Lattice modeling of a real gas revisited

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Abstract: The spin-half Ising model has been used with remarkable success in describing magnetism and phase transition in magnetic materials. Likewise, the lattice gas model, which uses the spin-1 Ising model, was employed to investigate the phase transition in liquid-gas systems. In all the earlier lattice gas models, the kinetic energy of atoms occupying the various lattice sites were not considered for finding the equation of state. In this paper we use the Hamiltonian with kinetic energy and a modified equation of state is obtained. The isotherms of this model show the behavior of real gases at all pressures and they also exhibit phase transition.

Key words: Equation of state, real gas, Ising model, lattice gas

1. Introduction

Real gases satisfy the ideal gas equation of state (EoS) only at low densities, and so an improvement on the EoS was suggested by van der Waals in 1873 [1], which was remarkably successful in representing the qualitative features of real fluids, including the gas-liquid phase transition. The van der Waals equation contains corrections to the ideal gas EoS taking into account the interaction between particles and the volume of gas molecules. The EoS for van der Waals gas with pressure P, volume V, and temperature T is:

$$(P + \frac{a}{V^2})(V - b) = RT, \tag{1.1}$$

where R is the universal gas constant and a and b are constants. Later studies showed much progress towards an understanding of the structure and properties of van der Waals gas [2–5]. Over the years, improved equations have followed the van der Waals equation. These equations predict results more accurately, but they also become increasingly more complex to analyze [6]. In a system consisting of atoms or molecules there will be interatomic or intermolecular forces. The vectorial treatment for modeling such a system is a difficult one. In earlier studies interatomic potentials were used for obtaining the EoS of real gas, but later Ising energy, which has an interaction term, was used for modeling and to look for the possibility of phase transitions [7–9].

The spin-half Ising model was initially introduced to simulate the structure of a ferromagnetic substance [10]. In this model, the system is considered as an array of N fixed points called lattice sites, which form an n-dimensional periodic lattice ($n = 1, 2, 3, …$). Each lattice site is assigned a spin that determines the magnetic nature of the system. Later the Ising model was used to describe nonmagnetic properties of completely different systems [11]. Modeling of the particles on lattices was used to explain liquid-gas phase transitions,

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percolation, and fragmentation [12]. In studies of nuclear matter, isospin lattice gas models were used to explain phase transition [13].The term "lattice gas" was first coined by Yang and Lee in 1952 [14,15], though the interpretation of the model as a gas was known earlier [16]. In this lattice gas model, it is assumed that a fluid system is divided into a regular lattice of cells of volume roughly equal to the particle (atom, molecule) volume [17], and this volume may or may not be occupied by the atoms. Here discreteness is introduced in the classical description of fluids. If the lattice constant, which is the spacing between the lattice points, is allowed to approach zero, and adding ideal gas pressure to the EoS, the model corresponds to a real gas of atoms, interacting with one another [17]. For a more realistic approach, in this paper we include the kinetic energy along with an interaction term in the Hamiltonian and obtain a new EoS. To simplify the interaction energy Bragg–William approximation is used [18].

2. Lattice gas and Ising model

The basic use of a lattice gas model is to describe a fluid, where the particles are located on the sites of a lattice instead of continuously occupying any position in space. Each lattice site can be occupied by at most one atom. Let

N = total number of lattice sites,

N_+ = total number of atoms filling the lattice sites,

N_{++} = total number of nearest neighbor pairs of atoms.

Lattice gas with nearest neighbor interaction is mathematically equivalent to the Ising ferromagnet. The occupied sites correspond to up spins and vacancies to down spins.

The correspondence with the Ising model is established, relating the local density of a

fluid with the local magnetization density of an Ising model. The chemical potential plays the role of the magnetic field. In the case of lattice gas, the free energy and pressure are each other's Legendre transform. Each can be obtained from the other by a Legendre transform or both contain the same information about the system, and hence either of them can be used to study the thermodynamic behavior of the lattice gas [19]. We use the equivalence of the canonical ensemble of the ferromagnets with the grand canonical ensemble of the lattice gas. From this comparison, pressure can be obtained from the following equation:

$$P_{LG} = -\left(\frac{A}{N} + \frac{1}{2}qJ - \mu B \right), \tag{2.1}$$

where A is the Helmholtz free energy, J is the coupling constant, μ is the magnetic moment, q is the coordination number, and B is the external field, with the support of the following equations:

