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Uncertainty as a stabilizer of the head-tail ordered phase in carbon-monoxide monolayers on graphite

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$(CO)_{1-x}(Ar)_x$ mixtures physisorbed on graphite experimentally display a novel phenomenon of increasing phase-transition temperature (stabilizing the system) with increasing Ar impurity concentration or uncertainty [H. Wiechert and K.-D. Kortmann, Surf. Sci. **441**, 65 (1999)]. We develop a two-dimensional Ising-type model that accurately captures the phase transition and its temperature dependence. The anomaly in transition temperature is due to formation of pinwheel regions of CO around Ar atoms. The dilemma of whether the ground state is head-to-head or head-to-tail ordered is reconciled in favor of the latter. The phase-transition curve in the presence of uncertainty in Ar impurity is computed using Monte Carlo (MC) and probabilistic collocation method (PCM). PCM computes the first two moments ≈2000 times faster than MC.

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I. INTRODUCTION

Self-organization of physical systems is a series of steps the system elements follow in order to find a stable state by actively interacting with each other. Some applications of self-organization include structural phase transitions and spontaneous magnetization in physics,[1,2] molecular self-assembly and liquid crystals in chemistry,[3,4] folding of proteins and flocking in biology,[5] cellular automata and robot swarms in mathematics and engineering, etc. Because of the numerous applications of self-organization and its simple underlying principle, targeted self-organization is becoming an increasingly important field of research.[2,6] The target system can be a material with desired physical properties, a molecular cluster for efficient drug delivery, or a formation of autonomous vehicles for search and surveillance missions.

In this paper we study a herringbone to head-tail-ordered herringbone phase transition of a two-dimensional diatomic crystal in the presence of impurities. Our understanding of the effect of impurities on this novel phase transition will provide a recipe for robust targeted self-organization of anisotropic physical systems.[7,8] Namely, we will show that stability of a system designed through the particle-particle and particle-substrate interaction can be increased by introducing a short-range particle-impurity interaction.

Uncertainty is an important factor in the design of physical models. Usually significant effort is needed to minimize uncertainty in the output of a model subject to input uncertainty. Phase transitions in statistical thermodynamics of condensed matter are some of the most vivid manifestations of the effect of uncertainty on the state of a system.[9,10] In particular, defects in the form of vacancies, interstitial, and quenched impurities give rise to random fields which are known to catalyze phase transitions.[11,12] Disorder and nonequilibrium effects are known to modify structural phase transitions in pure periodic systems.[13] Even small amounts of impurities in monolayers of adsorbed gases can induce significant changes in the phase behavior and phase transitions. Impurities tend to distort the sublattices of the adsorbed phase and hence lead to a phase transition into an "intermediate" phase significantly prior to that observed for a pure monolayer.[14] Low-temperature phase transitions in some systems can be regarded as realizations of two-dimensional (2D) Ising-type systems.[15]

Recently, Carbon Monoxide (CO) monolayers with Argon (Ar) impurities physisorbed on graphite have been studied experimentally and found to exhibit unique physical properties.[12,16] When adding Ar impurities to head-tail ordered CO monolayers, the order in the system is slowly destroyed and the phase transition is found to be completely suppressed when the impurity concentration reaches ≈7%.[12] Unlike any other known physical system, the disorder induced in a CO monolayer by Ar impurities results in a higher phase-transition temperature, thereby stabilizing the head-tail ordered phase.[12] The phase transition of interest (called head-tail ordering transition) occurs at ≈5.18 K.[17,18] In this paper we develop a model of the CO-Ar system and explain the origin of the observed phenomena.

CO-Ar mixtures physisorbed on graphite can be considered as experimental realizations of 2D Ising-type models. In the following we design an Ising-type model that captures the head-tail ordering transition along with the anomalous shift in the transition temperature with increasing Ar concentration. The stabilization of the phase with uncertainty is successfully captured by the Ising-type model when the experimentally observed pinwheel structure[12] of CO molecules around the Ar sites is correctly modeled (see Fig. 1). We study the phase-transition curve as a function of Ar concentration in the presence of uncertainty. The unpredictability in the exact concentration of Ar atoms is another source of uncertainty. The latter uncertainty transforms the phase-transition curve into a phase-transition region, which can be captured by computing the moments of phase-transition region at every nominal concentration of Ar. The moments are obtained using Monte Carlo (MC) and Polynomial Chaos (PCH) techniques. The two methods are compared and it is

