

## Gas-liquid phase transition II: The van der Waals' models

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MS received 7 June 1977; revised 22 August 1977

**Abstract.** On the basis of a recently proposed theory of first order phase transition we discuss (i) the exact equation of state in the critical region and (ii) examine the van der Waals' gas model.

**Keywords.** First order phase transition; Mayer clusters; isotherms van der Waals' gas; law of rectilinear diameter.

### 1. Introduction

In a recent paper (Biswas 1976) the author discussed a new approach to the problem of gas-liquid phase transition. The approach is based on the well-known Mayer expansion (Mayer and Mayer 1940) of the partition function. The important features of the theory are:

1. The necessary condition for a first order phase transition\* is that there exists a *physical* solution  $\rho = \rho_0$  of the equation

$$\frac{\partial^2 \tilde{\phi}}{\partial \rho^2} = 0 \quad (1)$$

where

$$\tilde{\phi} = \text{Lt}_{\substack{V \rightarrow \infty \\ N/V = \rho}} \frac{1}{V} \log Q(\beta, N, V) \quad (2)$$

$Q(\beta, N, V)$  being the canonical partition function (Notations in this paper are the same as in (Biswas 1976) referred to as paper I).

2. The sufficient condition for a first order phase transition is that there exists a temperature  $T_c$  below which all Mayer clusters  $b_l$  are positive.

3. If there is *only one* physical solution of eq. (1) then the isotherms of the systems are given by

$$\left. \begin{aligned} \frac{P}{\mathcal{H}T} &= \sum_{l=1}^{\infty} \bar{g}_l \bar{z}^l \\ \rho &= \sum_{l=1}^{\infty} l \bar{g}_l \bar{z}^l \end{aligned} \right\} \bar{z} < 1 \quad (3)$$

\*In this paper by 'phase transition' we shall mean phase transition with a critical point.

$$\left. \begin{aligned} \frac{P}{\mathcal{K}T} &= \sum_{l=1}^{\infty} \bar{g}_l \\ \rho_G &= \sum_{l=1}^{\infty} l \bar{g}_l \leq \rho \leq \rho_L = 2\rho_0 - \sum_{l=1}^{\infty} \bar{g}_l \end{aligned} \right\} \bar{z}=1 \quad (4)$$

$$\left. \begin{aligned} \frac{P}{\mathcal{K}T} &= 2\rho_0 \log \bar{z} + \sum_{l=1}^{\infty} \bar{g}_l \left(\frac{1}{\bar{z}}\right)^l \\ \rho &= 2\rho_0 - \sum_{l=1}^{\infty} l \bar{g}_l \left(\frac{1}{\bar{z}}\right)^l \end{aligned} \right\} \bar{z} > 1 \quad (5)$$

where  $P$ =pressure,  $\rho$ =density,  $T$ =temperature, and  $\rho_G, \rho_L$ =gas and liquid specific densities of coexistence respectively,

$$\bar{g}_l = \lim_{V \rightarrow \infty} \frac{1}{V} g_l(V, T)$$

$$g_l = b_l z_0^l$$

$z_0$ =radius of convergence of the series  $\sum_{l=1}^{\infty} b_l z^l$ ,  $z$  being the fugacity and  $\bar{z}=z/z_0$

The relations (3), (4) and (5) give respectively the isotherms for the gas, saturated vapour and the liquid phases.

We also have from (4)

$$\rho_G + \rho_L = 2\rho_0 \quad (6)$$

The purpose of this article is to examine the well-known van der Waals' model for gas-liquid phase transition in the context of our theory. We shall particularly concern ourselves with the existence and temperature dependence of  $\rho_0$  in these models. Before we proceed to do that we shall discuss the existence of  $\rho_0$  in the context of the general Mayer theory.

## 2. Existence of $\rho_0$

In our theory  $\rho_0$  is given by the physical solution of eq. (1) which is equivalent to

$$\left. \frac{\partial P}{\partial \rho} \right|_{\rho=\rho_0} = 0 \quad (7)$$

where  $P(\rho)$  is the pressure expressed as a function of density in the low density region.

