

## The law of rectilinear diameter for the liquid-gas phase transition

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**Abstract.** A rigorous semi-microscopic derivation of the law of rectilinear diameter for the liquid-gas phase transition has been provided.

**Keywords.** Liquid, phase transition.

### 1. Introduction

The law of rectilinear diameter for the liquid-vapour equilibrium phase was discovered by Cailletet and Mathias in 1886. Since then it has been used by many experimentalists to measure the critical density. Apart from its intrinsic significance the law is of tremendous practical importance since the determination of the critical density by direct measurement is extremely difficult due to the fact that small changes in pressure produce large changes in density along the critical isothermal. A theoretical derivation of the law of rectilinear diameter, however, is missing except for a very specific lattice model (Lee and Yang 1952). Widom and Rowlinson (1970) suspected the validity of the law for continuum models. Recently, Cornfeld and Carr (1972) have provided strong experimental evidence supporting the validity of the law for continuum fluids.

### 2. Analysis

In what follows we propose to derive the law of rectilinear diameter from a recently developed theory (Biswas 1973) of the liquid-gas phase transition on the basis of Mayer's cluster expansion (Munster 1969). In fact it has been shown (Ruelle 1969) that for any stable potential  $\sum u(|r_i - r_j|)$  where the summation is carried out for  $i > j$  with the particles having hard repulsive cores the following theorem holds for a many-particle system.

*Theorem:* If there exists a temperature  $T = T_c$  at and below which all Mayer cluster  $b_l^1$ 's (except perhaps a finite number of them) are positive then a first order phase transition does occur and the isotherms for  $T \leq T_c$  are given as

$$\frac{p}{kT} = \sum_{l=1}^{\infty} g_l \bar{z}^l; \quad \frac{1}{v} = \sum_{l=1}^{\infty} l g_l \bar{z}^l \quad \text{for } \bar{z} < 1 \text{ defining the gas state.} \quad (1)$$

$$\frac{p}{kT} = \sum_{l=1}^{\infty} g_l; \rho_G = \left[ \sum_{l=1}^{\infty} l g_l \right] \geq \frac{1}{v} \geq \left[ 2\rho_0 - \sum_{l=1}^{\infty} l g_l \right] = \rho_L \quad (2)$$

for  $\bar{z}=1$  defining the saturated vapour region.

$$\frac{p}{kT} = 2\rho_0 \log \bar{z} + \sum_{l=1}^{\infty} g_l \left( \frac{1}{\bar{z}} \right)^l; \frac{1}{v} = 2\rho_0 - \sum_{l=1}^{\infty} l g_l \left( \frac{1}{\bar{z}} \right)^l \quad (3)$$

for  $\bar{z} > 1$  defining the liquid-state where  $g_l = b_l z_0^l$  and  $\bar{z} = z/z_0$  being the fugacity and  $z_0$ , the radius of convergence of the series  $\sum_{l=1}^{\infty} b_l \bar{z}^l$  for  $T \leq T_c$ ,  $p$  and  $v$  have the usual meaning of pressure and specific volume;

$$\rho_0 = \rho_0(T) = \lim_{V \rightarrow \infty} \frac{\bar{N}(V, T)}{V} \quad (4)$$

where  $\bar{N}(V, T)$  is defined as the least positive root of  $\mathcal{Z}(\bar{N}, V, T) = 0$  for a given volume  $V$  and temperature  $T$  (see Biswas 1973). Equivalently one can say that  $\bar{N}$  is the least number of particles contained in the volume  $V$  at temperature  $T$  at which the free energy becomes infinite.

From equation (2) it follows that

$$\frac{1}{2}[\rho_L + \rho_G] = \rho_0(T) \quad (5)$$

In principle one can evaluate  $\rho_0(T)$  by finding the least value of  $\mathcal{N} = \bar{N}$  for which

$$\mathcal{Z}(\mathcal{N}, V, T) = \frac{d^{\mathcal{N}}}{d\mathcal{N}} \exp \left( V \sum_{l=1}^{\infty} b_l x^l \right) / x = 0 \quad (6)$$

vanishes and then evaluate the limit  $\bar{N}(V, T)/V$  as  $V \rightarrow \infty$ . The existence of such a value of  $\bar{N}$  is ensured by the hard-core nature of the interaction at short distances.

