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Gas-liquid phase transition*

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Abstract. A theorem has been proved giving a sufficient condition for a first order phase transition in a gas. The corresponding fugacity expansions for the isotherms in the different phases have been derived.

Keywords. Partition function; Massieu-Planck function; thermodynamic stability; grand partition function; first order phase transition; analytic continuation; thermodynamic limit; isotherms.

1. Introduction

The problem of gas-liquid phase transition has been known to be one of the most fundamental problems in theoretical physics. Though a good advance has been made in this direction in the last decade or so, the basic problem still remains. The question we ask ourselves here is "Given a many-particle system with an interaction function $\sum_{i>j} \phi(r_{ij})$ in equilibrium (i) can one give a sufficient condition that the system will undergo first order phase transition? (ii) the condition being satisfied what will be the forms of the isotherms in the saturated vapour phase and the liquid phase?" We start with the partition function given by

$$Q(\beta, N, V) = \frac{1}{N!} \int e^{-\beta \sum_{i>j} \phi(r_{ij})} dr_1 \ldots dr_N. \tag{1}$$

We put the thermal wave length equal to unity and in (1), $\beta = 1/KT$, T being the temperature; K the Boltzmann constant; N and V respectively are the number of particles and the total volume of the system.

We shall write (1) in terms of the generating function as derived by Mayer and Mayer (1940) namely

$$Q_N = Q(\beta, N, V) = \frac{1}{2\pi i} \oint_C \frac{e^{V\sum_{l=1}^{\infty} b_l(V,T)\zeta^l}}{\zeta^{N+1}} d\zeta \tag{2}$$

where $b_l(V, T)$ are the well-known cluster integrals and C is a closed contour

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around $\zeta = 0$ in the complex ζ-plane so that on C, $\sum_{l=1}^{\infty} b_l \zeta^l$ is convergent.

In dealing with the question of phase transition we must first enquire how the canonical Massieu-Planck function (Münster 1969) should behave at the point of a transition if any. This is discussed in detail by Münster (1969). The answer is that the canonical distribution to be physically meaningful should be thermodynamically stable with respect to fluctuations. At the point of a phase transition this stability breaks down. In that case for a given temperature there exists a density $\rho_0(\beta)$ beyond which the canonical partition function does not make sense. In fact for densities ρ greater than $\rho_0(\beta)$ the canonical ensemble does not lead to the same asymptotic average as the micro-canonical ensemble and hence is physically meaningless and the corresponding canonical partition functions should be omitted from the sum giving the Grand-Partition function of the system. This fact must be taken into account in formulating a theory of phase transition. The Grand Canonical Partition function for a system of particles in a finite volume V is thus a polynomial of degree $\bar{N}_0 = V\rho_0$ where ρ_0 is the density for which the canonical partition function becomes *unstable*. This number $\bar{N}_0$ is *not* the close-packed number and in fact must be much less than the later. This observation will bring a point of difference of our formulation in the next section in terms of the Grand Partition function from that of Lee and Yang (1952).

The second point of observation we make is that since the Grand-Partition function for *finite* V is a polynomial of degree $\bar{N}_0$ we must be able to find the Grand-Partition function for the whole complex fugacity plane before the thermodynamic limit (Ruelle 1969) is taken. This should be possible because if we know the polynomial in any part of the complex plane we can analytically continue it to any other part of the same complex plane. It is only when we take the thermodynamic limit that we should be able to see whether the free energy tends to different limits in different regions of the fugacity plane. The above observations will motivate the philosophy of the following analysis. We shall confine our discussion to systems which have (if any) only one phase transition.

