

Cellular Automata Simulations of Vapor–Liquid Equilibria

Paul G. Seybold,^{A,B,E} Matthew J. O'Malley,^A Lemont B. Kier,^C and Chao-Kun Cheng^D

^A Department of Chemistry, Wright State University, Dayton, OH 45435, USA.

^B Department of Biochemistry, Wright State University, Dayton, OH 45435, USA.

^C Department of Medicinal Chemistry, Virginia Commonwealth University, Richmond, VA 23298, USA.

^D Department of Mathematical Sciences, Virginia Commonwealth University, Richmond, VA 23298, USA.

^E Corresponding author. Email: paul.seybold@wright.edu

Phase transitions and phase equilibria are among the most fundamental phenomena in the physical and environmental sciences. In the present work an asynchronous stochastic cellular automata model for the equilibrium between a liquid and its vapor is presented. The model is visual, dynamic, and employs just two rules—an attraction probability and a gravitational preference. Application of the attraction rule alone yields a ‘mist’ within the vapor, whereas application of the gravitational rule by itself yields an isothermal atmospheric profile. Application of both rules together causes the vapor to evolve to a liquid phase with a vapor phase above it. Introduction of a third rule for short-range attraction/repulsion more clearly resolves the liquid/vapor interface.

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Understanding the intrinsic features governing phase changes and phase equilibria has long been a major thrust within the physical sciences. Phase phenomena typically involve the interactions between a great many individual ingredients, and although the ingredients may themselves be rather simple, their multiple interactions can generate complex behaviors. In particular, the condensation of a vapor to its liquid and the resulting equilibrium between these two phases have been subjects of intense study for some time.^[1–3] Most commonly, theoretical approaches to the study of vapor–liquid equilibrium have employed Monte Carlo^[4–8] and molecular dynamics simulations,^[9,10] often with special attention focussed on aqueous systems because of their enormous environmental importance.^[11–19] These theoretical studies have been highly enlightening and have yielded a great deal of specific information regarding the molecular details of the equilibrium conditions at vapor/liquid interfaces.^[20]

An alternative approach to the examination of phase transition mechanisms involves the use of cellular automata models.^[21–27] In contrast to the Monte Carlo and molecular dynamics approaches, which employ classical force fields to estimate molecular interactions, cellular automata models are rule-based and do not employ the expressions (e.g. the differential equations) typically used in classical physics. The cellular automata models are in a sense ‘stripped-down’ models compared to the more elaborate Monte Carlo and molecular dynamics simulations. They represent intermolecular interactions only in very general terms, with the disadvantage that they do not yield the specific energetic information commonly produced by the more elaborate approaches, but also the advantages that (a) they are normally much

less computationally demanding than these more formal approaches and (b) they can frequently yield highly instructive pictures of features governing complex phenomena that may fall outside the range of the formal approaches.

In cellular automata models the activities of the ingredients take place on a grid (normally two-dimensional) composed of cells between which the ingredients can move and interact according to user-specified model rules. The interactions between the ingredients are entirely local, occurring either at the interface between adjacent cells or, at most, across an empty space between two ingredients. The rules in these ‘agent-based’ models can be deterministic—specified exactly—or probabilistic. In these models time advances in time-steps (iterations) during which the rules are uniformly applied to all of the ingredients. Thus not only are the ingredients of a cellular automata ‘universe’ themselves discrete, but so too are space (the cells) and time (the iterations) within this universe.

We have developed a variety of cellular automata models and applied them to several different physical and chemical systems.^[27,28] The rules in these models are probabilistic (stochastic) and are of two general types: *transition rules*, which establish the probability that an ingredient will change to a new type of ingredient during an iteration, and *movement rules*, which govern the movements of the ingredients about the grid. The transition rules are not required in the present context. Of the movement rules, three are relevant to the present examination of vapor–liquid phase changes and equilibria. In the absence of constraints the ingredients move in random walks about the grid. However, the ingredient movements can be restricted or modified by (a) interactions

