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On the Gas–Liquid Phase Transition

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A new approach to the problem of the gas-liquid phase transition, based on the Mayer cluster expansion of the partition function, is proposed. It is shown that the necessary and sufficient condition for phase transition to occur is that there exist a temperature $T = T_c > 0$ such that for $T \leqslant T_c$, all the $\bar{b}_l$ (except perhaps a finite number of them) are positive, where the $\bar{b}_l$ are the cluster integrals (as defined by Mayer) in the thermodynamic limit. Explicit expressions for the isotherms for gas-saturated vapor and liquid phases are given.

KEY WORDS: Partition function; cluster expansion; grand partition function; fugacity expansion; analyticity; phase transition; isotherms.

1. INTRODUCTION

Let us consider a system of N particles enclosed in a volume V at temperature T and interacting through a potential $\phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{k<l} \phi(\mathbf{r}_{kl})$. It is an old problem[1] to derive the correct isotherms starting from the partition function $Z(N, V, T)$, where

$$Z(N, V, T) = (1/\lambda^{3N} N!) \int_V \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp\Big[-\beta \sum_{i<j} \phi(r_{ij})\Big] \qquad (1)$$

with $\beta = 1/kT$, k being the Boltzmann constant, $\lambda^2 = h^2/2\pi mkT$, m is the mass of a particle, and h is Planck's constant. The necessity for introducing $N!$ and h in (1) has been discussed by Uhlenbeck.[1] We shall not discuss these points here and refer the reader to Ref. 1, the notations of which we shall mostly use. Only the new notations introduced in this article will be explained.

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Starting from (1), we know that the grand partition function

$$Z_{gr}(V, T, z) = \sum_{N=0}^{\infty} Z(V, T, N)(\lambda^3 z)^N, \qquad Z(V, T, 0) = 1 \tag{2}$$

(we shall for simplicity put $\lambda = 1$) and the function

$$X(V, T, z) = \sum_{l=1}^{\infty} b_l(V, T)\, z^l$$

satisfy the relation

$$Z_{gr}(V, T, z) = e^{VX(V,T,z)} \tag{3}$$

Expressions for b_l are given in Ref. 1 and have been discussed in detail in many books.[2] The important thing is that $\lim_{V\to\infty} b_l(V, T) = b_l(T)$ exists. Writing

$$X(z, T) = \lim_{V\to\infty} X(V, T, z) = \sum_{l=1}^{\infty} \bar{b}_l(T)\, z^l \tag{4}$$

one can show[1] that if the series (4) is convergent, then the pressure p and the specific volumes v are given by

$$\begin{aligned} p/kT &= X(z, T) = \sum_{l=1}^{\infty} \bar{b}_l(T)\, z^l \\ 1/v &= z\,\partial X/\partial z = \sum_{l=1}^{\infty} l\bar{b}_l(T)\, z^l \end{aligned} \tag{5}$$

Relations (5) are the parametric equations derived by Mayer giving the isotherms for the gas state. The parameter z is a positive-definite physical quantity known as the fugacity and is given by

$$z = (1/\lambda^3)\, e^{\mu/kT} = e^{\mu/kT} \tag{6}$$

where μ is the chemical potential.

It is well known that the Mayer theory, though constituting the first major advance in the theory of isotherms since the van der Waals equation, could not give a satisfactory description of the critical phenomena. Equations (5) are exact for the low-density region. They are by no means valid for higher densities, where the virial expansion (i.e., the expansion of pressure p as a function of $\rho = 1/v$) breaks down. It is easy to see that the expressions (5) are true for small z (e.g., the zeroth-order approximation gives the perfect gas law and the first-order expression gives the Onnes virial expansion, as is experimentally verified). It is obvious that (5) is valid so long as the series

[2] See Ref. 2 for an excellent review of the Mayer theory and subsequent work.

$\sum_{l=1}^{\infty} \bar{b}_l z^l$ is convergent. In other words, if $z = z_0$ is the radius of convergence of the series $\sum_{l=1}^{\infty} \bar{b}_l z^l$, then (5) is valid up to $z = z_0$. This clearly indicates that Mayer theory gives the possibility of a phase transition at $z = z_0$. Mayer himself took the idea and tried to give a theory of the phase transition which has met ample criticism. We shall not discuss the Mayer theory of condensation now. In the next section, we shall discuss the theory we propose without any reference to any other existing theories of condensation. In the following section, we shall discuss some aspects of the theory of the phase transition proposed by Mayer[3] in the context of our theory.

2. PHASE TRANSITION

We have the partition function $Z(N, V, T)$ given by

$$Z(N, V, T) = (1/2\pi i) \oint_C e^{VX(\zeta, V, T)} \zeta^{-N-1} \, d\zeta \tag{7}$$

where $X(\zeta, V, T) = \sum_{l=1}^{\infty} b_l(V, T)\zeta^l$ is the generating function for $Z(N, V, T)$, and C is any closed contour around $\zeta = 0$ (in the complex ζ-plane) such that $\sum_{l=1}^{\infty} \bar{b}_l \zeta^l$ is convergent on C.

Theorem 1. The necessary and sufficient condition for phase transition to occur is that there exist a temperature $T = T_c > 0$ at and below which all $\bar{b}_l$ (excepting perhaps a finite number of them) are positive.

Proof. (i) The condition is necessary. Let us first note that if the series $\sum_{l=1}^{\infty} \bar{b}_l \zeta^l$ is analytic for all positive values of ζ at all temperatures, there does not exist a discontinuity in the isotherms obtained from (5) and hence phase transition does not occur. Thus for phase transition to occur it is necessary[4] that $X(\zeta, T)$ have a singularity on the positive real axis in the complex ζ-plane. As temperature goes to infinity, it is known[5] that the $\bar{b}_l$ alternate in sign as the system behaves as hard spheres. From the theory of complex variables,[6] it is wellknown that the necessary and sufficient condition for a series of the form $X(\zeta, T) = \sum_{l=1}^{\infty} b_l \zeta^l$ to have a singularity on the positive real axis is that all the $\bar{b}_l$ (excepting perhaps a finite number of them) be positive.

