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メタデータ	
	言語:
	出版者: 琉球大学工学部
	公開日: 2008-03-31
	キーワード (Ja):
	キーワード (En): liquidus and gaseous line, phase diagram, critical temperature, latent heat, vapor pressure, Kamerlingh-Onnes' constant
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URL	http://hdl.handle.net/20.500.12000/5448

Liquidus and Gaseous Line in Phase Diagram

Tatsuhiro YOGI* and Minoru YAGA*

Abstract

This paper describes that negative pair-interaction energy averaged over all particles and its density dependence gives van der Waals' equation of state through mean-field modeling and that liquidus and gaseous line for vapor-liquid phase are rigorously calculated from the equation of state, so that latent heat of vaporization and vapor pressure are obtained. Phase diagram is constructed from these lines and it is shown that the critical temperature depends not only on the size of molecule and the averaged magnitude of interaction energy but also on the mass of molecule. As a property of such system Kamerlingh-Onnes' constant is obtained.

Key Words: liquidus and gaseous line, phase diagram, critical temperature, latent heat, vapor pressure, Kamerlingh-Onnes' constant

1. Introduction

The phase transition problems have been always attracted physicist and chemists in fundamental and industrial application field both from the practical view point of seeking for useful theory of properties of matter and from the further understanding the discontinuities associated with phase transitions in thermodynamic functions. So it is useful to describe some typical works for phase transition briefly. Mayer's work has been well known in the field of the theory of condensation of gases [1]~[5], however Lee and Yang have shown the inadequacy of Mayer's method for dealing with a condensed phase [6]~[7]. They have also shown that an example of two-dimentional lattice regions in p-V diagram is exactly calculated. Hill has treated the question of whether or not "loop" should be expected in $\mu - N/V$ or $p - N/V$ curve for an exact theory of first-order phase transition using canonical ensemble [8]. A careful argument has been described by Van Hove showing that no loop is obtained from complete evaluation of canonical ensemble partition function of fluid [9]. The phase transition is to be characterized by the fact that the partition function of finite system suffers a sudden change at some value of parameters. Katsura has calculated the partition function of the system which has finite number of lattice points as its volume and described the possibility of cooperative phenomena even in pretty small systems [10]~[11]. Many description on the lattice gas model have been shown in textbooks [12]~[15]. The Percus-

Yevick equation of state for the Lennard-Jones 6-12 potential derived not only from the compressibility for several isotherms but also from the pressure equation is not in agreement with experimental data. Particularly in coexistent state of liquid and vapor this equation has no solution of experimental flat region[18]. Liquidus and gaseous lines are conventionally understood by the existence of double local minimum of Gibbs energy in a given system. The previous work of such problems for matter have not given satisfactory explanation for results of experiments. The occurrence of the discontiniuties associated with phase transitions will be further understood by the more correct liquidus and gaseous line. This leads us much intensive study for existence of liquidus and gaseous line, so that we can construct phase diagram not only with coexistent state but also with separate phases of vapor and liquid. Therefore this paper will be concerned with two curves representing liquidus and gaseous line below critical temperature. We have studied the first-order phase transition for simple matter by using canonical emsemble with mean-field approach, which is quite simple and fairly practical and indeed show the existence of two separate phases and coexistent state of both liquid and vapor. If we neglect the interaction between particles both in liquid and vapor phases, the partition function with the mean field approximation is available to obtain the distribution of interaction energy par particle and the linear dependence of the energy on density in each phase by MD computer simulation. The contribution of mean-field theory to the distribution and density-dependence of interaction energy par particle is acceptable over a wide temperature range for many substance. The canonical partition function in the

present paper gives van der Waals' equation of state in each phase. We suppose that thermal and mechanical equilibrium are established in the system(i.e.,$T_1 = T_2$ and $p_1 = p_2$), therefore liquidus and gaseous lines are derived from the equation of state only without Maxwell's equiareal rule and the vapor pressure are obtained for several simple substance at any given temperature. We show that above two lines separate the parts of liquid, vapor and coexistent state in phase diagram and examine the thermodynamic properties of such system. The present paper shows that Maxwell's equiareal rule based on these lines is satisfied near critical temperature. Our theory provides that the isotherms stay flat in coexistent state between liquidus and gaseos line and that the isotherms is a function only of temperature. These feature is quite different from Mayer's theory and Lee and Yang's theory. The characteristic feature of liquidus and gaseous line experimentally determined are well reproduced by the theory. Thermodynamic properties such as latent heat of vaporization are satisfactory in the region between liquidus and gaseous line. It sholud be emphasized that the purpose of this paper is to derive liquidus and gaseous line in vapor-liquid coexistent state and to derive thermodynamic properties of such system through mean-field approach. we will show the solution for the discrepancy for molecular size between van der Waals and quantum mechanics. In section 2, we introduce practical method for liquidus and gaeous line and construct phase diagram for simple matter. We analyze and discuss the usefulness of this method for results in section 3. The conclusion is described in section 4.