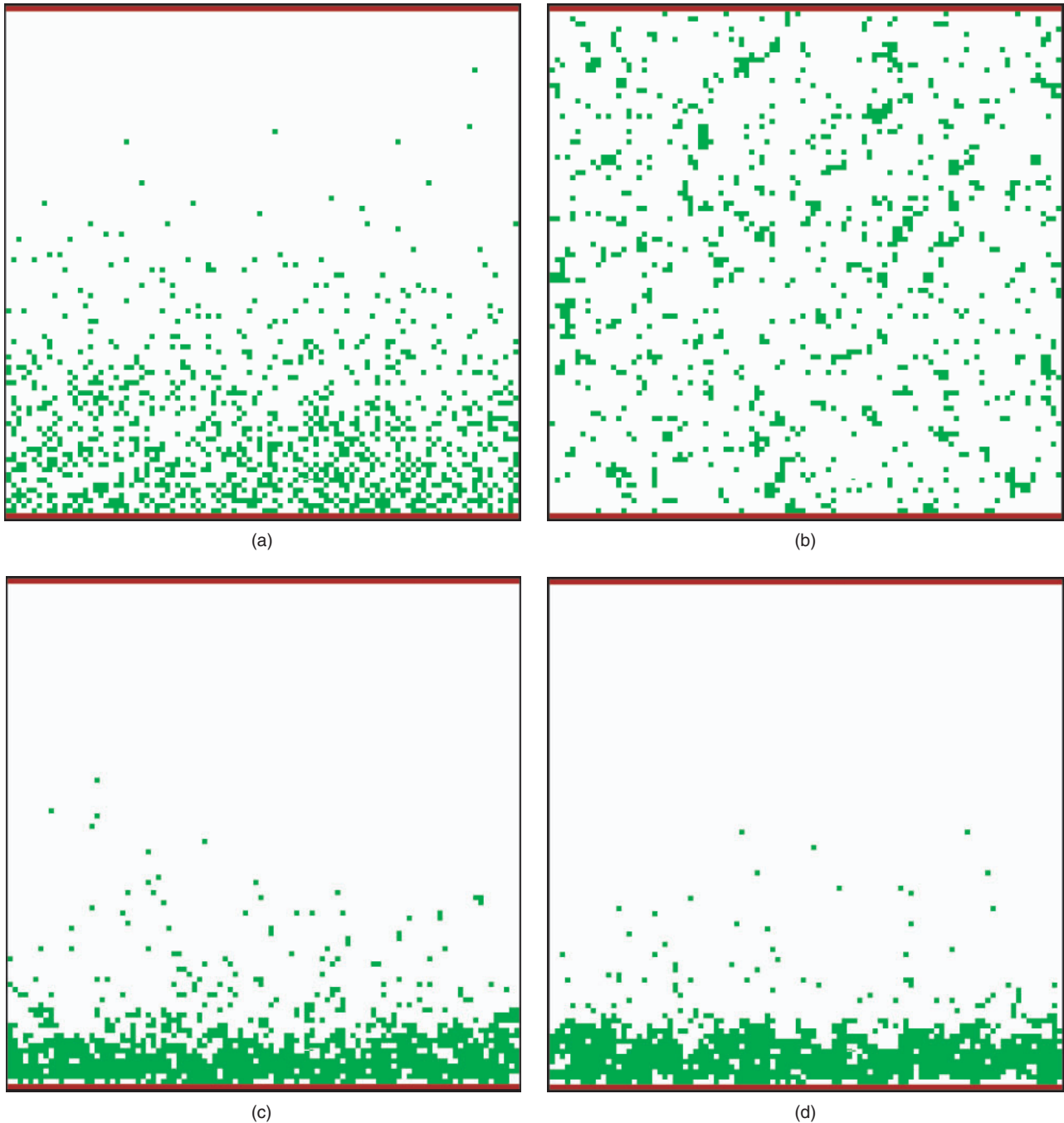


Fig. 1. Snapshots from the cellular automata simulations of 1000 ingredients moving on a 100×100 grid. (a) Applying the gravitational rule only: $G_A(A) = 0.15$. (b) Applying the breaking parameter only: $P_B(AA) = 0.25$. (c) Using both parameters: $G_A(A) = 0.10$, $P_B(AA) = 0.25$. (d) Adding the joining parameter: $G_A(A) = 0.10$, $P_B(AA) = 0.25$, $J(AA) = 2.0$.

with other ingredients or (b) a favored direction of motion. The *breaking probability* $P_B(AA)$ defines the probability that when two ingredients, both of type A, move to adjacent cells on the grid they will separate at the next iteration. Thus a value $P_B(AA) = 0.3$ would specify a 30% probability of breaking apart during an iteration, and P_B can be set between 0.0 and 1.0. $P_B(AA)$ therefore represents the adhesion between the A ingredients, with lower P_B values indicating greater ‘stickiness’. The *joining probability* $J(AA)$ specifies the relative probability that an ingredient A on the grid separated from

a second A by an empty cell will move toward the second A during the next iteration. (In completely free movement this probability is 0.25 because the ingredient can move up, down, right, or left.) A $J(AA)$ value of 1.0 is neutral, whereas $J > 1.0$ indicates an increased tendency to move toward the second A and $J < 1.0$ indicates a reduced tendency. Finally, the gravity parameter $G_A(A)$ specifies a greater than normal probability that the ingredient A will move downward on the grid, compared to the other three directions of possible motion. Thus a value $G_A(A) = 0.1$, for example, indicates a slight tendency

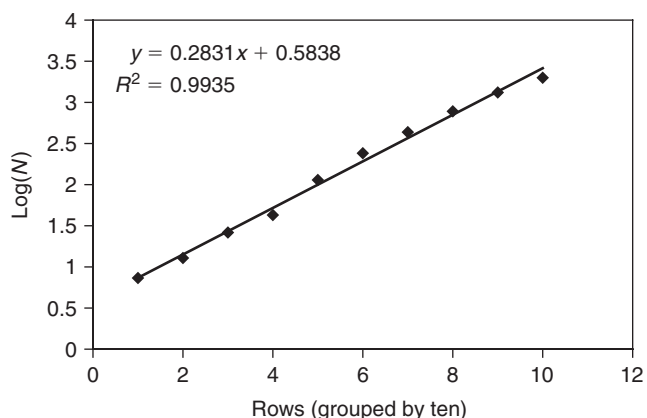


Fig. 2. Test of the atmospheric concentration profile, with $G_A(A) = 0.15$ for the simulation in Fig. 1a. Time averaged concentrations collected by bins of 10 rows each. The bins start at the top of the grid and proceed downward.

to move downward. The specific details of the simulations are described more completely in refs [27,28].