2. The Massieu-Planck function

Let us define the functions ϕ_l by

$$\log Q(\beta, N, V) = N\phi_l(\beta, v, V) = V\tilde{\phi}_l(\beta, \rho, V). \tag{2}$$

We follow closely the notations of Münster. As has been discussed by Münster (1969) in detail the canonical partition functions $Q(\beta, N, V)$ has a domain of stability on the set $\{N\}$. This domain of stability is defined by the set $\{\bar{N}\}$ such that $\bar{N} = V\rho$, where ρ satisfies

$$\frac{\partial^2 \tilde{\phi}_l^{\infty}}{\partial \rho^2} < 0 \tag{3}$$

where

$$\tilde{\phi}_l^{\infty} = \mathrm{Lt}_{V\to\infty}\, \tilde{\phi}_l(\beta, N, V)$$

$$\frac{N}{V} = \rho. \tag{4}$$

The boundary of the domain of stability is given by

$$\frac{\partial^2 \tilde{\phi}_l^{\infty}}{\partial \rho^2} = 0. \tag{5}$$

Let $\rho_0(\beta)$ be the solution of (5). Then $\bar{N}_0 \simeq V\rho_0$ gives the largest value of N for which the canonical partition function is stable *with respect to statistical fluctuations.* The existence of a *finite* $\rho_0(\beta)$ is a necessary (but not sufficient) condition for phase transition. We shall assume in what follows that a *finite* $\rho_0(\beta)$ exists.

3. Grand-Partition function

Let $z = e^{\mu/KT}$ be the fugacity where μ is the chemical potential of the system. In terms of μ and z equation (5) is equivalent to the existence of a $z = z_0$ such that at $z = z_0$

$$\frac{\partial \mu}{\partial \rho} = \frac{\partial z}{\partial \rho} = 0. \tag{6}$$

Then we define the Grand-Partition function as

$$Z_{gr}(\beta, V, z) = \sum_{N \in \{\bar{N}\}} Q_N z^N = \sum_{N=0}^{\bar{N}_0} Q_N z^N \tag{7}$$

$$= \frac{1}{2\pi i} \oint_C \frac{1 - \left(\frac{z}{\zeta}\right)^{\bar{N}_0+1}}{1 - \left(\frac{z}{\zeta}\right)} e^{V \sum_{l=1}^{\infty} b_l(V, \beta)\, \zeta^l} \frac{d\zeta}{\zeta} \tag{8}$$

using (2).

Let $z_0(V)$ be the radius of convergence of the series $\sum_{l=1}^{\infty} b_l(V, \beta)\, z^l$ and we assume that

(i) $\mathrm{Lt}_{V\to\infty}\, z_0(V) = \bar{z}_0 > 0$ exists.

(ii) $\sum_{l=1}^{\infty} \bar{b}_l \bar{z}_0^{\,l}$ and $\sum_{l=1}^{\infty} l \bar{b}_l \bar{z}_0^{\,l}$ are finite.

where

$$\bar{b}_l = \mathrm{Lt}_{V\to\infty}\, b_l(V, \beta).$$

Then the function $Z_{gr}(\beta, V, z)$ is analytic for $|z| \leq z_0$ in the complex z-plane

Let us define $\bar{z} = z/z_0$ then

$$Z_{gr}(\beta, V, \bar{z}) = \frac{1}{2\pi i} \oint \frac{1 - \left(\frac{z}{\zeta}\right)^{\bar{N}_0+1}}{1 - \frac{\bar{z}}{\zeta}} e^{V \sum_{l=1}^{\infty} g_l(V, T)\, \zeta^l} \frac{d\zeta}{\zeta} \tag{9}$$

is analytic in the complex $\bar{z}$-plane in the domain $|\bar{z}| \leq 1$; on $\bar{C}$ in the complex ζ-plane $|\zeta| \leq 1$,

$$g_l(V, T) = b_l(V, T)\, z_0^{\,l}. \tag{10}$$

4. Thermodynamic pressure and density

We shall define the isothermal pressure p and the density ρ by the relations (Ruelle 1969)

$$\frac{p}{KT} = \mathrm{Lt}_{V\to\infty} \frac{1}{V} \log Z_{gr}(\beta, V, Z) \tag{11}$$

$$\rho = \mathrm{Lt}_{V\to\infty} \frac{\langle N\rangle}{V} = \mathrm{Lt}_{V\to\infty} \frac{1}{V} z \frac{\partial}{\partial z} \log Z_{gr}(\beta, V, z). \tag{12}$$

We have assumed above that the interaction $\sum_{i>j} \phi(r_{ij})$ satisfies the stability criterion (Ruelle 1969) and the limit in (11) and (12) is realised in the sense of Fisher (Ruelle 1969) which is a smoothness condition on sequences imagined in passing to the limit of infinite volume.