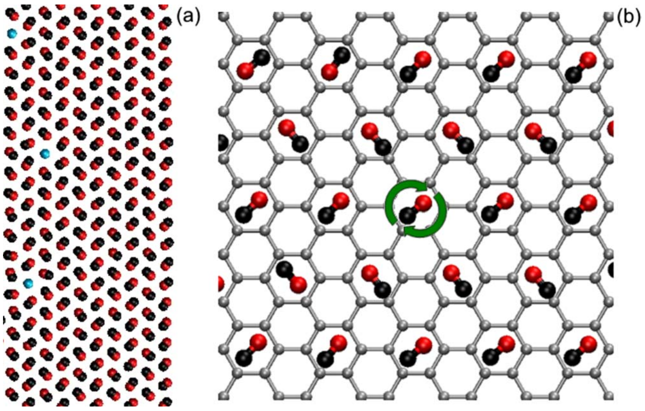

FIG. 1. (Color online) CO-Ar on graphite. (a) Pinwheel structure formed around the Ar impurities. (b) Flip of CO molecule in Metropolis-Hastings.

found that PCH captures the moments of the uncertain phase-transition curve ≈2000 times faster than standard MC.

II. DETAILS OF THE MODEL

Previous lattice dynamics calculations[19,20] have used realistic interaction potential based on an *ab initio* pair potential. The total CO-CO interaction potential is written as a sum of exchange, dispersion, and electrostatic pair interactions between the carbon and oxygen atoms or between sites on the CO bond axes.

$$V_{AB} = \sum_{i \in A} \sum_{j \in B} v_{iA,jB}(R_{iA,jB}) \tag{1}$$

where $v_{iA,jB}$ is the interaction between site i on molecule A and site j on molecule B, and $R_{iA,jB}=|\mathbf{R}+\mathbf{r}_j-\mathbf{r}_i|$ is the distance between interaction sites.

$$v_{iA,jB}(R_{iA,jB}) = v^{\text{exch}}_{iA,jB}(R^{\text{exch}}_{iA,jB}) + v^{\text{disp}}_{iA,jB}(R^{\text{disp}}_{iA,jB}) + v^{\text{elect}}_{iA,jB}(R^{\text{elect}}_{iA,jB}) \tag{2}$$

The exchange and dispersion contributions are described using a spherical expansion of the *ab initio* potential.

$$v^{\text{exch}}_{i,j}(R_{iA,jB}) = A_{ij} \exp(-B_{ij} R_{iA,jB}) \tag{3}$$

$$v^{\text{disp}}_{iA,jB}(R_{iA,jB}) = -C_{ij} R^{-6}_{iA,jB} \left[1 - \sum_{k=0}^{6} \frac{(B_{ij} R_{iA,jB})^k}{k!} \right] \times \exp(-B_{ij} R_{iA,jB}) \tag{4}$$

The positions of sites (r_O and r_C) and the parameters A_{ij}, B_{ij}, and C_{ij} were found in Ref. 20. The electrostatic contribution to the site-site potential is represented by three point charges on the CO bond axis; one on the oxygen atom, one on the carbon atom, and one in the center of mass. These point charges were chosen such that the dipole and quadrupole moments of the CO molecule are reproduced.[20]

TABLE I. Interaction parameters of CO-Ar pair potential.

i,j	$A_{i,j}$ (K)	$B_{i,j}$ (Å^{-1})	$C_{i,j}$ (KÅ^6)
C,Ar	16606500	3.20748	548639
O,Ar	48119500	3.64995	295445

$$v^{\text{elect}}_{iA,jB}(R_{iA,jB}) = \frac{q_i q_j}{R_{iA,jB}} \tag{5}$$

The CO-Ar interaction potential is similar but with no electrostatic contribution. We use an empirical approximation of the parameters A, B, and C.[21] The parameters are given in Table I.

The interactions of the molecules with the graphite surface is modeled using Steele's Fourier decomposition of the periodic Lennard-Jones interaction between a semi-infinite graphite substrate and a carbon or an oxygen atom similar to the one in Ref. 22. The interaction parameters are taken from Ref. 23.