To illustrate the application of this approach to the vapor–liquid phase equilibrium phenomenon we place 1000 ingredients on a 100×100 grid of cells. A cylindrical grid is employed with barriers at the top and bottom of the grid; these barriers prevent vertical motions beyond those points. (For other applications one might use either a box or a toroid grid.) Left–right movement is unrestricted, so that ingredients moving off the grid on the right side appear at the left of the grid, and those moving off to the left appear on the right. In all cases the ingredients are initially placed in random positions on the grid and the system is allowed to evolve subject to the applied rules. As a first example we apply only the gravitational rule, with $G_A(A) = 0.15$, and assume that there are no attractions or repulsions between the ingredients ($P_B = J(AA) = 1.0$). In this case after some time the system, although continually fluctuating, takes on the general appearance of an ‘isothermal atmospheric profile’, or barometric distribution,^[29] as illustrated by the snapshot shown in Fig. 1a. This dynamic configuration is an ‘emergent property’ generated by application of the $G_A(A)$ rule. One can test the average density variation with height for this case to see if the expected exponential decrease in concentration is present in this model ‘atmosphere’. The result is shown in Fig. 2, which plots $\log(N)$ versus height, with N representing the number of ingredients at a given height. (Note that ‘bins’ of 10 rows each were employed in Fig. 2, and the bin counts begin at the top of the grid and proceed downward.) In general, increasing $G_A(A)$ squeezes the atmospheric distribution downward, and lowering $G_A(A)$ raises it, in much the same way that a planet’s gravitational field affects its atmosphere’s extent.

A different situation arises if the gravitational rule is turned off (by setting $G_A(A) = 0.0$) and the attraction or ‘stickiness’ probability rule is applied. Setting $P_B(AA) = 0.25$ causes the system to evolve to a dynamic ‘mist’, wherein small clusters of ingredients continually form and dissipate but the ingredients do not settle. The snapshot in Fig. 1b illustrates the general appearance of the system for this case. This simulation mimics the situation in which a mist forms in a

humid atmosphere where the gravitational force is negligible compared to the attractive forces between the molecules.

When both the gravitational rule and the attraction rule are in force the system evolves, after ~ 5000 – 10000 iterations, to a steady-state condition in which a condensed phase forms below, and this phase is in equilibrium with an overlying vapor phase. This is illustrated in the snapshot in Fig. 1c for $G_A(A) = 0.15$ and $P_B(AA) = 0.25$. It is to be emphasized that this is a dynamic condition in which ingredients continually enter and leave the ‘liquid’ phase. Note that the interface between the two phases is a highly dynamic region extending over several rows of the grid, in effect over several molecular diameters. This agrees with experimental and theoretical studies, which commonly describe a transition zone/interface of several molecular diameters between liquid and vapor phases.^[13,19,30] Phillips has described the molecular-scale liquid–vapor interface as ‘a zone of rapid, chaotic motion, where condensing and evaporating molecules continuously arrive and depart and the measured values of bulk quantities such as density vary continuously over a distance of the order of a few tens of Ångströms.’^[31] The cellular automata model of the vapor/liquid interface is entirely consistent with this description.

If one adds the short-range attraction/repulsion parameter $J(AA)$ to the above simulations, taking $J = 2.0$ as an attractive contribution, the interface transition region becomes somewhat more distinctly resolved, although the interface itself remains rough and dynamic. This is shown in Fig. 1d. This general picture, taking into account short-range attractive forces between the molecules, most likely presents a more realistic description of the interface region for a polar substance such as water.

Einstein once remarked that ‘The grand aim of all science is to cover the greatest number of empirical facts by logical deduction from the smallest number of hypotheses or axioms.’^[32] Cellular automata models have proven to have considerable value in the modeling and simulation of a wide variety of complex physical, chemical, and biological phenomena. The simulations are based on simple, heuristic rules, are visual and dynamic, are computationally undemanding, and, most importantly, yield realistic representations of the phenomena addressed. In the present case, in determining the minimum number of parameters or rules required to simulate the traditional condensation of a vapor to its liquid and the subsequent equilibrium between the two phases, that minimum number of rules or parameters appears to be two. Addition of a third rule enhances the description. In the future we anticipate extending this model to encompass a variety of more diverse examples such as mixtures of liquids^[33,34] and the participation of ions in the liquid phase.^[35]

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