Graph-based lattice models

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0 Preliminaries

Lattice models abound in seemingly disparate areas of statistical mechanics. Many are isomorphic to one another, and these are known by a number of names (depending on field): the Ising model of magnetism, the lattice gas model, the regular solution model, the binary alloy (order-disorder) model, etc. In each of these cases, every lattice cell is defined to contain up to one molecule.[1] Though we may account for freedom of mobility of the molecules within each cell, we will only consider constant energies of interaction between the various possible types of cells (thus, should a cell be filled, the relative location of the contained molecule is immaterial).

1 Energy expression

We are interested in using a lattice gas model to understand the mixing of two dense gases (or, perhaps, two liquids). We consider a lattice composed of N cells, in which each cell contains a molecule of either type A or B. Thus

$$N = N_{\mathrm{A}} + N_{\mathrm{B}}, \tag{1}$$

where N_i is the number of cells containing a molecule of type i. Each cell has a coordination number z. We can count and partition the neighboring interactions as follows,

$$zN_{\mathrm{A}} = 2N_{\mathrm{AA}} + N_{\mathrm{AB}}, \tag{2}$$
$$zN_{\mathrm{B}} = 2N_{\mathrm{BB}} + N_{\mathrm{AB}}, \tag{3}$$

where N_{ij} is the number of interactions between any cell containing a molecule of type i and a neighboring cell containing a molecule of type j. Note that, because we are counting all z interactions for every cell (i.e., zN total interactions), each interaction will be double-counted. Thus, we find

$$zN = 2N_{\mathrm{AA}} + 2N_{\mathrm{BB}} + 2N_{\mathrm{AB}}. \tag{4}$$

This is verified by multiplying (1) by z and then substituting (2) and (3) accordingly,

$$zN = z(N_{\mathrm{A}} + N_{\mathrm{B}}), \tag{5}$$
$$= zN_{\mathrm{A}} + zN_{\mathrm{B}}, \tag{6}$$
$$= 2N_{\mathrm{AA}} + N_{\mathrm{AB}} + 2N_{\mathrm{BB}} + N_{\mathrm{AB}}, \tag{7}$$
$$= 2N_{\mathrm{AA}} + 2N_{\mathrm{BB}} + 2N_{\mathrm{AB}}. \tag{8}$$

[1] A *cell model* is one in which each cell is constrained to contain one and only one molecule. A *hole model* relaxes this constraint by allowing cells to be either *empty* (i.e., they contain no molecules), or *filled* (i.e., they contain one molecule).

Since the energy E of such a system depends only on the interactions between neighboring cells, we find

$$E = \varepsilon_{\mathrm{AA}} N_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}} N_{\mathrm{BB}} + \varepsilon_{\mathrm{AB}} N_{\mathrm{AB}}, \tag{9}$$

where ε_{ij} is the interaction energy between a cell containing a molecule of type i and a neighboring cell containing a molecule of type j. We may usefully write (9) in terms of one variable N_{AB} (and the constants z, $\varepsilon_{\mathrm{AA}}$, $\varepsilon_{\mathrm{BB}}$, $\varepsilon_{\mathrm{AB}}$, N_{A}, and N_{B}). We begin by rearranging (2) and (3) to obtain

$$N_{\mathrm{AA}} = \frac{1}{2} z N_{\mathrm{A}} - \frac{1}{2} N_{\mathrm{AB}}, \tag{10}$$

$$N_{\mathrm{BB}} = \frac{1}{2} z N_{\mathrm{B}} - \frac{1}{2} N_{\mathrm{AB}}. \tag{11}$$

Substituting these into (9), we find

$$E = \varepsilon_{\mathrm{AA}} \left(\frac{1}{2} z N_{\mathrm{A}} - \frac{1}{2} N_{\mathrm{AB}} \right) + \varepsilon_{\mathrm{BB}} \left(\frac{1}{2} z N_{\mathrm{B}} - \frac{1}{2} N_{\mathrm{AB}} \right) + \varepsilon_{\mathrm{AB}} N_{\mathrm{AB}}, \tag{12}$$