We fix the molecules with their center of rotation (center of force) on the ideal sites of a completely covered herringbone monolayer $(\sqrt{3}\times\sqrt{3})R\ 30°$ commensurate with graphite lattice ($a=2.456$ Å). The center of mass of each molecule is shifted by a distance d_c from the center of the hexagonal lattice cell in which it is located [see Fig. 2(a)]. The center of mass offset d_c is a very important parameter of the model. For the critical value $d_{\text{crit}}=0.203$ Å, the ground-state energy for the head-to-head and head-to-tail configurations are equal [see Fig. 2(b)]. In the absence of impurities, we observe head-to-tail ordering for $d_c < d_{\text{crit}}$ while $d_c > d_{\text{crit}}$ results in head-to-head ordering. Previous theoretical and experimental studies of CO on graphite molecule arrangement at low temperature have not been able to conclude decisively on the ordering.[24,25]

The lowest energy in Fig. 2(b) corresponds to the head-to-head ordered configuration with $d_c \approx 0.4$ Å. However, $d_c \approx 0.4$ Å gives the ordering transition temperature that is more than an order of magnitude higher than the one observed experimentally. This is due to the fact that our 2D Ising-type model does not take into account out-of-plane excitations that lower the transition temperature. The ordering transition temperatures for $d_c \approx d_{\text{crit}}$ are close to the experimentally observed value. Thus, our model is applicable for $d_c \approx d_{\text{crit}}$, where the energy of the system is almost the same for both head-to-head and head-to-tail configurations. In order to probe the nature of the ground state of the system, we will study the effect of Ar impurities on the system.

Only pair interactions with the six nearest neighbors are included. The initial angle configuration is set to have a herringbone structure with head-to-tail ordering if $d_c < d_{\text{crit}}$. To form the head-to-tail herringbone structure we initialize the angles to be $\frac{\pi}{4}$ on odd rows and $\frac{3\pi}{4}$ on even rows [see Fig. 2(a)]. If $d_c > d_{\text{crit}}$, the initial configuration is set to have a head-to-head structure with angles $\frac{\pi}{4}$ on odd rows and $\frac{3\pi}{4}+\pi$ on even rows. The six CO nearest neighbors of an argon impurity form a pinwheel structure. If an argon impurity is

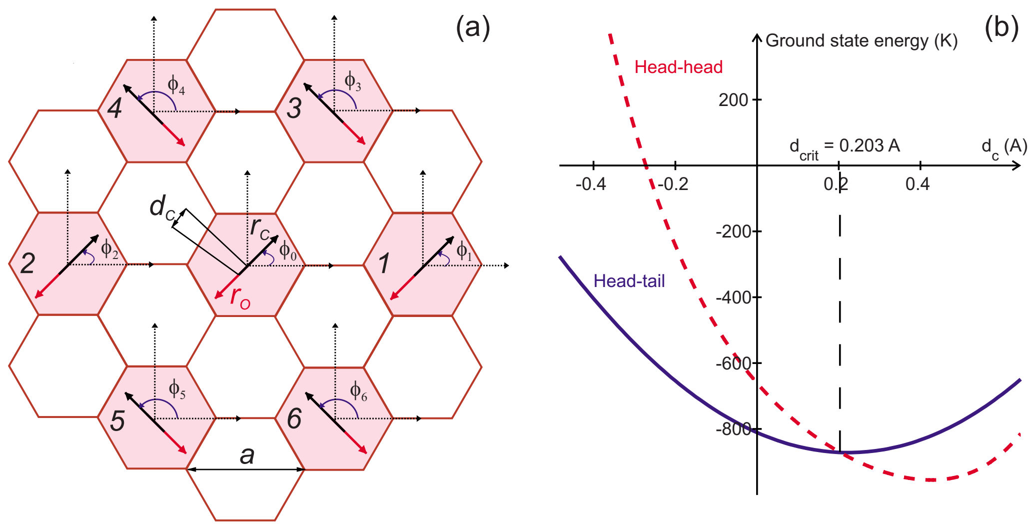

FIG. 2. (Color online) (a) CO on graphite. Initial configuration for head-to-tail case with angles $\phi_0=\phi_1=\phi_2=\frac{\pi}{4}$ and $\phi_3=\phi_4=\phi_5=\phi_6=\frac{3\pi}{4}$. The center of mass of each CO molecule is shifted from the center of the cell by a distance d_c. The positions from the center of mass of the C sites and O sites are denoted r_C and r_O, respectively. (b) Dependence of the ground-state energy on distance d_c for a head-to-head configuration (dashed curve) and a head-to-tail configuration (solid curve).

placed on site 0 [see Fig. 2(a)], the pinwheel structure is achieved by rotating the angles ϕ_3 and ϕ_5 by $-\frac{\pi}{6}$ and the angles ϕ_4 and ϕ_6 by $+\frac{\pi}{6}$.