5. First order phase transition

Definition 1. We shall define a first-order phase transition in the above-defined system if at a fixed temperature T the density ρ becomes a discontinuous function of the fugacity z whereas the pressure p remains continuous. In this context we shall prove the following theorem.

THEOREM 1: *The sufficient condition that a first order phase transition occurs in the system is that there exists a temperature $T = T_c > 0$ below which all $b_l(V, T)$'s* (except perhaps a finite number of them) *are positive* for $V > V_0$, some finite value.

Proof.—The proof of the theorem consists of the following steps:

Lemma 1.—For $\bar{z} < 1$

$$\mathrm{Lt}_{V\to\infty} \frac{1}{V} \log Z_{gr}(\beta, V, \bar{z}) = \sum_{l=1}^{\infty} \bar{g}_l \bar{z}^l \tag{13}$$

where

$$\bar{g}_l = \mathrm{Lt}_{V\to\infty} g_l(V, T).$$

The relation (13) is well known (Mayer and Mayer 1960). We shall, however, rederive the same starting from (9) for the sake of completeness.

Proof.—We start from relation (9). We choose the real axis in the ζ-plane such that the phase of $\bar{z}$ is zero, *i.e.*, $\bar{z} = |\bar{z}|$. Since $\bar{z} < 1$, let us choose $\bar{C}$ to be the circle $|\zeta| = \bar{z}$ and substitute $\zeta = \bar{z}e^{i\theta}$ in (8) to get

$$Z_{gr}(\beta, V, \bar{z}) = \frac{1}{2\pi i} \oint_{|\zeta|=\bar{z}} \frac{1-\left(\frac{\bar{z}}{\zeta}\right)^{\bar{N}_0+1}}{1-\frac{\bar{z}}{\zeta}} e^{V\sum_{l=1}^{\infty} g_l \zeta^l} \frac{d\zeta}{\zeta} \tag{14}$$

i.e.,

$$Z_{gr}(\beta, V, \bar{z}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1-e^{-i(\bar{N}_0+1)\theta}}{1-e^{-i\theta}} e^{V\sum_{l=1}^{\infty} g_l \bar{z}^l e^{il\theta}} d\theta. \tag{15}$$

We now note that

$$\mathrm{Lt}_{\bar{N}_0\to\infty} \frac{1-e^{-i(\bar{N}_0+1)\theta}}{1-e^{-i\theta}} \to \delta(\theta)$$

where $\delta(\theta)$ is the Dirac delta. This immediately gives

$$\mathrm{Lt}_{V\to\infty} \frac{1}{V} \log Z_{gr}(\beta, V, \bar{z}).$$

$$= \sum_{l=1}^{\infty} \bar{g}_l \bar{z}^l \qquad \bar{z} < 1 \tag{16}$$

We assume that $\mathrm{Lt}_{V\to\infty} \sum g_l \bar{z}^l = \sum_{l=1}^{\infty} \bar{g}_l \bar{z}^l$. A sufficient condition for this interchange of the 'limit' and 'summation' to be possible has been discussed by Katsura (1963).

Hypothesis 1. Let

$$\exists_{T_c} \exists_{V_0} \forall_{T<T_c} \forall_{V>V_0} \; b_l(V, T) > 0 \quad \text{for all } l,$$

i.e.,

$$\exists_{T_c} \exists_{V_0} \forall_{T<T_c} \forall_{V>V_0} \; g_l(V, T) > 0 \quad \text{for all } l. \tag{17}$$

Observation 1. If hypothesis 1 is true then the series $\sum_{l=1}^{\infty} \bar{g}_l \bar{z}^l$ must have a singularity (Titchmarsh 1939) at $\bar{z} = 1$ in the complex $\bar{z}$-plane and hence the relation (16) does not hold for $\bar{z} \geq 1$. On the other hand since the series $\sum_{l=1}^{\infty} \bar{g}_l \bar{z}^l$ and its derivatives are analytic within the circle $|\bar{z}| = 1$, according to definition 1 the system does not have a phase-transition for $|\bar{z}| < 1$ and at $\bar{z} = 1$ equation (6) is satisfied defining the domain of stability of the system in the fugacity plane.