$$= \left(\varepsilon_{\mathrm{AB}} - \frac{1}{2} \varepsilon_{\mathrm{AA}} - \frac{1}{2} \varepsilon_{\mathrm{BB}} \right) N_{\mathrm{AB}} + \frac{1}{2} z \varepsilon_{\mathrm{AA}} N_{\mathrm{A}} + \frac{1}{2} z \varepsilon_{\mathrm{BB}} N_{\mathrm{B}}, \tag{13}$$

$$= w N_{\mathrm{AB}} + \frac{1}{2} z \varepsilon_{\mathrm{AA}} N_{\mathrm{A}} + \frac{1}{2} z \varepsilon_{\mathrm{BB}} N_{\mathrm{B}}, \tag{14}$$

where the *interchange energy* w is

$$w \equiv \varepsilon_{\mathrm{AB}} - \frac{1}{2} \varepsilon_{\mathrm{AA}} - \frac{1}{2} \varepsilon_{\mathrm{BB}}. \tag{15}$$

2 Metropolis algorithm

The lattice gas model easily lends itself to manipulations and analysis via a Metropolis algorithm. The general procedure is considered below.

1 Randomly pick a pair of A and B cells (independent of distance) and determine the system energy E_{i}.

2 Swap the molecular character (A becomes B, and vice versa), and calculate the new system energy E_{f}.

3 Determine whether or not to keep the swap based on the probability law

$$P = \begin{cases} e^{-\beta(E_{\mathrm{f}} - E_{\mathrm{i}})}, & \text{if } E_{\mathrm{f}} - E_{\mathrm{i}} > 0, \\ 1, & \text{otherwise}, \end{cases} \tag{16}$$

where $\beta = (k_{\mathrm{B}} T)^{-1}$ (where k_{B} is the Boltzmann constant and T is the temperature).

4 Repeat Steps 1 – 3 until equilibrium is obtained.

Step 3 is more straightforward than it appears. Since E is only dependent on N_{AB}, we may determine P based on how many $\mathrm{A} - \mathrm{B}$ intercell interactions are introduced or eliminated by a given move. In turn, this is weighted by w, whose components are user-specified. Using (14), we may determine the energy difference dependence on N_{AB} as follows,

$$E_{\mathrm{f}} - E_{\mathrm{i}} = \left[w (N_{\mathrm{AB}})_{\mathrm{f}} + \frac{1}{2} z \varepsilon_{\mathrm{AA}} N_{\mathrm{A}} + \frac{1}{2} z \varepsilon_{\mathrm{BB}} N_{\mathrm{B}} \right] - \left[w (N_{\mathrm{AB}})_{\mathrm{i}} + \frac{1}{2} z \varepsilon_{\mathrm{AA}} N_{\mathrm{A}} + \frac{1}{2} z \varepsilon_{\mathrm{BB}} N_{\mathrm{B}} \right], \tag{17}$$

$$= w [(N_{\mathrm{AB}})_{\mathrm{f}} - (N_{\mathrm{AB}})_{\mathrm{i}}], \tag{18}$$

where $(N_{\mathrm{AB}})_{\mathrm{i}}$ and $(N_{\mathrm{AB}})_{\mathrm{f}}$ are N_{AB} before and after a move, respectively. Since most A − B intercell interactions remain static following a move, we only need to determine how many are introduced or eliminated in the immediate local environment of the flipped cell; we will refer to this local change due to a single move as n_{AB}, defined as

$$n_{\mathrm{AB}} = (N_{\mathrm{AB}})_{\mathrm{f}} - (N_{\mathrm{AB}})_{\mathrm{i}}. \tag{19}$$

Considering (18) and (19), our probability law may be simplified to

$$P = \begin{cases} e^{-\beta w n_{\mathrm{AB}}}, & \text{if } n_{\mathrm{AB}} > 0 \\ 1, & \text{otherwise.} \end{cases} \tag{20}$$

References

The starting point and inspiration for this derivation were the treatments in Chapter 8 and Appendix C of G. de With, *Liquid-State Physical Chemistry*, Wiley-VCH, Weinheim, Germany, 2013. Other helpful resources included the Ising model Wikipedia page (`https://en.wikipedia.org/wiki/Ising_model`), and Chapter 5 of D. Chandler, *Introduction to Statistical Mechanics*, Oxford University Press, Oxford, UK, 1987.