$$\frac{1}{2}\left(\frac{M_I}{N} + 1 \right) = \frac{1}{v}, \tag{2.2}$$

$$\mu B = qJ - \frac{kT}{2}\ln z, \tag{2.3}$$

where M_I is magnetization, $v = V/N$ is the specific volume, T is the absolute temperature, k is the Boltzmann constant, and z is the fugacity. According to the Ising model, the interaction energy is:

$$E_{int} = -J\sum_{<ij>} \sigma_i\sigma_j - \mu B\sum_{i=1}^{N} \sigma_i, \tag{2.4}$$

where σ_i can be ± 1 depending on whether the site is occupied or not and $< ij >$ indicates that only nearest neighbor interactions are considered. This energy is modified suitable to a lattice gas using Bragg–Williams approximation as described below.

2.1. Bragg–Williams (BW) approximation

The basic assumption in BW approximation is that the energy of an atom in a system is given by the average degree of order prevailing in the entire system. We can see that the number $\frac{N_+}{N}$ requires no correlation between the nearest neighbors. If this number is known in the neighborhood of a given filled site, no matter how far we go away from the given site, the order measured by it remain the same, since the number of atoms is constant (provided that no atoms evaporate from or condense on the lattice). Hence, the number $\frac{N_+}{N}$ is a measure of the long-range order in the lattice. If we know that a given site is occupied then $\frac{N_{++}}{(qN/2)}$ is the fraction of its nearest neighbors with occupied sites. It is a measure of local correlation and hence it is considered to be a measure of short-range order. Defining the long-range order parameter as L and the short-range order parameter as s, we get:

$$\frac{N_+}{N} = \frac{1}{2}(1+L) \qquad -1 \leq L \leq +1, \tag{2.5a}$$

$$\frac{N_{++}}{qN/2} = \frac{1}{2}(1+s) \qquad -1 \leq s \leq +1, \tag{2.5b}$$

From Eq. (2.5a) and using the relation $N = N_+ + N_-$, we get

$$L = \frac{N_+ - N_-}{N}.$$

Then

$$N_+ = \frac{N(1+L)}{2} \qquad \text{and} \qquad N_- = \frac{N(1-L)}{2}. \tag{2.6}$$

Also, we can write

$$\sum_i \sigma_i = N_+ - N_- = 2N_+ - N,$$

$$\frac{N_+}{N} = \frac{1}{2}\left(\frac{\sum_i \sigma_i}{N} + 1\right) = \frac{1}{2}(L+1).$$

Hence, $\sum_i \sigma_i = NL$.

Using the relations [8] $qN_+ = 2N_{++} + N_{+-}$,

$$qN_- = 2N_{--} + N_{+-},$$

$$\sum_{i,j} \sigma_i \sigma_j = N_{++} + N_{--} - N_{+-} = 4N_{++} - 2qN_+ + \frac{qN}{2},$$

$$\frac{\sum \sigma_i \sigma_j}{qN/2} = \frac{4N_{++}}{qN/2} - \frac{2qN_+}{qN/2} + 1 = 4\left(\frac{1}{2}(s+1)\right) - 4\left(\frac{1}{2}(L+1)\right) + 1,$$

we have

$$\sum \sigma_i \sigma_j = \frac{qN}{2}(2s - 2L + 1). \tag{2.7}$$

Hence, we get

$$E_{int} = -J\frac{qN}{2}(2s - 2L + 1) - \mu BNL. \tag{2.8}$$

In BW approximation, there is no short-range order other than that which follows from long-range order [17], and hence

$$\frac{1}{2}(s + 1) = \left(\frac{1}{2}(L + 1)\right)^2, \tag{2.9}$$

$$s = \frac{1}{2}(L + 1)^2 - 1. \tag{2.10}$$

Substituting in Eq. (2.4), we get the interaction energy for a lattice gas in terms of the order parameter as

$$E_{int} = -\frac{NqJL^2}{2} - \mu BNL. \tag{2.11}$$

3. Partition function for lattice gas

If we consider the energy of individual particles along with the interaction energy, the total energy is

$$E = E_{int} + \sum_{N_+=0}^{N} \frac{p_{N_+}^2}{2m}, \tag{3.1}$$

where p is the temporal average of the momentum of particles. In the lattice gas, the particles are supposed to move from site to site. The partition function is given by [9]

$$Q = \sum \Omega(E)e^{-\beta E}, \tag{3.2}$$

where $\beta = \frac{1}{kT}$ and $\Omega(E)$ is the number of ways in which we can distribute N_+ particles among the N lattice sites:

$$\Omega(E) = \frac{N!}{N_+!N_-!} = \frac{N!}{N_+!(N - N_+!)}. \tag{3.3}$$

Thus, the partition function becomes

$$Q(N_+, T) = \sum_{N_+=0}^{N} \frac{N!}{N_+!(N - N_+!)}e^{-\beta E}. \tag{3.4}$$