In order to find the correct series expansion for the Free Energy for $|\bar{z}| > 1$ we shall first find an analytic representation of the function $Z_{gr}(\beta, V, \bar{z})$ given by (9) in the region $|\bar{z}| \geq 1$ in such a way that the thermodynamic limit can be conveniently taken. As already noted such an analytic representation is possible in the complex z-plane before the thermodynamic limit is taken since $Z_{gr}(\beta, V, \bar{z})$ is then a polynomial in the $\bar{z}$-plane.

Lemma 2. For given V and $\bar{N}_0$ (may be very large but finite)

$$Z^{+}_{gr}(\beta, V, \bar{z}) = \frac{1}{2\pi i} \oint_{|\zeta| = \frac{1}{|\bar{z}|}} \frac{1-\left(\frac{\bar{z}}{\zeta}\right)^{\bar{N}_0+1}}{1-\frac{\bar{z}}{\zeta}} \, e^{V\sum_{l=1}^{\infty} g_l \zeta^l} \frac{d\zeta}{\zeta} \tag{18}$$

analytically represents $Z_{gr}(\beta, V, \bar{z})$ for $|\bar{z}| \geq 1$ in the complex $\bar{z}$-plane.

Proof. (i) We first note that $Z_{gr}(\beta, V, \bar{z})$ and $Z^{+}_{gr}(\beta, V, \bar{z})$ are analytic in the regions $|\bar{z}| \leq 1$ and $|\bar{z}| \geq 1$ respectively.

(ii) On the circle $|\bar{z}| = 1$

$$Z_{gr}(\beta, V, \bar{z}) \equiv Z_{gr}^{+}(\beta, V, \bar{z})$$

(iii) $1/\bar{z}$ is the *unique*-function except for a phase factor which transforms *homographically* (Copson 1935) all points *outside* the circle $|\bar{z}| = 1$ uniquely to those *inside* and those on the circle onto themselves (the point at infinity is chosen to be transformed due to symmetry, to the centre of the unit circle) in the complex $\bar{z}$-plane. [To be precise, if $|\zeta| = |R(\bar{z})|$ is the radius of the contour in (18) then the statements $|\bar{z}| \geq 1$ and $|R(\bar{z})| \leq 1$ should uniquely imply one another and $R(\infty) = 0$, this gives $R(\bar{z}) = 1/\bar{z}$].

Lemma 3. $\mathrm{Lt}_{V\to\infty} \dfrac{1}{V} \log Z_{gr}^{+}(\beta, V, \bar{z})$

$$= 2\rho_0 \log \bar{z} + \sum_{l=1}^{\infty} \bar{g}_l \left(\frac{1}{\bar{z}}\right)^l, \qquad \bar{z} > 1$$

where

$$\rho_0 = \mathrm{Lt}_{V\to\infty} \frac{\bar{N}_0}{V}. \tag{19}$$

Proof. As in Lemma 1 we shall again choose the real-axis in the ζ-plane such that the phase of $\bar{z}$ is zero. We then put in (18) $\zeta = 1/\bar{z}\, e^{i\theta}$ to get

$$Z_{gr}^{+}(\beta, V, \bar{z}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1 - (\bar{z}^2 e^{-i\theta})^{\bar{N}_0+1}}{1 - \bar{z}^2 e^{-i\theta}}\, e^{V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l e^{il\theta}}\, d\theta$$

$$= \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1 - (\bar{z}^2 e^{i\theta})^{\bar{N}_0+1}}{1 - \bar{z}^2 e^{i\theta}}\, e^{V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l e^{-il\theta}}\, d\theta$$

$$= \frac{1}{4\pi} \int_{-\pi}^{\pi} d\theta\, e^{V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \cos l\theta} \left[\cos \left\{V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \sin l\theta\right.\right.$$

$$\left.\times R_l \frac{1 - (\bar{z}^2 e^{-i\theta})^{\bar{N}_0+1}}{1 - \bar{z}^2 e^{-i\theta}}\right\} + \sin \left\{V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \sin l\theta\right.$$

$$\left.\left.\times I_m \frac{(1 - \bar{z}^2 e^{-i\theta})^{\bar{N}_0+1}}{1 - \bar{z}^2 e^{-i\theta}}\right\}\right] \tag{20}$$