2. Theoretical Frame

We consider one component closed system and assume that one particle interacts with other particles with attractive potential function. Let N and V be the number of particles and volume in system with the restriction of N(const.) and V(variable). We can write the canonical ensemble partition function as follows;

$$Q = \frac{1}{N!h^{3N}} \int e^{-\beta K} \prod_{i=1}^{N} dP_i \int e^{-\beta U} \prod_{i=1}^{N} dr_i \qquad (1)$$

where

$$K = \sum_{i=1}^{N} \frac{P_i^2}{2m} \qquad (2)$$

and

$$U = \sum_{i=1}^{N} \sum_{j>i}^{N} \phi_{ij} \qquad (3)$$

Since the interaction between particles exists in single phase above equation(1) can not be analytically calculated except some simple cases. Therefore we should

expect the problem to represent somewhat less serious mathematical difficulties than rigorous way. We calculate an averaged interaction energy a particle around all other particles by computer simulation(MD), so we obtain the concentration-dependence of energy in each of liquid and vapor phases. We investigate the subject that an averaged interaction energy is of attractive type, so we suppose that the interaction potential is of Lennard-Jones type as typical one of attractive force. We consider a monoatomic gas or liquid with the interaction

$$U = 4\epsilon((\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^6) \qquad (4)$$

where r_{ij} is the distance between the i-th and j-th atoms in a phase and σ the diameter of atoms and ϵ a coupling constant(the magnitude of interaction), in detail, $4\epsilon = 320k_B$ and $\sigma = 3.56A$ for Ar. The value of ϵ is different from that used in Rahman[16]. All sampling for statistics was averaged over the next 10000 steps after the initial 4000 steps calculation for equilibrium with $\delta t^* = 0.0064$ as a scaled time step). The usual periodic boundary condition, in which the simulated box is surrounded by images of itself, is applied and we used Nose's method to controle the temperature of a system[20],[21]. Let ϕ be the averaged energy a particle. In the most probable state for energy obtained by MD simulation, the representative particles is thought of as moving in some averaged potential due to all the other particles in the system, we thus approximate the energy function in phase as follows;

$$\sum_{i=1}^{N} \sum_{j>i}^{N} \phi_{ij} \approx N\phi \qquad (5)$$

$$= N(-|\epsilon|\rho + \alpha)), \qquad (6)$$

where $|\epsilon|$ is an averaged interaction energy a particle and ρ is density of phases(see fig.1).

It is shown from eqs.(5) and(6) that the averaged interaction energy is of attractive type. ϕ is commonly written by a linear function only of density over liquid and vapor phases. Each molecule is assumed to be free to move in the volume V-Nv_0(v_0 is a molecular volume), therefore we obtain the canonical partition function as follows;

$$Q = \frac{1}{N!h^{3N}}(\frac{2m\pi}{\beta})^{\frac{3N}{2}}(V - Nv_0)^N e^{-N\beta\phi}, \qquad (7)$$