III. RESULTS OF THE SIMULATION

To simulate the system at different temperatures we employed the Metropolis-Hastings algorithm. A CO site is picked at random and its spin is flipped (i.e., the molecule is rotated by π, see Fig. 1). If the total energy of the modified system decreases, the spin flip is accepted, otherwise the flip is accepted with probability associated with the Boltzmann distribution.[26] At each temperature, the fluctuation in energy U gives us the heat capacity (C_v).[26] The impurities are chosen randomly on the two-dimensional lattice with the restriction that no CO molecules can have more than one impurity in their six nearest neighbors. The locations of impurities on the lattice are found to make no difference for the transition temperatures. This is confirmed by a molecular-dynamics (MD) simulation (similar to the one in Ref. 27) with the interaction potentials described in the previous section. Using the MD simulation, we have also verified that CO on graphite self-assembles into a herringbone lattice and that a pinwheel structure is formed around Ar impurities (see Fig. 1).

We first performed Ising-type simulations on a 24×24 lattice for four values of d_c close to d_{crit} (see Fig. 3). The values $d_c=0.202$ Å and $d_c=0.205$ Å correspond to the experimentally observed position of the heat-capacity peak. When the center of mass offset d_c lies outside of the interval [0.195;0.212], the system exhibits "classical" behavior with high phase-transition temperatures which decrease with increased impurity concentration as the system becomes less stable. For the head-to-head ordered monolayer with $d_c=0.205$ Å, the phase-transition temperature does not depend on the impurity concentration. Finally, for the head-to-tail ordered monolayer with $d_c=0.202$ Å, the phase-transition temperature shifts to higher temperatures with the inclusion of impurities. In addition to the fact that our model is able to explain the anomalous increase in transition temperature with impurity concentration, it also reconciles the dilemma of whether the ground state is head-to-head or head-to-tail ordered in favor of the latter.[12]

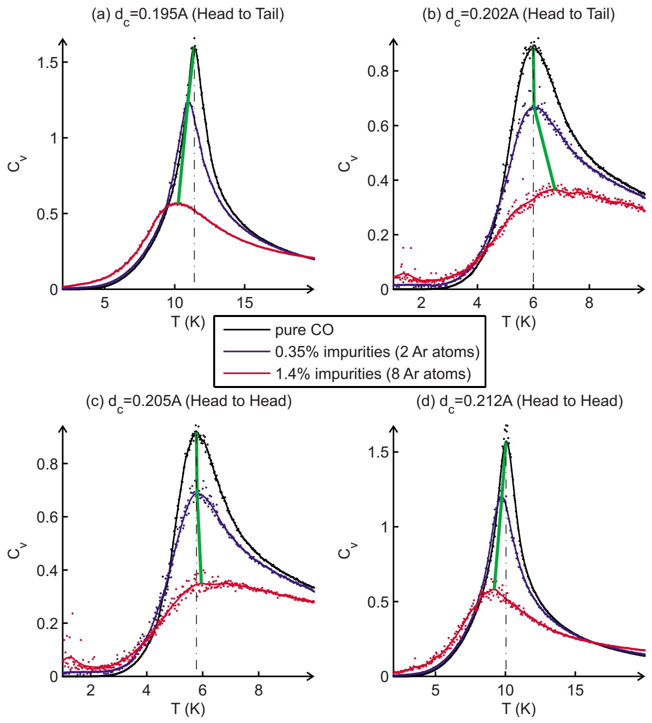

FIG. 3. (Color online) Heat capacity C_v for different concentrations of Ar impurities on a 24×24 lattice. (a) Head-to-tail ordering with $d_c=0.195$ Å. (b) Head-to-tail ordering with $d_c=0.202$ Å. (c) Head-to-head ordering with $d_c=0.205$ Å. (d) Head-to-head ordering with $d_c=0.212$ Å.