We start from the Mayer expansion of  $P(\rho)$  (Mayer and Mayer 1940) (see section 3 below) namely

$$P(\rho) = \rho - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k \rho^{k+1} = \rho \left[ 1 - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k \rho^k \right] \tag{8}$$

where  $\beta_k$ 's are the irreducible Mayer clusters.  $\rho_0$  is given by the solution of the equation

$$\sum_{k=1}^{\infty} k \beta_k \rho_0^k = 1. \tag{9}$$

Let us note that in the Mayer theory of condensation (Mayer and Mayer 1940) eq. (9) presumably defines the density at which condensation actually takes place (i.e.  $\rho_0$  is identified with  $\rho_G$ ). According to our theory condensation takes place at a density  $\rho_G < \rho_0$ .  $\rho_0$  equals the diameter  $\frac{1}{2}(\rho_G + \rho_L)$  for  $T \leq T_c$  and becomes equal to the critical density  $\rho_c$  at the critical temperature  $T_c$ .

We shall now prove the following theorem:

*Theorem.* If for  $0 \leq T < T_c$  all the irreducible cluster  $\beta_k$ 's are positive, the system has one and only one first order phase transition.

*Proof.* Let us define

$$f(\rho) = 1 - \sum_{k=1}^{\infty} k \beta_k \rho^k \tag{10}$$

and make the following observations regarding the functions  $P(\rho)$  and  $f(\rho)$  represented by the series on the r.h.s. of (8) and (10) respectively.

*Observations.* Let  $\beta_k > 0$  for all  $k$  then,

1. The series (8) and (10) have the same radius of convergence  $R$  given by

$$\lim_{k \rightarrow \infty} (k \beta_k)^{-1/k} = \lim_{k \rightarrow \infty} \left( \frac{k}{k+1} \beta_k \right)^{-1/k} = R$$

2. Both  $P(\rho)$  and  $f(\rho)$  are analytic functions of  $\rho$  for  $0 \leq \rho < R$ .
3. At  $\rho=0$ ,  $P(0)=0$ ,  $f(0)=1$ . At  $\rho=R$ ,  $P(R)$  and  $f(R)$  both have negative signs (This is true even though  $\rho=R$  is a point of singularity of these functions).
4. From (10)  $\frac{\partial f}{\partial \rho} = - \sum_{k=1}^{\infty} k^2 \beta_k \rho^{k-1} < 0$  for  $\rho > 0$ .

Hence  $f(\rho)$  is a monotonic decreasing function of  $\rho$  and hence  $f(\rho)$  vanishes only once i.e.  $\rho_0$  is unique (see figure 1).

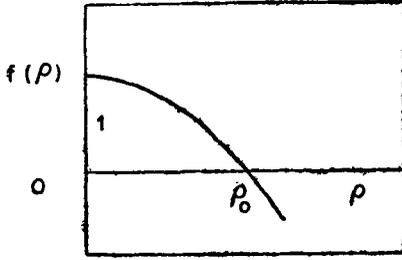
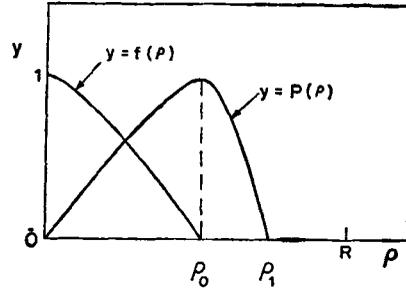


Figure 1. Qualitative form of  $f(\rho)$  as a function of  $\rho$ .



Figures 1-2. Qualitative forms of  $f(\rho)$  and  $P(\rho)$  as functions of  $\rho$ .

5. Since at  $\rho = \rho_0$ ,  $\partial P / \partial \rho = f(\rho) = 0$  and  $\partial^2 P / \partial \rho^2 = \partial f / \partial \rho < 0$  we have  $P(\rho)$  has a unique point of maximum at  $\rho = \rho_0$  (see figures 1-2).

6. The function  $P(\rho) > 0$  for  $0 < \rho < \rho_1$  and vanishes at  $\rho = \rho_1$  such that  $0 < \rho_0 < \rho_1 < R$  (see figures 1-2). The density  $\rho_1$  in fact, corresponds to the close-packed density.