where $\beta = (k_B T)^{-1}$ and k_B is Boltzmann constant. The theory can be easily generalized to diatomic gas or liquid; the rotational and vibrational energy are easily calculated in canonical partition function, however, these energy terms are disappeared by the settlement of the conditions of $T_1 = T_2$ and $p_1 = p_2$, which must be satisfied in an equilibrium state. The result shows the linear dependence of energy on density and the attractive type of
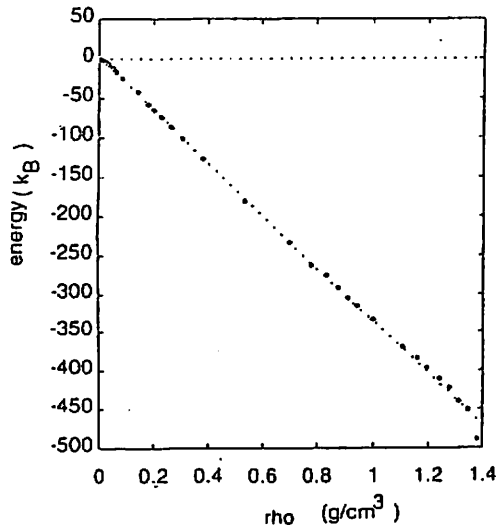
Fig. 1. The density dependence and attractive type of energy for Ar over a wide temperature range. Other substance shows the same as the linear dependence of energy on density and attractive type.
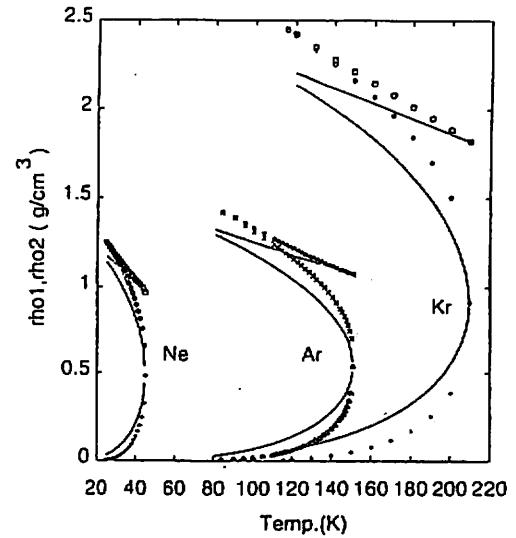

Fig. 2. Liquidus and gaseous line Ne, Ar and Kr, when use the relation $d/b_c = 1/3$, which is independent of the molecular size. These are not quantitatively but qualitatively in good agreement with experimental data. Ne: dashed and solid lines: calculation, □ and ×: experiments. Ar: dash-dooted and dashed lines: calculation, × and △: experiments. Kr: dotted lines: calculation, ◇ and +: experiments.

interaction, therefore we progress to calculate the canonical partition function for system dealing with the interaction energy by the mean field theory. The problem of seeking the liquid and vapor curves is to find the solution which satisfy $T_1 = T_2$ and $p_1 = p_2$ in the coexistent state. The state equation for phases are

$$
\begin{aligned}
p &= -kT\frac{\partial \ln Q}{\partial V} \\
&= kT(\frac{N}{V - Nv_0} + \beta\phi(\frac{N}{V})^2) \quad (8) \\
&= \frac{c}{\beta}(\frac{1}{1 - cv_0} - bc), \quad (9)
\end{aligned}
$$

where $b = \beta|\epsilon|m$ and c is number density of phase N/V. Above eqns.(8) and (9) are indeed van der Waals' equation of state, so we derive the critical temperature from the local maximum and minimum value(denoted by asterisk).

$$
c_1^* = \frac{2}{3v_0}(1 - \cos(\frac{\pi - \theta}{3})), \quad (10)
$$

$$
c_2^* = \frac{2}{3v_0}(1 - \cos(\frac{\pi + \theta}{3})), \quad (11)
$$

$$
c_3^* = \frac{2}{3v_0}(1 + \cos(\frac{\theta}{3})), \quad (12)
$$

where $\tan\theta = 6\sqrt{3D}/(27 - D)$, $D = 8b/v_0 - 27$. If $\theta = 0$ at a temperature in eqs.(10) and (11), then c_1^* and c_2^* coincide with each other, therefore we obtain the well known relation for critical temperature

$$
T_c = \frac{8|\epsilon|m}{27v_0 k_B}. \quad (13)
$$

It is remarked that the critical temperature depends not only on v_0 and $|\epsilon|$ but also on the mass of molecule. We define the number density $c_1 = N/V_g$ in vapor and

$c_2 = N/V_l$ in liquid phases, respectively. The liquidus and gaseous line is obtained at $T_1 = T_2$ and $p_1 = p_2$, if the following relations is satisfied

$$
\frac{1}{1 - c_1v_0} - bc_1 = dc_2, \quad (14)
$$

and

$$
\frac{1}{1 - c_2v_0} - bc_2 = dc_1, \quad (15)
$$

where the constant d is determined by experiments as shown in later. Therefore we have

$$
c_1(T) = \frac{1}{2v_0}(f - gQ), \quad (16)
$$

and

$$
c_2(T) = \frac{1}{2v_0}(f + gQ), \quad (17)
$$

where $f = 1 - d/b$, $g = 1 + d/b$ and $Q = \sqrt{1 - 4(v_0/b)/(g^2 f)}$. This means that Maxwell's equal-areal rule is not necessarily required to determine the vapor and liquid lines in a coexistent state(see figs.2 ~ 5).