(R_l = Real part and I_m = Imaginary part so that $x = R_l x + I_m x$).

Since $\cos l0 = 1 - 2\sin^2 l\theta/2$ from (20) we have after a bit of manipulation,

$$J(\beta, V, \bar{z}) = Z_{gr}^{+}(\beta, V, \bar{z})\,(\bar{z})^{-2\bar{N}_0}\, e^{-V\sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l}$$

$$= \frac{1}{4\pi}\int_{-\pi}^{\pi} G(\theta)\, e^{-2V\sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \sin^2\frac{l\theta}{2}}\, d\theta \tag{21}$$

where

$$G(\theta) = \Big\{\cos\,[Vf(\theta) + \bar{N}_0\theta] - \frac{1}{\bar{z}^2}\cos\,[Vf(\theta) + (\bar{N}_0 + 1)\,\theta]$$

$$-\left(\frac{1}{\bar{z}_0^{\,2}}\right)^{\bar{N}_0+1}\cos\,[Vf\,(\theta) - \theta] + \left(\frac{1}{\bar{z}_0^{\,2}}\right)^{\bar{N}_0+2}\Big\}$$

$$\times\left\{\left(1 - \frac{\cos\theta}{\bar{z}^2}\right)^2 + \frac{\sin^2\theta}{\bar{z}^4}\right\}^{-1} \tag{22}$$

with

$$f(\theta) = \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \sin l\theta$$

From (21)

$$\frac{1}{V}\log Z_{gr}^{+} = \frac{2\bar{N}_0}{V}\log\bar{z} + \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l + \frac{1}{V}\log J\,(\bar{N}_0, V)$$

or

$$\mathrm{Lt}_{V\to\infty}\frac{1}{V}\log Z_{gr}^{+} = 2\rho_0\log\bar{z} + \sum_{l=1}^{\infty} \bar{g}_l \left(\frac{1}{\bar{z}}\right)^l$$

$$+\ \mathrm{Lt}_{V\to\infty}\frac{1}{V}\log J\,(\bar{N}_0, V) \tag{23}$$

Proposition 1. $J\,(\bar{N}_0, V)$ is a non-zero positive quantity for any finite $\bar{N}_0$ and V.

Proof. This follows from the identity (21). Since Z_{gr}^{+} is a non-zero positive quantity as it is a polynomial consisting of a sum of positive definite terms for real $\bar{z} > 1$ and finite $\bar{N}_0$ and V, see (18),

Proposition 2.

$$\mathrm{Lt}_{V\to\infty}\frac{1}{V}\log J\,(\bar{N}_0, V) = 0.$$

Proof. We first note that for finite $\bar{N}_0$ and V, $G\,(\theta)$ is a continuous function of θ in the interval $-\pi \le \theta \le \pi$. Using the integral mean value theorem we have

$$J(\bar{N}_0, V) = \frac{G(\delta)}{2\pi} \int_{-\pi}^{\pi} d\theta \; e^{-2V \sum_{l=1}^{\infty} g_l \left(\frac{1}{z}\right)^l \sin^2 \frac{l\theta}{2}} \tag{24}$$

where δ is a value of θ in the interval $[-\pi, \pi]$ and a function of $\bar{N}_0$ and V.

Due to proposition 1, $G(\delta)$ is non-zero positive.