Integrating over the momentum space independently,

$$Q(N_+, T) = \frac{1}{\lambda^{3N_+}N_+!}\sum_{N_+=1}^{N} \frac{N!}{N_+!(N - N_+!)}e^{-\beta E_{int}}, \tag{3.5}$$

where $\lambda = \frac{h}{\sqrt{2\pi mkT}}$ is the thermal wavelength. The contribution of the integration in momentum space can be incorporated into the chemical potential [7], but here we treat this term independently. We write this as $Q(N_+, T) = Q_K Q_{int}$, where

$$Q_K = \frac{1}{\lambda^{3N_+} N_+!} \text{ and } Q_{int} = \sum_{N_+=1}^{N} \frac{N!}{N_+!(N-N_+!)} e^{-\beta E_{int}}. \tag{3.6}$$

4. Helmholtz free energy

Taking the logarithm $\ln Q(N_+, T) = \ln(Q_K Q_{int}) = \ln Q_K + \ln Q_{int}$ and evaluating the first term,

$$\ln Q_K(N_+, T) = \ln Q(L, T) = \ln \left[\frac{1}{\lambda^{3N_+} N_+!} \right]$$

$$= -\frac{N(1+L)}{2} \left[\ln \lambda^3 + \ln \frac{N(1+L)}{2} - 1 \right]. \tag{4.1}$$

Maximizing $\frac{\ln Q_K}{N}$ with respect to L,

$$\ln \lambda^3 = -\ln \frac{N}{2}(1+L^*), \tag{4.2}$$

where L^* is the value of L that maximizes $\frac{\ln Q_K}{N}$.

Then the Helmholtz free energy is

$$\frac{A_K}{N} = \frac{-kT \ln Q_K}{N} = kT \frac{N(1+L^*)}{2} \left[\ln \lambda^3 + \ln \frac{N(1+L^*)}{2} - 1 \right]. \tag{4.3}$$

Using the maximizing condition, we obtain

$$\frac{A_K}{N} = -kT \frac{(1+L^*)}{2}. \tag{4.4}$$

On evaluating the second term, we consider a system of infinite number of particles, and as $N \to \infty$, $\ln Q_N$ is equal to the logarithm of the largest term in the summand. Using Stirling's approximation,

$$\ln Q_{int} = \beta N \left(\frac{qJ\bar{L}^2}{2} + \mu B L \right) - \frac{N(1+\bar{L})}{2} \ln \frac{(1+\bar{L})}{2} - \frac{N(1-\bar{L})}{2} \ln \frac{(1-\bar{L})}{2}. \tag{4.5}$$

Here $\bar{L}$ is the value of L that maximizes the summand. By maximizing $\frac{1}{N} \ln Q_{int}$ with respect to the order parameter, the Helmholtz free energy is

$$\left(\frac{A}{N} \right)_{int} = \frac{qJ\bar{L}^2}{2} - \frac{kT}{2} \ln \left(\frac{1-\bar{L}^2}{4} \right). \tag{4.6}$$

Combining Eq. (4.4) and Eq. (4.6), the Helmholtz energy of the lattice gas is

$$\frac{A}{N} = \frac{A_K}{N} + \frac{A_{int}}{N} = -kT \frac{(1+L^*)}{2} + \frac{qJ\bar{L}^2}{2} - \frac{kT}{2} \ln \left(\frac{1-\bar{L}^2}{4} \right). \tag{4.7}$$

5. Equation of State

Pressure by Eq. (2.1) is

$$P = \mu B - \frac{qJ}{2} - \frac{qJ\bar{L}^2}{2} + \frac{kT}{2} \ln\left(\frac{1 - \bar{L}^2}{4}\right) + \frac{kT}{2}(1 + L^*). \tag{5.1}$$