The vapor pressure in coexistent state is written

$$
p(T) = \frac{d}{\beta}c_1(T)c_2(T), \quad (18)
$$

where p is a function only of temperature(see fig.6).

The rectilinear diameter rule is given by

$$
\begin{aligned}
\rho_1 + \rho_2 &= m(c_1 + c_2) \\
&= \frac{m}{v_0}f \quad (19)
\end{aligned}
$$

and the so-called order parameter is

$$
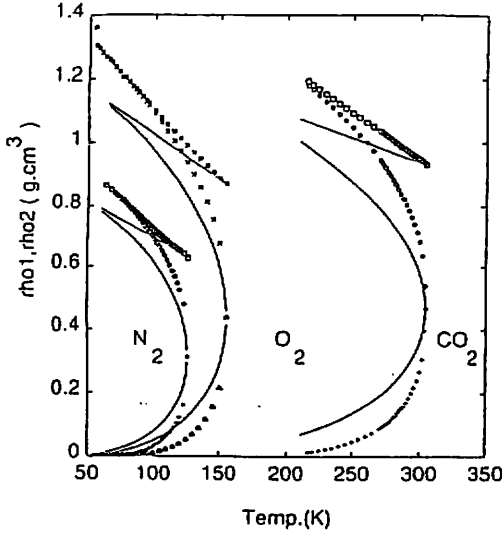\rho_2 - \rho_1 = \frac{m}{v_0}gQ \quad (20)
$$

Fig. 3. Liquidus and gaseous line for N_2, O_2 and CO_2, when use the relation $d/b_c = 1/3$, which is independent of the molecular size. As shown in fig.(2), these are not quantitatively but qualitatively in good agreement with experimental data. N_2: dashed and solid lines: calculation, □ and ×: experiments. O_2: dash-dotted and dashed lines: calculation, × and △: experiments. CO_2: dotted lines: calculation, ◊ and +: experiments.

Fig. 4. Liquidus and gaseous line for Ne, Ar and Kr, when use use eq.(24) as d/b_c. A good agreement with experiment is better than that of fig.(2) quantitatively. Ne: dashed and solid lines: calculation, □ and ×: experiments. Ar: dash-dotted and dashed lines: calculation, × and △: experiments. Kr: dotted lines: calculation, ◊ and +: experiments.

where ρ_1 and ρ_2 are density of vapor and liquid state, respectively. Ising models of lattice gas have generally shown the relation of $\rho_1 + \rho_2 = $ const. [7], but the theory shows that eq.(19) is a function only of temperature. Our method will give a good qualitative behavior as an approximate theory. The latent heat of vaporization is given by Clausius-Clapeyron's equation

$$\frac{dp}{dT} = \frac{L}{T(V_g - V_l)}$$

$$= \frac{L}{kT^2}(\frac{v_0}{d})\frac{p}{gQ}. \qquad (21)$$

Equation (21) yields the latent heat $L(T)$ after using $p(T)$ and dp/dT in eq.(18)(see figs.7 and 8).

This is not in good agreement with the experiments, however, if eq.(21) is connected to the empirical equation for vapor pressure [17], the good agreement is obtained as follows:

$$\frac{dp}{p} = 5.4T_c\frac{dT}{T^2} \qquad \text{(empirical formula)}, \quad (22)$$

then

$$L = \frac{5.4gQ}{\beta_c}(\frac{v_0}{d})^{-1}. \qquad (23)$$

Above latent heat of vaporization is shown as fig.9. The well known experimental fact that $c_1(T_c) = c_2(T_c)$ and $L(T_c) = 0$ requires Q to vanishes at a critical temperature. so we obtain the value d

$$d = \frac{m}{2\rho_c v_0}(1 - \frac{2\rho_c v_0}{m})(1 - \frac{\rho_c v_0}{m})^{-2}v_0 \qquad (24)$$