From the above observations we conclude that (i) eq. (7) has a unique solution  $\rho = \rho_0$  in the whole density range and (ii) the series (8) representing  $P(\rho)$  loses its physical meaning for  $\rho > \rho_0$ . This follows from the fact that in the neighbourhood of  $\rho = \rho_0$ ,  $P(\rho)$  is given by

$$P(\rho) = P(\rho_0) + \frac{(\rho - \rho_0)^2}{2!} \left. \frac{\partial^2 P}{\partial \rho^2} \right|_{\rho = \rho_0} \tag{11}$$

and since  $\left. \frac{\partial^2 P}{\partial \rho^2} \right|_{\rho = \rho_0} < 0$  we have  $P(\rho_0 + \epsilon) < P(\rho_0)$  where  $\epsilon$  is a small positive

quantity. Hence the thermodynamic stability condition is violated at  $\rho = \rho_0$  (see Biswas 1976) (Obviously van Hove's theorem does not hold for  $\rho > \rho_0$ ). The system, therefore, can have only one first order phase transition at a density less than  $\rho_0$ .

We next observe that since the cluster integral  $b_l$  is given by

$$b_l = \frac{1}{l^2} \sum_{\{n_k\}} \prod_k \frac{(l\beta_k)^{n_k}}{n_k!}, \quad \sum_k kn_k = l - 1 \tag{12}$$

we have if  $\beta_k$ 's are all positive  $b_l$ 's are also positive for all  $l$ . Hence by the theorem proved in paper I the system does undergo a first order phase transition.

*Remark.* Though there does not exist any general proof, the numerical calculations indicate beyond doubt that all the  $\beta_k$ 's for a Lennard-Jones potential are positive at very low temperatures (Hirschfelder *et al* 1954, Barker *et al* 1966). This implies that according to our theory a Lennard-Jones gas undergoes only one first order phase transition.

### 3. The critical region

In this section we shall try to analyse the critical region on the basis of the equations of state derived from (3), (4) and (5).

Equations (3) are the usual Mayer equations for the gas phase, i.e.

$$\frac{P}{\mathcal{H}T} = \sum_{l=1}^{\infty} b_l z^l \tag{13}$$

$$\rho = \sum_{l=1}^{\infty} l b_l z^l. \tag{14}$$

It is known that one can invert (14) to get

$$z = \rho \exp \left( - \sum_{k=1}^{\infty} \beta_k \rho^k \right) \tag{15}$$

and substituting (15) in (13) one gets the well-known gas-phase equation of state

$$\frac{P}{\mathcal{H}T} = \rho - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k \rho^{k+1}. \tag{16}$$

Now let us take eqs (5) which can be written for  $z > z_0$  as

$$\frac{P}{\mathcal{H}T} = 2\rho_0 \log \frac{z}{z_0} + \sum_{l=1}^{\infty} b_l \left( \frac{z_0^2}{z} \right)^l \tag{17}$$

$$\rho = 2\rho_0 - \sum_{l=1}^{\infty} l b_l \left( \frac{z_0^2}{z} \right)^l. \tag{18}$$

We can write (18) as

$$\hat{\rho} = 2\rho_0 - \rho = \sum_{l=1}^{\infty} l b_l \left( \frac{z_0^2}{z} \right)^l. \tag{19}$$

Comparing (19) with (14) we have

$$\frac{z_0^2}{z} = \hat{\rho} \exp \left( - \sum_{k=1}^{\infty} \beta_k \hat{\rho}^k \right). \tag{20}$$

Substituting (20) in (17) we have

$$\frac{P}{\mathcal{H}T} = 2\rho_0 \log \frac{z_0}{\hat{\rho}} + 2\rho_0 \sum_{k=1}^{\infty} \beta_k \hat{\rho}^k + \hat{\rho} - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k \hat{\rho}^{k+1} \tag{21}$$

which gives the equation of state for the liquid phase.