We write

$$J(\bar{N}_0, V) = G(\delta)\, U(V) \tag{25}$$

where

$$U(V) = \frac{1}{2\pi} \int_{0}^{\pi} d\theta \; e^{-2V \sum_{l=1}^{\infty} g_l \left(\frac{1}{z}\right)^l \sin^2 \frac{l\theta}{2}} \tag{26}$$

Since $g_l > 0$ for all l, we have (for $V > V_0$)

$$\sum_{l=1}^{\infty} g_l \left(\frac{1}{z}\right)^l \sin^2 \frac{l\theta}{2} \leq \left\{ \sum_{l=1}^{\infty} g_l \left(\frac{1}{z}\right)^l l^2 \right\} \frac{\theta^2}{4} \tag{27}$$

for all θ, and

$$\sum_{l=1}^{\infty} g_l \left(\frac{1}{z}\right)^l \sin^2 \frac{l\theta}{2} \geq g_1 \frac{1}{z} \sin^2 \frac{\theta}{2} \geq \frac{\theta^2}{\pi^2} \tag{28}$$

$$\left\{ -\pi \leq \theta \leq \pi,\; g_1 \frac{1}{z} = b_1 = 1 \right\}. \tag{28}$$

Hence

$$\frac{1}{2\pi} \int_{0}^{\pi} e^{-2V \left\{ \sum_{l=1}^{\infty} g_l \left(\frac{1}{z}\right)^l l^2 \right\} \theta^2} d\theta$$

$$\leq U(V) \leq \frac{1}{2\pi} \int_{0}^{\pi} e^{-\frac{2V\theta^2}{\pi^2}} d\theta \tag{29}$$

or

$$\frac{1}{2\pi}\, \theta \left(\pi \sqrt{2V \sum_{l=1}^{\infty} g_l \left(\frac{1}{z}\right)^l l^2} \right)$$

$$\leq U(V) \leq \frac{1}{2\pi} \frac{\theta(\pi\sqrt{2V})}{\sqrt{2V}} \tag{30}$$

where $\theta(x) = \int_0^x e^{-x^2} dx$ is the well-known error function.

We now note that

(i) $G(\delta)$ is a uniformly bounded *non-zero positive* quantity for all $\bar{N}_0$ and V.

(ii) The error function $\theta(x) \to 1$ as $x \to \infty$.

These immediately give from (30) and (25),

$$\mathrm{Lt}_{V\to\infty} \frac{1}{V} \log J(\bar{N}_0, V) = 0. \tag{31}$$

Hence lemma 3 is proved.

We can now derive expression for the isotherms from (13) and (19) using (11) and (12).

We get

$$\left.\begin{aligned} \frac{p}{KT} &= \sum_{l=1}^{\infty} \bar{g}_l \bar{z}^l \\ \rho &= \sum_{l=1}^{\infty} l \bar{g}_l \bar{z}^l \end{aligned}\right\} \quad \bar{z} < 1 \tag{32}$$

$$\left.\begin{aligned} \frac{p}{KT} &= 2\rho_0 \log \bar{z} + \sum_{l=1}^{\infty} \bar{g}_l \left(\frac{1}{\bar{z}}\right)^l \\ \rho &= 2\rho_0 - \sum_{l=1}^{\infty} l \bar{g}_l \left(\frac{1}{\bar{z}}\right)^l \end{aligned}\right\} \quad \bar{z} > 1. \tag{33}$$

To get the isotherms at $\bar{z} = 1$ we continue the isotherms from both sides to $\bar{z} = 1$ by Abel's theorem (Whittaker and Watson 1963) and then make use of relation (6).

$$\left.\begin{aligned} \frac{p}{KT} &= \sum_{l=1}^{\infty} \bar{g}_l \\ \rho_G &= \sum_{l=1}^{\infty} l \bar{g}_l \leq \rho \leq \rho_L = 2\rho_0 - \sum_{l=1}^{\infty} l \bar{g}_l \end{aligned}\right\} \quad \bar{z} = 1. \tag{34}$$

From (32), (33), (34) we see that a *first order phase transition* does take place and Theorem 1 is proved.