Substituting Eq. (2.3),

$$P = \frac{qJ}{2} - \frac{kT}{2} \ln z - \frac{qJ\bar{L}^2}{2} + \frac{kT}{2} \ln\left(\frac{1 - \bar{L}^2}{4}\right) + \frac{kT}{2}(1 + L^*). \tag{5.2}$$

From the relation $\sum_i \sigma_i = M_I = NL$ and using Eq. (2.2),

$$\frac{1}{2}[L + 1] = \frac{1}{v},$$

and replacing $\bar{L}$ and L^*,

$$P = \frac{qJ}{2} - \left(\frac{kT}{2}\right) \ln z - \frac{qJ}{2}\left(\frac{2}{v} - 1\right)^2 - \frac{kT}{2} \ln\left(\frac{1 - (\frac{2}{v} - 1)^2}{4}\right) + \frac{kT}{v}. \tag{5.3}$$

This is the modified EoS for a lattice gas incorporating the kinetic energy in the Hamiltonian. The p-v diagrams of the lattice gas with and without kinetic energy for different values of temperature are plotted in Figure 1 and Figure 2, respectively, where p and v are scaled pressure (P/qJ) and volume (V/N), respectively. In addition to the liquid-gas coexistence region, the p-v relation is studied under constant temperature conditions. Arbitrary temperatures were chosen to visualize the phase transition. From these graphs, the relationships of molar volume versus pressure at each of the isotherms can be compared with the experimental data [20]. This EoS can be used to obtain the critical parameters of different gases if we know the exchange interaction J and the coordination number q of the given lattice structure. A comparison is made by drawing the p-v−T diagrams for ideal gas EoS (Figure 3), van der Waals EoS (Figure 4), and lattice gas EoS with and without kinetic energy (Figures 5 and 6). The EoS obtained without considering the individual particle's kinetic energy shows phase transition, but it deviates from the real gas nature as pressure decreases. Even if the phenomenon of phase transition is essentially a consequence of interaction energy among the atoms, we have shown that in order to obtain the actual behavior of real gases the kinetic energies of the atoms occupying the various lattice sites must be considered.

6. Conclusion

The EoS provides a starting point for the evaluation of thermodynamic properties of substances; a large amount of experimental data can be orderly summarized and can be interpolated accurately between the experimental data points with the help of the EoS. Expressing the pressure-volume-temperature relationships as continuous functions helps in the calculation of physical properties using differentiation and integration. In this paper we used a lattice gas model for modeling real gases. By including the kinetic energy in the Ising Hamiltonian, the EoS of the system is modified. We plotted the isotherms for the lattice gas with and without kinetic energy. A comparative study of our EoS with ideal gas, van der Waals gas, and lattice gas without kinetic energy was done by plotting the p-v−T diagrams. Our study could show the existence of a phase transition together with the actual behavior of a real gas using the Ising model.

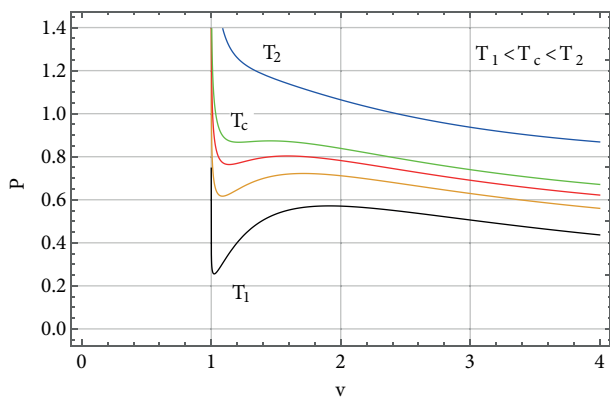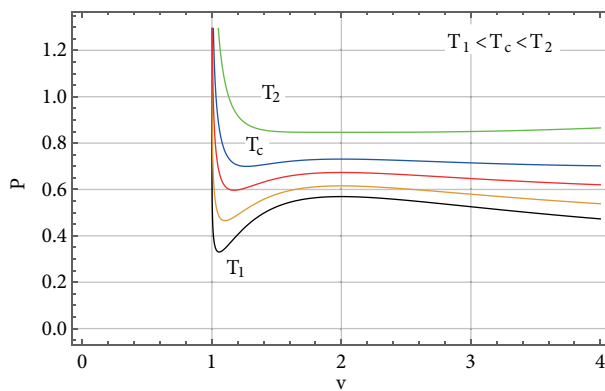**Figure 1**. Isotherms for lattice gas with kinetic energy.