We shall now show that  $\rho = \rho_0$  is a point of true minimum of the liquid pressure defined by (21). From (21) we have

$$\frac{\partial P}{\partial \hat{\rho}} = -\frac{\partial P}{\partial \rho} = -\frac{2\rho_0}{\hat{\rho}} + 2\rho_0 \sum_{k=1}^{\infty} k \beta_k \hat{\rho}^{k-1} + 1 - \sum_{k=1}^{\infty} k \beta_k \hat{\rho}^k. \tag{22}$$

For  $\rho = \rho_0$ ,  $\hat{\rho} = 2\rho_0 - \rho_0 = \rho_0$ .  
 Substituting  $\hat{\rho} = \rho_0$  in (22) we have

$$\frac{\partial P}{\partial \rho} = -2 + 2 \sum_{k=1}^{\infty} k \beta_k \rho_0^{k-1} + 1 - \sum_{k=1}^{\infty} k \beta_k \rho_0^k = 0 \text{ due to (9).}$$

Again

$$\frac{\partial^2 P}{\partial \rho^2} = \frac{\partial^2 P}{\partial \hat{\rho}^2} = \frac{2\rho_0}{\hat{\rho}^2} + 2\rho_0 \sum_{k=1}^{\infty} k(k-1)\beta_k \hat{\rho}^{k-2} - \sum_{k=1}^{\infty} k^2 \beta_k \hat{\rho}^{k-1} \text{ so that at } \rho = \rho_0$$

we have due to (9)

$$\begin{aligned} \frac{\partial^2 P}{\partial \rho^2} &= \frac{2}{\rho_0} + 2 \sum_{k=1}^{\infty} k^2 \beta_k \rho_0^{k-1} - 2 \sum_{k=1}^{\infty} k \beta_k \rho_0^{k-1} \\ &= \sum_{k=1}^{\infty} k^2 \beta_k \rho_0^{k-1} = \sum_{k=1}^{\infty} k^2 \beta_k \rho_0^{k-1} > 0 \end{aligned} \tag{23}$$

since  $\beta_k > 0$  for all  $k$ .

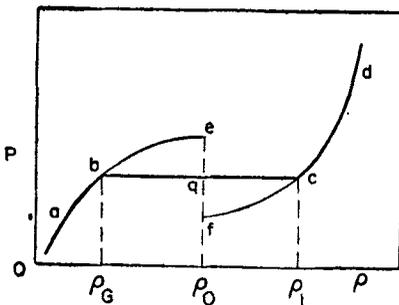


Figure 3. An isotherm below  $T_c$ .

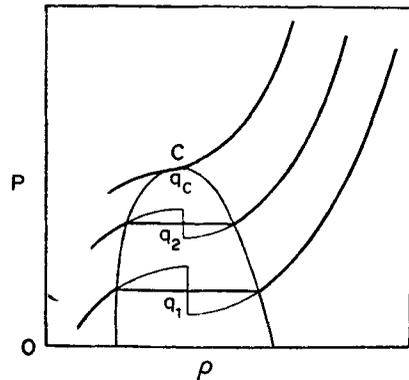


Figure 4. Isotherms below  $T_c$  and at  $T_c$ .

A typical isotherm for  $T < T_c$  is shown in figure 3. The curves *ab*, *bc* and *cd* represent respectively the gas, the saturated vapour and the liquid phases. The curves *be* and *cf* represent respectively the supercooled vapour and the superheated liquid. These are obviously states of metastable equilibrium. The locus of the point *q* as the temperature varies in the interval  $0 \leq T \leq T_c$  gives the diameter of the critical region (figure 4).

The virial series (16) does not have any singularity up to  $\rho = \rho_0$  where the stability region gets saturated. The phase transition, however, takes place at the point *b* where the fugacity series (13) and (14) encounter a singularity on the real positive axis. The fact that the virial series can be continued up to  $\rho = \rho_0$  from both sides indicate that the metastable phases *be* and *cf* are physically realisable in a thermodynamically continuous fashion. These states are, however, unstable to even the slightest of perturbations. (See Landau and Lifshitz (1969) for a discussion of metastable states).