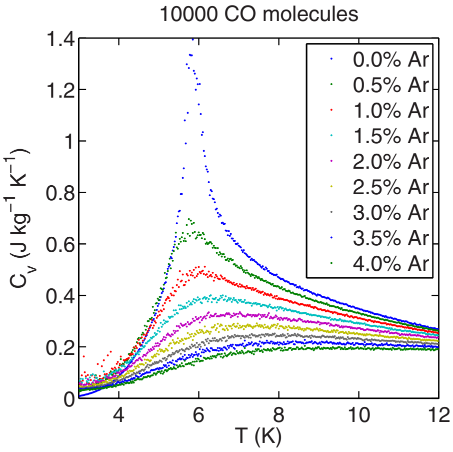

FIG. 4. (Color online) Heat capacity C_v for different concentrations of Ar impurities (d_c=0.202 Å).

The results presented thereafter are obtained for a 10^4-site Ising-type system and 2×10^4 flips are performed per CO site. For each concentration of Ar, a heat-capacity curve is computed with d_c=0.202 Å (see Fig. 4). It can be seen in Fig. 4 that the effect of Ar impurities on the C_v curves match experimental observations.[12] Both the suppression of the heat-capacity curve along with its anomalous shift to higher transition temperatures[12] are captured. To the best of our knowledge, the Ising-type model implemented in this paper is the only model that captures the anomalous shift of the phase-transition temperature caused by formation of pinwheel structures around Ar impurity sites.

From Fig. 4 the transition temperatures can be plotted against the concentration of Ar (we pick the transition temperature at the peak for every curve in Fig. 4). The transition temperatures with increasing Ar density are plotted in Fig. 5, demonstrating the anomalous shift found experimentally.[12] The noisy curve obtained from the Ising-type model (see Fig. 5) is approximated by a quadratic fit to ease the computation of the phase transition in the presence of uncertainty. Moreover, our theoretical predictions are found to lie within experimental error of Ref. 12 as shown in Fig. 5.

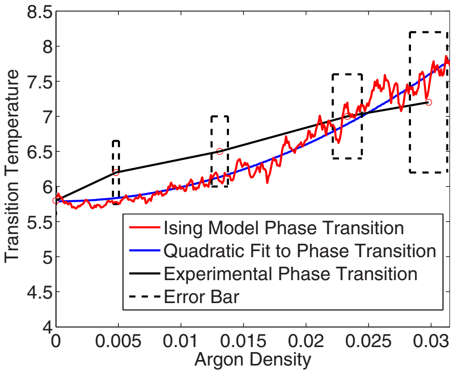

FIG. 5. (Color online) Phase-transition temperature as a function of Ar impurity density extracted from the Ising-type model (red curves) and its quadratic fit (blue curve). Experimental data (black curve) and error bars are taken from Ref. 12.

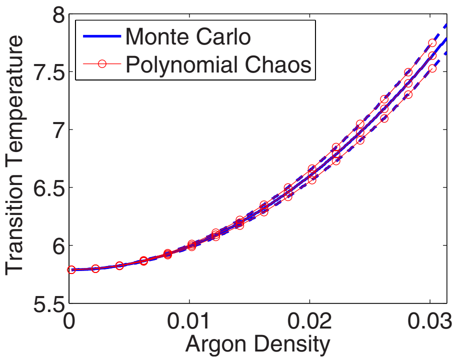

FIG. 6. (Color online) Comparison of the mean and one standard-deviation phase-transition curves computed using Monte Carlo and Polynomial Chaos.

IV. UNCERTAINTY IN THE ARGON CONCENTRATION

In the experiments, there is always uncertainty in the concentration of impurities. This, in turn, makes the phase-transition curve uncertain. Hence, different experimental realizations of CO-Ar mixtures on graphite will give rise to slightly different phase-transition curves. In the following we quantify the variability in the phase-transition curve in the presence of uncertainty in the concentration of Ar impurities. To compute the variability we use two different approaches. The first approach, the MC technique, is a fairly standard statistical analysis method. This method is, however, very inefficient. A significant speedup in the computation of the uncertainty in the phase-transition curves can be obtained by employing PCH techniques.[28,29]