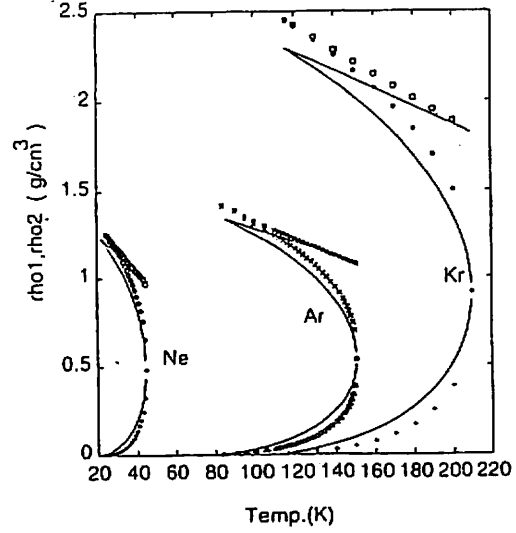where v_0 is a molecular volume. Van der Waals' equation of state conventionally yields the critical volume

$V_c = 3v_0$. If one uses the relation $\rho_c = m/(3v_0)$, then $d = 9v_0/8$ but the value of v_0 will not give correct molecular size, in this case thermodynamic properties are not in good agreement with experiments(e.g. latent heat of vaporization or vapor pressure). This discrepancy can be solved by $2\rho_c = m(1 - d/b_c)/v_0$, if one fits the value of v_0 with a true value, then the value of d/b_c is determined at a critical temperature, so that the curves of $c_1(T)$ and $c_2(T)$, $L(T)$ and $p(T)$ are in good agreement with each experiment. Thus we will give a role of fitting parameter to the volume of molecule v_0. This is the advantage of our theory. The value of v_0 is not necessarily determined only within the frame of thermodynamics. We examine the Maxwell's equiareal rule as an integral of $p(T)$ over the range of V_l and V_g at a temperature written by

$$\int_{V_l}^{V_g} pdV = p(T)\int_{V_l}^{V_g} dV \qquad (25)$$

This rule is usually used to determine the vapor pressure , V_l and V_g at a desired temperature and holds on near the critical temperature, however, the coincidence of two values is not good in the low temperature near triple point when using $d = 9v_0/8$. On the other hand, this rule holds on well in our theory, if an appropriate value of v_0 is employed.(see figs.10 ~ 12).

Kamerlingh Onnes' constant is given by

$$K_m = p_c V_c \beta_c, \qquad (26)$$

$$= \frac{e_2}{2e_1^2}, \qquad (27)$$

where $e_1 = 1 - \rho_c v_0/m$ and $e_2 = 2e_1 - 1$. This is in good agreement with experimental value, for example, eq.(26) gives $K_m = 0.3412$ at $r = 2.200$A and $K_m =$
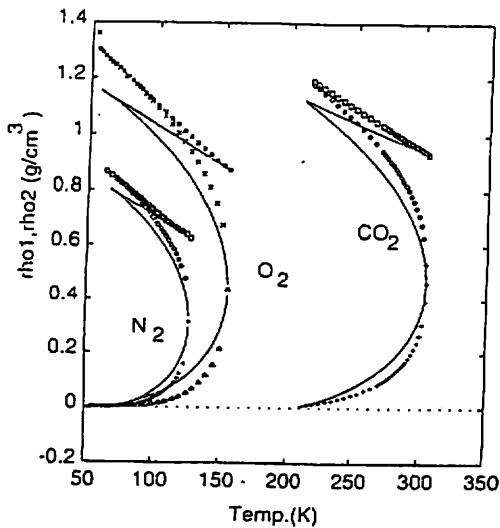
Fig. 5. Liquidus and gaseous line for N_2, O_2 and CO_2, when use eq.(24) as d/b_c, which is dependent on a molecular size. As shown in fig.(4), these are qualitatively in good agreement with experimental data. N_2: dashed and solid lines: calculation, □ and ×: experiments. O_2: dash-dotted and dashed lines: calculation, × and △: experiments. CO_2: dotted lines: calculation, ◇ and +: experiments.
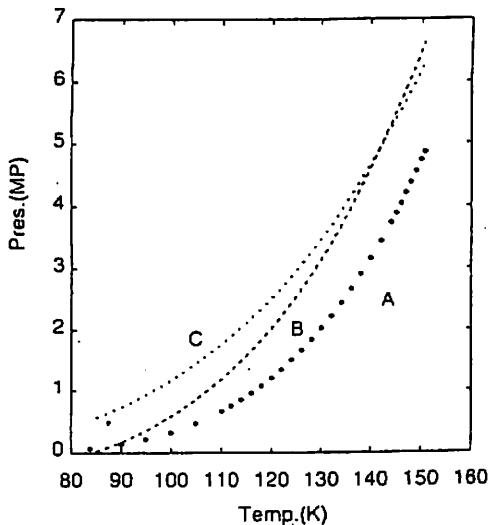

Fig. 6. The vapor pressure curves of Ar. (a) Experiments. (b) when use eq.(24) with r=2.105 A. (c) when use d/b_c = 1/3. When use r=2.105 A in eq.(24), the agreement is better than that of d/b_c = 1/3.