#### 4. van der Waals' gas

The pioneering van der Waals' equation of state which marked the first significant step towards an understanding of the problem of gas-liquid phase transition was given hundred years back (van der Waals 1873). Our qualitative understanding of the problem is still very much confined to this equation. The equation was arrived historically as a phenomenological equation but there have been serious attempts at understanding the equation on the basis of the microscopic theory (Ornstein 1908, Uhlenbeck 1962, Smith and Alder 1959). It is now known that this equation can be derived as some sort of a mean field approximation of the partition function. To be specific let

$$Q(\beta, N, V) = \frac{1}{N!} \int \dots \int_V \exp \left[ -\beta \sum_{i>j} \phi(\mathbf{r}_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (24)$$

be the partition function (in usual notations) and let  $g(r, \rho, T)$  be the two particle distribution function (see Munster 1969). We know from Mayer's theory that  $g(r, \rho, T)$  can be written as a density expansion in the form

$$g(r, \rho, T) = g_0(r, T) + \rho g_1(r, T) + \dots \quad (25)$$

For a potential with hard core radius  $r_0$  and an attractive tail one can write (see Uhlenbeck 1962) (24) as

$$Q = \frac{1}{N!} \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N \prod_{ij} S(\mathbf{r}_{ij}) \exp \left[ -\beta \sum_{i>j} \phi_{\text{attr}}(\mathbf{r}_{ij}) \right] \quad (26)$$

where

$$\begin{aligned} S(\mathbf{r}_{ij}) &= 1 && \text{for } |\mathbf{r}_{ij}| > 2r_0 \\ &= 0 && \text{for } |\mathbf{r}_{ij}| < 2r_0 \end{aligned} \quad (27)$$

Let us now replace the attractive potential  $\sum_{i>j} \phi_{\text{attr}}(\mathbf{r}_{ij})$  by its mean value

$$\begin{aligned} \langle \sum_{i>j} \phi_{\text{attr}}(\mathbf{r}_{ij}) \rangle &= \frac{N(N-1)}{2} \langle \phi_{\text{attr}}(r) \rangle \\ &= \frac{N(N-1)}{2V} \int \phi_{\text{attr}}(r) g(r, \rho, T) dr \end{aligned} \quad (28)$$

van der Waals' equation is obtained if one writes

$$\int \phi_{\text{attr}}(r) g(r, \rho, T) dr = -a \quad (29)$$

where  $a$  is a positive constant (see Uhlenbeck, 1962 for details). Note that in terms of density expansion it amounts to retaining only the first term in (25). It is this truncation which leads to the well-known van der Waals' instability. In this approximation the attractive part of the interaction appears only in the second virial coefficient whereas all higher virial coefficients are the same as those for a hard sphere gas. The resulting van der Waals' equation for the isotherms is given by

$$P = \frac{\mathcal{K}T\rho}{1-b\rho} - a\rho^2 \quad (30)$$

where  $a$  and  $b$  are positive constants being respectively the measure of the strength of the attractive part of the interaction and the hard core volume.

The Mayer irreducible cluster  $\beta_k$ 's are given in this model by

$$\left. \begin{aligned} \beta_1 &= 2 \left( \frac{a}{\mathcal{K}T} - b \right) \\ \beta_k (k \geq 2) &= -\frac{k+1}{k} b^k \end{aligned} \right\} \quad (31)$$

### Remark 2

From (27) we see that in this model only  $\beta_1$  becomes positive at low temperatures whereas all the higher  $\beta_k$ 's are negative. It is obvious that this is because in the van der Waals' approximation the attractive part of the interaction appears only in  $\beta_1$  whereas all the higher  $\beta_k$ 's are the same as those due only to the repulsive part of the interaction. One can see from (21) and (24) that if in the mean field description one writes

$$\langle \phi_{\text{attr}}(r) \rangle = \sum_{n=0}^{\infty} C_n(\tau) \rho^n [C_n > 0 \text{ for all } n] \quad (32)$$

and retains terms in all powers of  $\rho$  then the pressure  $P$  will be given by

$$P = \frac{\mathcal{K}T\rho}{1-b\rho} - \sum_{n=0}^{\infty} C_n \rho^{n+2} \quad (33)$$

so that

$$\beta_k = \frac{k+1}{k} \left[ \frac{c_{k-1}}{\mathcal{H}T} - b^k \right] \tag{34}$$

and there exists a temperature range near  $T = 0$  where all  $\beta_k$ 's are positive. In what follows we shall, however, concern ourselves with the van der Waals' model given by (30).