A typical isotherm for $T < T_c$ is shown in figure 1. The regions $\bar{z} < 1$, $\bar{z} = 1$ and $\bar{z} > 1$ characterise respectively the gas, saturated vapour and the liquid phases. ρ_G and ρ_L are respectively the gas and liquid specific densities of coexistence at equilibrium with the saturated vapour phase. The critical temperature is defined by vanishing of the order parameter $\rho_L - \rho_G$, *i.e.*, by the equation

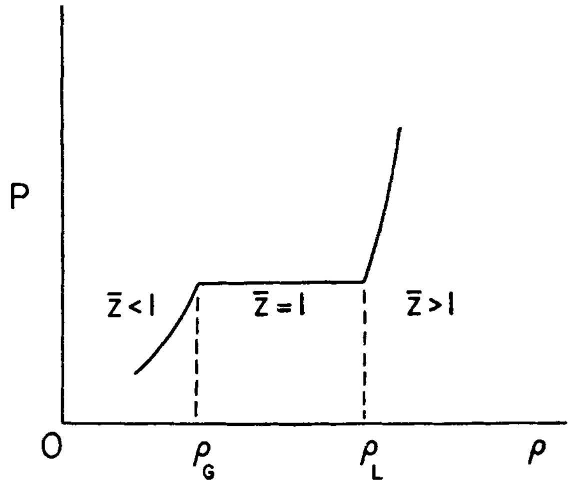

Figure 1. A typical isotherm for $T < T_0$.

$$\sum_{l=1}^{\infty} l\bar{g}_l(T_c) = 2\rho_0(T_c) - \sum_{l=1}^{\infty} l\bar{g}_l(T_c)$$

or

$$\sum_{l=1}^{\infty} l\bar{g}_l(T_c) = \rho_0(T_c) = \rho_C \tag{35}$$

where ρ_C is the critical density. We remember that ρ_0 is the solution of equation (5).

6. Discussion

The above considerations are valid for any potential $\sum_{i>j} \phi(r_{ij})$ which is stable, *i.e.*, there exists a $B \leq 0$ such that

$$\sum_{i>j} \phi(r_{ij}) \geq -nB \quad \text{for all} \quad n \geq 0. \tag{36}$$

It has been shown by Ruelle that under condition (36) the series $\sum_{l=1}^{\infty} \bar{b}_l z^l$ is convergent at least up to

$$z < e^{-2\beta B-1}[C(\beta)]^{-1} \tag{37}$$

where

$$C(\beta) = \int dk \mid e^{-\beta\phi(k)} - 1 \mid. \tag{38}$$

This means that the system does not have a phase transition in the region defined by (37). The region (37) defines the gas region. This also means that there is no phase transition at high temperature, since for small β the region (37) extends to the whole of the positive z-axis (*see* Ruelle 1969).

What we have shown above is that if below a certain temperature $T = T_c$ all b_l's are positive for large V, the system undergoes a first order phase transition (we have not discussed the case when a finite number of b_l's do not have a definite sign. However the generalisation to that case is not difficult).

The above discussion is qualitative and is not supposed to give a final answer to the problem. There remain the detailed investigations of the analytic properties of b_l's themselves which we have assumed to be true. This should be done in terms of some definite potential function satisfying (36). A quantitative test of the theory is possible. From (34) we have

$$\rho_L + \rho_G = 2\rho_0(\beta) \tag{39}$$

where $\rho_0(\beta)$ is determined by (5). For a realistic potential (39) should quantitatively describe the law of rectilinear diameter (Cailletet and Mathias 1886) when it holds good. One can also derive the following pressure-density relation for a liquid from (33)

$$\frac{p}{KT} = 2\rho_0 \log \frac{\bar{z}_0}{\hat{\rho}} + 2\rho_0 \sum_k \beta_k \hat{\rho}^{k+1} + \hat{\rho} - \sum_k \frac{k}{k+1} \beta_k \hat{\rho}^{k+1} \tag{40}$$

where β_k are the irreducible Mayer cluster integrals, $\hat{\rho} = 2\rho_0 - \rho$, ρ being the density of the liquid; $\bar{z}_0$ is as defined in section 3 (i). One can quantitatively test (40) with a realistic potential for a given liquid.

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