### 3. Discussion

In this note, however, we are more interested in finding the qualitative nature of the relation (5) from the microscopic point of view and as such we shall calculate  $\rho_0(T)$  from a van der Waal's type approximation of the partition function. We shall be interested in determining  $\rho_0$  in the neighbourhood of  $T = T_c$  (the critical temperature) to the lowest order in  $T_c - T$ . Since, the relation (5) has been derived from a rigorous microscopic theory, by a van der Waal's type calculation (which is exact upto the second virial coefficient) of  $\rho_0(T)$  we do not sacrifice any essential qualitative feature of the physical system. In this approximation it is easy to see (Mandle 1971) that

$$\mathcal{Z}(\mathcal{N}, V, T) \simeq \left( 1 - \frac{\mathcal{N}}{V} B(T) \right)^{\mathcal{N}} \quad (7)$$

so that

$$\rho_0(T) \simeq 1/B(T) \quad (8)$$

where

$$B(T) = 2\pi \int_0^{\infty} dr r^2 \left[ 1 - e^{-\frac{u(r)}{kT}} \right] \quad (9)$$

is the second virial coefficient. For  $kT \gg u_0$  where  $u_0$  is the minimum value of the potential  $u(r)$

$$B(T) \simeq b - a/kT \quad (10)$$

$b$  and  $a$  are as defined by Mandl (1971). Now, again, rigorously speaking  $T_c$  should be determined from

$$\rho_0(T_c) = \sum_{l=1}^{\infty} l g_l(T_c)$$

We shall rather start with the assumption\* that the critical specific volume

$$v_c = 1/\rho_c = b(a-1)/a \quad (11)$$

where  $a$  is a number greater than unity and will be treated as a parameter. Then from equation (8) [ $\because \rho_0(T_c) = \rho_c$ ] we have

$$kT_c = aa/b \quad (12)$$

We now expand  $\rho_0(T)$  in the neighbourhood of  $T = T_c$  and retain only the lowest power of  $T - T_c$  getting

$$\rho_0(T) = \frac{-\frac{b}{a}kT_c}{1 - \frac{b}{a}kT_c} + \frac{\frac{b}{a}kT_c}{\left(1 - \frac{b}{a}kT_c\right)^2} \frac{T_c - T}{T_c} = \rho_c \left[ 1 + \frac{1}{a-1} \frac{T_c - T}{T_c} \right] \quad (13)$$

so that (5) becomes

$$\frac{1}{2}[\rho_L + \rho_G] = \rho_c \left[ 1 + \frac{1}{a-1} \frac{T_c - T}{T_c} \right] \quad (14)$$

giving the law of rectilinear diameter. The relation (14) has the unknown parameter  $a$ ; we find that  $a = 4.55$  fits reasonably well the experimental data obtained by Cornfeld and Carr (1972) for xenon as well as the experimental data for hydrogen obtained by Mathias *et al* (1921) (see Hirschfelder *et al* 1954). Note that in both these experimental results temperature is plotted in 'centigrade'. One should convert the temperature to 'absolute' scales before comparing with the formula (14).

## References

- Biswas A C (1973) *J Statist. Phys.* **7** 131  
 Cailletet and Mathias E (1886a) *C. R. Acad. Sci. Paris* **102** 1202  
 Cailletet and Mathias E (1886b) *J Phys.* **5** 549  
 Cailletet and Mathias E (1887) *C. R. Acad. Sci. Paris* **104** 1563  
 Cornfeld A B and Carr C Y (1972) *Phys. Rev. Lett.* **29** 28  
 Hirschfelder J O, Curtiss C F and Bird R B (1954) *Molecular theory of gases and liquids* (New York: John Wiley & Sons) see p 362 fig 5.2-3  
 Lee T D and Yang G N (1952) *Phys. Rev.* **87** 410  
 Mandl F (1971) *Statistical physics* (London: John Wiley & Sons) pp 203-205  
 Munster A (1969) *Statistical thermodynamics* Vol. 1 (New York: Academic Press)  
 Ruelle D (1969) *Statistical mechanics, Rigorous results* (New York: W A Benjamin Inc.)  
 Widom B and Rowlinson J S (1970) *J Chem. Phys.* **52** 1670

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\*Note that our critical parameters  $T_c$ ,  $v_c$  etc. have got no connection with the van der Waal's theory of condensation. However, the assumption (11) on the dependence of  $v_c$  on  $b$  has been intuitively guided by van der Waal's theory; the latter, of course, highly overestimates  $v_c$ .