If one plots the  $P-\rho$  isotherm from (30) one gets with the help of Maxwell's construction the isotherms which have all the characters as possessed by the exact isotherms shown in figure 3. The van der Waals' isotherms, of course, also includes as unstable region  $e'f'$  below  $T_c$  (figure 5).

It is, therefore, not surprising that the van der Waals' model represents so well the qualitative forms of the gas-liquid isotherms. The part of the isotherm beyond  $e'$  (figure 5) has got no theoretical foundation. The saturated vapour and the liquid isotherms should in fact be calculated from (4) and (21) respectively by using the relevant values of  $\beta_k$ 's and  $b_i$ 's.

In what follows we shall concern ourselves mainly with the existence of  $\rho_0$  and its specific temperature dependence as given by the van der Waals' model. In this context, we shall try to comment on the so-called law of rectilinear diameter.

Since the Mayer cluster  $b_l$  is given by

$$b_l = \frac{1}{l^2} \sum_{\{n_k\}} \prod_k \frac{(\beta_k)^{n_k}}{n_k}, \quad \sum_k kn_k = l-1 \tag{35}$$

we see from (31) that all  $b_i$ 's become positive at very low temperatures where  $\beta_1$  term dominates all the other terms involving higher  $\beta_k$ 's (see appendix). The model therefore satisfies the sufficient condition for phase transition in our theory.

From (30) equation for  $\rho_0$  is given by

$$\frac{\partial P}{\partial \rho} = \frac{\mathcal{H}T}{(1-b\rho_0)^2} - 2a\rho_0 = 0 \tag{36}$$

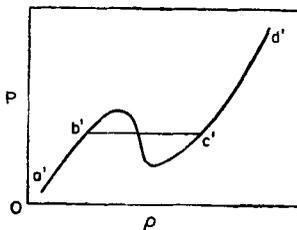


Figure 5. van der Waals' isotherm below  $T_c$ .

putting  $b\rho_0 = x$  we have

$$2 \frac{a}{b} x (1-x)^2 = \mathcal{X}T$$

or

$$x (1-x)^2 = \frac{b\mathcal{X}T}{2a} \quad (37)$$

we have to seek solution of (37) in the range  $0 \leq x \leq 1$ .

Let us make the substitution

$$y = x - \frac{1}{3} \quad (38)$$

in (37) and we should have

$$-\frac{1}{3} \leq y \leq \frac{2}{3} \quad (39)$$

equation (37) becomes

$$y^3 - y^2 + \frac{4}{27} \left[ 1 - \frac{27\mathcal{X}bT}{8a} \right] = 0. \quad (40)$$

One can easily verify that eq. (40) cannot have a real solution satisfying (39) for  $\mathcal{X}T > 8a/27b$ . This determines the critical temperature

$$T_c = 8a/27b \quad (41)$$

At  $T=T_c$ ,  $Y=0$  or 1. Only  $y=0$  corresponds to a physical solution. This gives

$$\rho_c = 1/3b \quad (42)$$

Let us write (40) as

$$y^3 - y^2 + \frac{4}{27} \left[ \frac{T_c - T}{T_c} \right] = 0. \quad (43)$$

For  $|(T_c - T)/T_c| \ll 1$  we have  $y \simeq 0$ , hence we can neglect  $y^3$  compared to  $y^2$  to get

$$|y| \simeq \left( \frac{4}{27} \right)^{\frac{1}{2}} \left( \frac{T_c - T}{T_c} \right)^{\frac{1}{2}}. \quad (44)$$

We get

$$\frac{|\rho_0 - \rho_c|}{\rho_c} \propto \left( \frac{T_c - T}{T_c} \right)^{\frac{1}{2}} \quad (45)$$

We note that this model does give a singularity of  $d\rho_0/dT$  at  $T = T_c$  and does not lead to the law of rectilinear diameter.

This qualitatively agrees with the recent views that the law of rectilinear diameter is violated near  $T_c$  (Widom and Rowlinson 1970, Mermin 1971, Green 1971, Raja Gopal 1974). The numerical value  $\frac{1}{2}$  of the exponent, and the multiplicity of the solution, however, are results of the van der Waals' approximation. We have discussed above that van der Waals' approximation is very crude from microscopic point of view. It is not even a mean field approximation to the partition function. The numerical value  $\frac{1}{2}$  of the exponent in (45) is therefore physically unreliable. A definite conclusion regarding the precise temperature dependence of  $\rho_0$  can only be arrived at by a rigorous calculation of  $\rho_0$  from (9) retaining in all the  $\beta_k$ 's contributions from the repulsive as well as the attractive part of the interaction.