For each value K_0 of Ar concentration in Fig. 5 we assume that the concentration of Ar is distributed binomially[30] with mean at K_0 and standard deviation of 3% (ϵ=0.03). The parameters of the binomial distribution N and p can be found from the following system:

$$Np = K_0$$

$$Np(1-p) = (\epsilon K_0)^2. \tag{6}$$

For each value of mean Ar concentration, we sample the corresponding binomial distribution in Ar concentration using MC techniques and compute the mean and standard deviation of the transition temperature. The results of the MC procedure are shown in Fig. 6 for 10^4 samples for each binomial distribution. As expected, the mean transition curve is the same as the quadratic fit in Fig. 5. The region between the outer curves in Fig. 6 is one standard deviation around the mean transition temperature. As the concentration of Ar atoms increases, the uncertainty in the phase-transition temperature also increases. This is because the standard deviation is defined relative to the Ar impurity (see Eq. (6)). Although MC methods succeed in computing the phase-transition curve in the presence of uncertainty, a very large number of samples (10^4) are necessary for a reliable estimate.

PCH techniques are used to quantify output uncertainty by expanding the output random variable of interest in an optimally chosen orthogonal basis.[29,31] Let us consider the following system:

$$\dot{x} = f(x,\lambda), \tag{7}$$

where x is the system output and λ is a vector of uncertain system parameters with associated probability distribution $w(\lambda)$. In PCH the output random variable is expressed as

$$x(t;\lambda) = a_0(t)\psi_0(\lambda) + a_1(t)\psi_1(\lambda) + \ldots \tag{8}$$

Here $\{\psi_i(\lambda): i \in 1, \ldots, \infty\}$ forms an orthogonal basis with respect to $w(\lambda)$. The coefficients $a_i(t)$ can be determined using Galerkin projections[29] when the equations of the system are explicitly known. In the case of the Ising-type model, the phase-transition temperature is a random variable and f is the Metropolis-Hastings code. Since f is not known explicitly, one can apply probabilistic collocation methods (PCM),[32] where the output random variable is expanded using Eq. (8). However, the system parameters are sampled using zeros of a polynomial orthogonal to the basis used in expansion Eq. (8) (typically if the order of expansion is n, ψ_{n+1} is chosen). A Lagrange interpolating polynomial is passed through the output and the resulting moments of the distribution are computed. The orthogonal polynomials corresponding to the binomial distribution are the Krawtchouk polynomials K_n.[33] The zeros of the polynomials K_n take noninteger values. Since the number of Ar atoms has to be discrete, we use the quadratic fit in Fig. 5 to compute the phase-transition temperature at a fractional number of Ar atoms.

The results of using PCM can be seen in Fig. 6. PCM captures the mean transition-temperature curve along with the one standard-deviation curves exceedingly well with just four input samples. The error in the mean and variance at the Ar concentration of 3% can be seen in Figs. 7(a) and 7(b). The results from PCM are obtained with the same magnitude of error as MC, 2000 times faster.

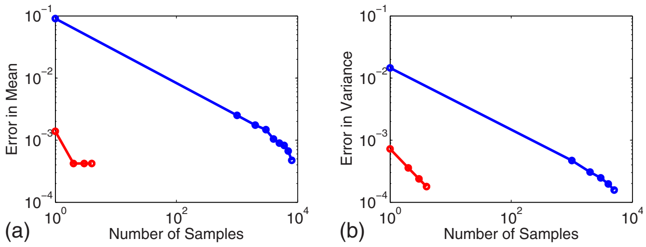

FIG. 7. (Color online) Comparison of the number of samples needed by Monte Carlo (upper curves) and Polynomial Chaos (lower curves) to obtain mean (left) and variance (right) of the phase-transition temperature in the CO-Ar system with 3% of Ar impurities.

V. CONCLUSIONS

In this paper we studied the effect of argon impurities on the head-tail ordering phase transition in CO monolayers physisorbed on graphite. We developed an Ising-type model that captures the head-tail ordering transition in CO-Ar mixtures in agreement with experimental data. The unique physical properties of the CO-Ar system have been explained and attributed to the formation of pinwheel regions of CO around the Ar impurities. To quantify the uncertainty in the number of Ar atoms, we have applied PCM and found it to be far superior to MC in this problem. This approach can be used to quickly bind the variation in phase transition curves when the impurity concentration is not known accurately.

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