Fig. 7. The latent heat of vaporization of N_2, O_2 and Ar, when use d/b_c = 1/3. Dashed and solid lines:calcualtion from eq.(21). Bold lines: drawn from eq.(23). △,× and ⋆ : experiments.

Fig. 8. The molecular-size dependence of latent heat for N_2, O_2 and Ar drawn by eqs.(21) and (24). Dashed and solid lines: r=2.130 A for Ar, r=2.270 A for N_2 and r=2.140 A for O_2. The peculiar behavior, appears in low temperature region, which intends to diverge. Bold lines: r=2.105 A for Ar, r=2.222 A for N_2 and r=2.092 A for O_2.

0.2548 at r = 2.300A with eq.(24) for Ar, on the other hand, if one employs the relation of d = $9v_0/8$, then K_m = 0.375. Equation(26) also gives fairly good value for another substance and we conjecture that the interval of K_m and $\rho_c v_0/m$ are $0 < K_m < 0.5$ and $0 < \rho_c v_0/m < 0.5$, respectively.

We can construct the isotherms in pvT diagram from eqs.(8),(9) and (18)(see fig.13).

3. Result and Discussion

Negative pair-interaction energy averaged over all particles and its density dependence gives van der Waals' equation of state and that liquidus and gaseous line for
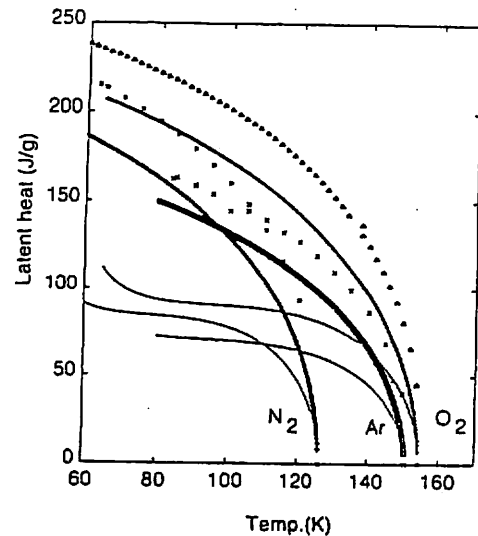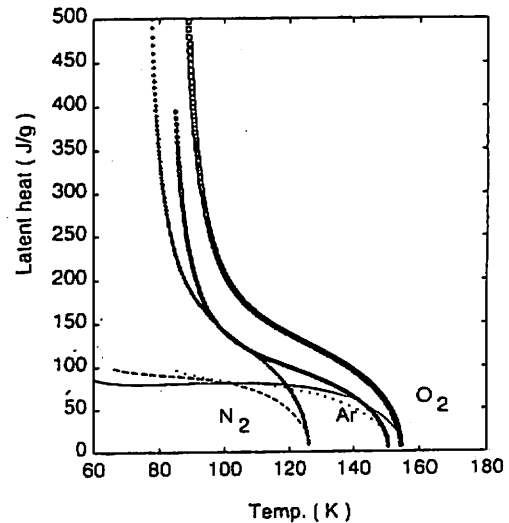
vapor-liquid phase are rigorously calculated from the e-quation of state. We found the existence of two phas-es of liquid and vapor and coexistent state through the canonical partition function with mean-field approach. The vapor, liquid and flat region phases are continuous-ly connected in phase diagram, thus we can identify the pvT diagram. The Percus-Yevick equation of state for the Lennard-Jones 6-12 potential derived not only from the compressibility for several isotherms but also from the pressure function is not in agreement with experi-mental data. Particularly in coexistent state of liquid and vapor this equation has no solution of experimen-tal flat region[18],[19]. Thermodynamic properties given by eq.(21) are less satisfactory in the latent heat of va-
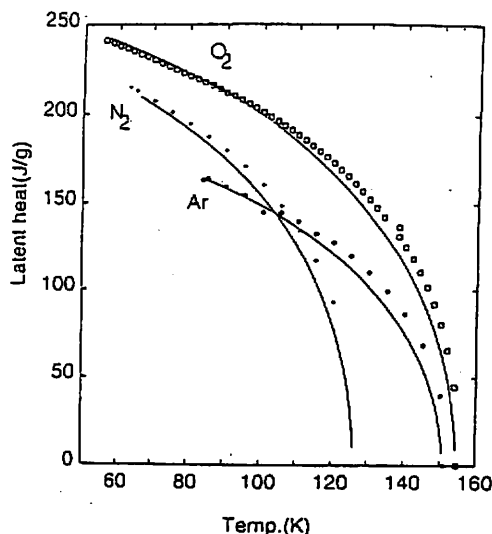
Fig. 9. The latent heat of vaporization of N_2, O_2 and Ar drawn by eqs.(23) and (24). r=2.105 A for Ar, r=2.222 A for N_2 and r=2.092 A for O_2, ○,+ and ×:experiments. Bold lines: drawn from eq.(23). These curves are in good agreement with experiments.
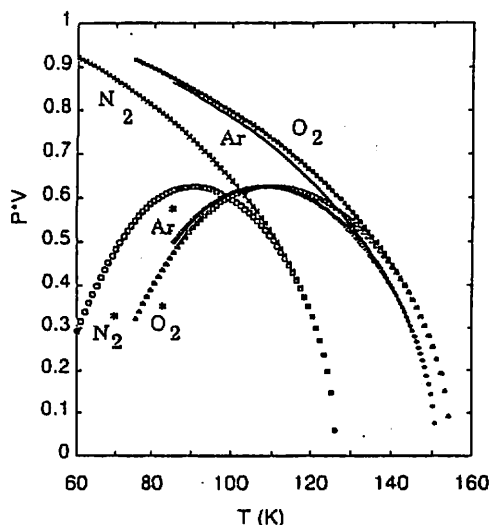