## 5. Discussion

We have discussed above the general features of the gas-liquid isotherms on the basis of a recent theory of first order phase transition proposed by the author. The purpose is to stress that a lot of information can be derived by knowing the temperature dependence of the Mayer clusters  $b_i$ 's and  $\beta_k$ 's. We encourage, therefore, that a detailed study of these functions is possible. We have compared the isotherms obtained from our theory with those of the van der Waals' gas. There is an interesting similarity of these curves. If one does not care for a rigorous foundation of van der Waals' model, the model as a phenomenological theory (along with the Maxwell's construction) represents qualitatively all the stable and metastable states of the system. As we have noted, van der Waals' model can be derived by a two-fold approximation of the partition function. The *first* one is to replace the attractive part of the interaction by its mean value. This if seriously done without making any truncation of the density series would not lead to the so called van der Waals' isotherms. But the second unphysical approximation namely retaining the attractive part of the interaction only in the second virial coefficient brings the part of the isotherm which look like that in the liquid state where the equation is not really valid. The model however is valid upon the critical density near the critical temperature. We have used this model to calculate the critical density and critical temperature on the basis of our theory. The critical values of these quantities are the same as those in the van der Waals' theory as, of course, expected. The quantity  $\rho_0(T)$ , however, has two values, whereas in a rigorous calculation we would have expected only one. We also see that  $d\rho_0/dT$  has a singularity at  $T = T_c$  and this violates the law of rectilinear diameter\*. It remains to be seen whether a rigorous calculation of  $\rho_0$  will retain this behaviour or not.

## Acknowledgement

My thanks are due to Virendra Singh for critical comments.

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\*An earlier paper by the author (1973 *Pramana* 1 109) in this connection was based on a theory which was revised later (see Biswas 1976).

### Appendix

We shall prove below that for the van der Waals' model the asymptotic  $b_l$ 's for large  $l$  are positive for  $\mathcal{X}T \leq 8a/27b$ .

*Proof:* For large  $l$  one can write (see Munster 1969, page 562)

$$l^2 b_l = \frac{\exp\left(l \sum_{k=1}^{\infty} \beta_k r^k\right)}{r^{l-1} \left[2\pi l \sum_{k=1}^{\infty} k^2 \beta_k r^k\right]^{\frac{1}{2}}}, \quad l \gg 1 \quad (\text{A.1})$$

where  $r$  satisfies

$$\sum_{k=1}^{\infty} k \beta_k r^k = 1 \quad (\text{A.2})$$

From (9) and (A.2) it is clear that  $r$  is identical to  $\rho_0$  defined in section 2.

With the values of  $\beta_k$ 's given by (31) this becomes

$$l^2 b_l = \frac{(1-br)^l \exp l \left[ \frac{2ar}{\mathcal{X}T} - \frac{br}{1-br} \right]}{r^{l-1} \left[ 2\pi l \left\{ \frac{2ar}{\mathcal{X}T} - \frac{2br}{(1-br)^3} \right\} \right]^{\frac{1}{2}}}. \quad (\text{A.3})$$

Hence all asymptotic  $b_l$ 's are positive if there exists a real positive  $r$  satisfying (A.2) and the condition.

$$0 < br \leq 1 - \left( \frac{b\mathcal{X}T}{a} \right)^{\frac{1}{3}}. \quad (\text{A.4})$$

Substituting the values of  $\beta_k$  in (A.2) the equation for  $br$  is obtained as

$$br(1-br)^2 = \frac{b\mathcal{X}T}{2a} \quad (\text{A.5})$$

which is exactly the eq. (37) to follow (see the text). We shall see that this equation does have a real solution satisfying (A.4) if (see (37) — (41) in the text)

$$\mathcal{X}T \leq \mathcal{X}T_c = 8a/27b \quad (\text{A.6})$$

Hence all asymptotic  $b_l$ 's are positive for  $\mathcal{X}T \leq 8a/27b$ .

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