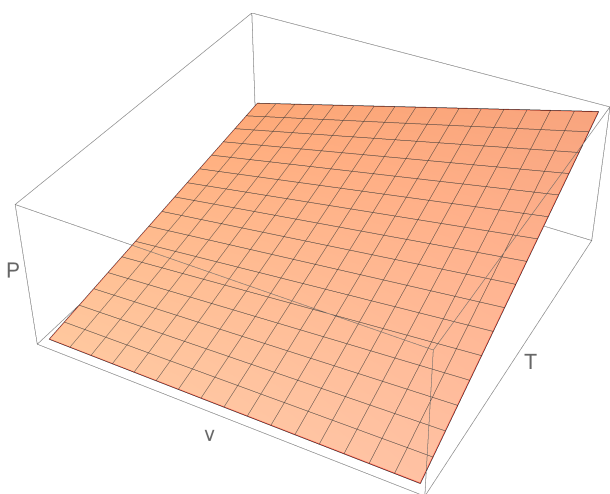**Figure 2**. Isotherms for lattice gas without kinetic energy.
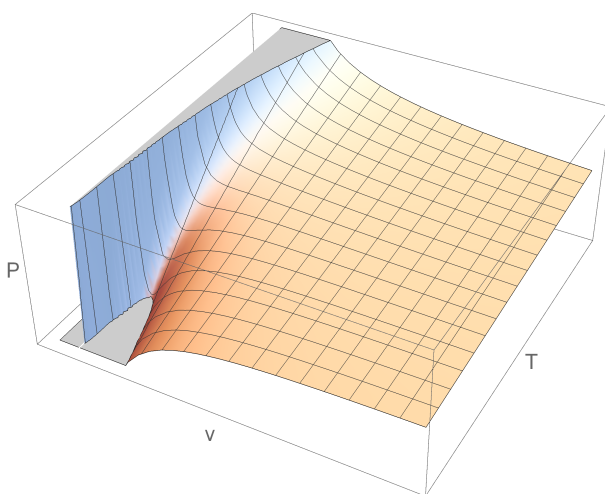

Figure 3. p-v-T diagram for ideal gas.

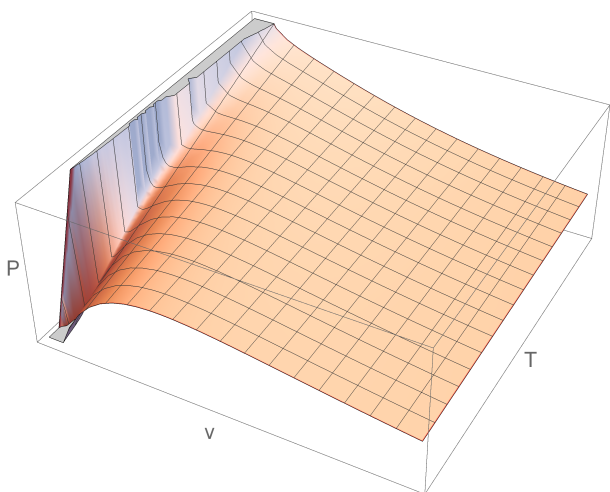**Figure 4**. p-v-T diagram for van der Waals gas.

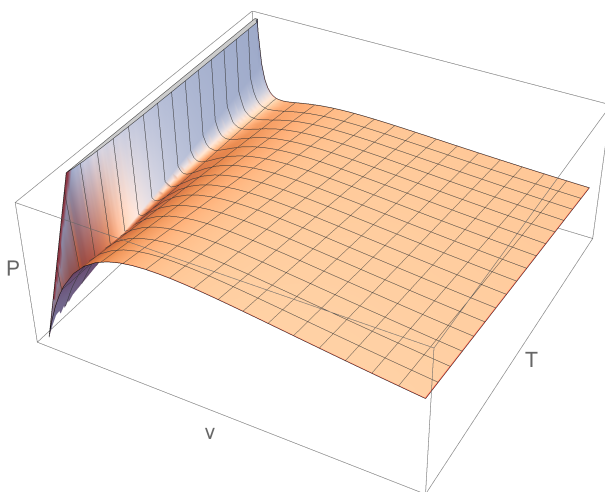**Figure 5**. p-v-T diagram for lattice gas with kinetic energy.

Figure 6. p-v-T diagram for lattice gas without kinetic energy.

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