4]D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd ed. (Taylor & Francis, 1992).