Fig. 10. The Maxwell's equiareal rule in eq.(25) with $d/b_c = 1/3$, apart from the factor β. This rule holds on near the critical temperature well, however this rule does not hold on in low temperature region. The curves denoted by asterisk means the left-hand side of eq.(25) and the other the right-hand side of eq.(25).

porization, which is smaller than the value calculated by empirical formula, however this results from the second law of thermodynamics. If the value of v_0 is conventionally employed by $\rho_c = m/(3v_0)$ in van der Waals' equation of state, then one obtains $d/b_c = 1/3$. However this value does not coincide with the value obtained from the relation $d/b_c = 1 - 2\rho_c v_0/m$ with appropriate value of v_0. The peculiar behavior in the latent heat of vaporization and Maxwell's equiareal rule disappear in the low temperature near triple point, if the appropriate value of v_0 is employed(see figs.9 and 11). The appropriate value of density along liquid and gaseous line should
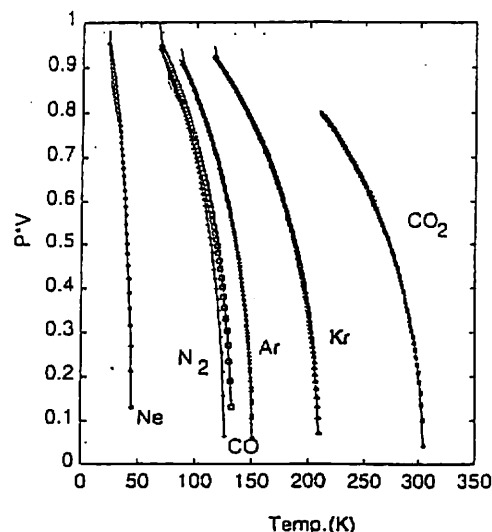

Fig. 11. The Maxwell's equiareal rule with eq.(24) and in eq.(25), apart from the factor β. This rule is satisfied in Ne, N_2, CO, Ar, Kr and CO_2 well, when r=2.126 A(Ar), 1.755 A(Ne), 2.282 A(Kr), 2.295 A(CO), 2.302 A(CO_2) and 2.258 A(N_2), respectively. If the suitable value of v_0 is employed, then a good agreement with experiments is obtained. Other substances shows good agreement with respective experiments, when the adequate values of v_0 are used.

be required for good agreement with experimental data precisely examined as shown in fig.8.

4. Conclusion

The computer simulation shows the attractive interaction as averaged energy over all particles and the density-dependence of pair-interaction energy in each phase. We showed alternative method deriving the equation of state both of liquid and vapor phases through mean field modeling with attractive type force. There have been some attempts with models, as seen in previous section, our theory will be a simple and one of the practical approximation methods. The liquidus and gaseous line in phase diagram are derived and is in good agreement with experimental data for several simple substance. We can identify the liquid, vapor and transition regions in the pvT diagram and the isotherms thus obtained are flat in the transition region and rise very rapidly with decreasing volume in the liquid phase. The vapor pressure is calculated and is somewhat higher than experimental value for simple substance in higher temperature, however in low temperature the pressure is fairly in good agreement with experiment for vapor pressure. It should be remarked that a critical temperature is concerned with structure of molecule, mass of molecule and the averaged magnitude of interaction energy a particle in the phase. The latent heat of vaporization obtained in eq.(21) is compared with experimental value and the agreement with experiment is not good (about half of experimental data), The heat of vaporization of eq.(23) is in good agreement with experimant. The discrepancy
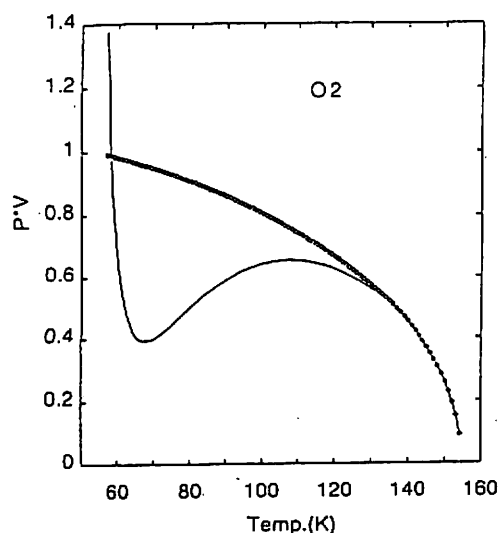
Fig. 12. The Maxwell's equiareal rule for O_2 in eq.(24) and (25), apart from the factor β. These curves do not satisfied the rule, even when r=2.129 A. This rule is fulfilled near the critical temperature, however does not hold on in low temperature. solid line: the left-hand side of eq.(25). o: the right-hand side of eq.(25).
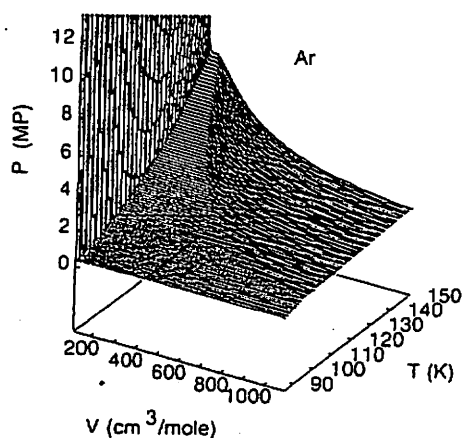

Fig. 13. The isotherms for Ar in pvT diagrams. One can identify the flat region of coexistence of vapor and liquid. Other substance reveals the same behavior as Ar.

between our results and experiments(or empirical formula) will indicate not to results from neglecting the interaction between particles in both phases but to result from the second law of thermodynamics. The thermodynamic properties are shown to be sensitive to the molecular size in this paper; if the equation $\rho_c = m/(3v_0)$ is used to determine the volume of molecule, this value does not coincide with other theory (e.g., quantum mechanics etc.), on the other hand, our theory has an advantage that one can employ correct values of critical density and molecular size in eq.(28). Liquidus and gaseous line, the latent heat of vaporization and Maxwell's equiareal rule should be satisfied by using suitable values of v_0, therefore we will have to reexamine these thermodynam-

ic values. Although our theory should be restricted to a system whose potential is of attractive type through the mean-field theory, by comparison of our results with experimental data, we conclude that such mean-field approach work more satisfactorily than those of previous work [1]~[3],[6]~[8],[10],[18]. If the interaction between particles is of repulsive type as shown in eqs.(5) and (6), we will predict the negative critical temperature from eq.(13). This remarkable result corresponds to the situation of ferromagnetism with Curie temperature and antiferromagnetism with Neel temperature in the second order phase transition of magnetism. Therefore we will show the classification of phase transition by whether the interaction between particles in fluid system is attractive or repulsive.

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