(ii) The condition is sufficient. Let $v_0 = 1$ be the particle hard-core volume. This puts a restriction on the maximum number of particles that can be put in a volume V. Mathematically, this fact is equivalent to adding potential $U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \sum_k U(\mathbf{r}_k)$ to $\phi(\mathbf{r}_1, ..., \mathbf{r}_N)$ in (1), where

$$\begin{aligned} U(\mathbf{r}_k) &= 0 \qquad \text{if the } k\text{th particle is in } V \\ &= \infty \qquad \text{if the } k\text{th particle is outside } V \end{aligned} \tag{8}$$

Let $\bar{N}$ be the maximum number of particles that can be accommodated in V; then, due to (8), we have

$$Z(N, V, T) = 0 \qquad \text{for} \quad N > \bar{N} \tag{9}$$

and $\lim_{V\to\infty}(\bar{N}/V) = 1$. Along with this, we note that the thermodynamic limit is given by

$$\lim_{V\to\infty} (N/V) = 1/v = 1/\text{specific volume} = \text{density}$$

Assuming stable interactions, the pressure p and specific volume v are given by (see Ref. 7, p. 57)

$$p/\kappa T = X(z, T) \qquad 1/v = z[\partial x(z, T)/\partial z] \tag{10}$$

where $X(z, T) = \lim_{V\to\infty}(1/v) \log Z_{gr}(V, T, z)$ and where $V \to +\infty$ in the sense of Fisher, which is a smoothness condition on sequences imagined in passing to the limit of infinite volume. Now, for an interaction with hard, repulsive cores,

$$X(z, T) = \lim_{V\to\infty} (1/V) \log \sum_{N=0}^{\bar{N}} Z(N, V, T) z^N \tag{11}$$

We shall take (10) as the defining equations for the pressure p and the specific volume v. Starting from Eq. (7) and using the definition (10), we shall evaluate in this section the function $X(\bar{z}, T)$ for the intervals $0 < \bar{z} < 1$ and $1 < \bar{z} < \infty$ and then, using (11), show that at $\bar{z} = 1$ $(T < T_c)$, the isotherms exhibit a first-order phase transition. The value of $\bar{z} = 1$ is to be approached after the thermodynamic limit has been taken. $\bar{z} = z/z_0$, and z_0 is defined below.

We have

$$Z(N, V, T) = (1/2\pi i) \oint_C e^{VX(\zeta, T)} \zeta^{-N-1} \, d\zeta \tag{12}$$

where

$$X(\zeta, T) = \sum_{l=1}^{r} b_l(V, T) \zeta^l \tag{13}$$

[we shall not distinguish between $X(V, T, z)$ and $\lim_{V\to\infty} X(V, T, z) = X(z, T)$ when the limit exists], and C is a contour as already specified.

Let $z = z_0$ be the radius of convergence of the series (13). We shall write (13) as

$$X(\bar{\zeta}, T) = \sum_{l=1}^{\infty} g_l \bar{\zeta}^l \tag{14}$$

where

$$g_l = b_l z_0^{\,l} \qquad \text{and} \qquad \bar{\zeta} = \zeta/z_0 \tag{15}$$

It is clear that (14) is convergent for $\bar{\zeta} < 1$.

We can write (12) as

$$Z(N, V, T) = (z_0^{-N}/2\pi i) \oint_C \{\exp[VX(\bar{\zeta}, T)]\}\, \bar{\zeta}^{-N-1}\, d\bar{\zeta} \tag{16}$$

where C is a contour around $\bar{\zeta} = 0$ (in the complex $\bar{\zeta}$-plane) such that $|\bar{\zeta}| \leqslant 1$ on C.

To find the function $X(\bar{z}, T)$ for the whole range of $\bar{z} = z/z_0$, we shall start from (16) and (10).

From (16), we have

$$Z_{\mathrm{gr}}(V, T, z) = \sum_{N=0}^{\bar{N}} Z(N, V, T)\, z^N = \frac{1}{2\pi i} \oint_C [\exp VX(\bar{\zeta}, T)]\, \frac{1 - (\bar{z}/\bar{\zeta})^{\bar{N}+1}}{1 - (\bar{z}/\bar{\zeta})}\, \frac{d\bar{\zeta}}{\bar{\zeta}} \tag{17}$$

Case 1. $z/z_0 = \bar{z} \leqslant 1$. In (17), let us choose C to be a circle of radius $\bar{z}$, so that we can put

$$\bar{\zeta} = \bar{z}\, e^{i\theta}, \qquad -\pi \leqslant \theta \leqslant \pi$$

From (17), we have

$$Z_{\mathrm{gr}}(V, T, \bar{z}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1 - \exp[-i(\bar{N}+1)\theta]}{1 - \exp(-i\theta)} \exp\left[V \sum_{l=1}^{\infty} g_l \bar{z}^l \exp(il\theta)\right] d\theta \tag{18}$$

To find $X(\bar{z}, T)$ from (18), let us first note that

$$\lim_{\bar{N}\to\infty} \frac{1 - \exp[-i(\bar{N}+1)\theta]}{1 - \exp(-i\theta)} = \lim_{\bar{N}\to\infty} \left(\exp \frac{iN\theta}{2}\right) \frac{\sin[(\bar{N}+1)\theta/2]}{\sin(\theta/2)} = \delta(\theta)$$

where $\delta(\theta)$ is the Dirac delta function.

From (18), one easily derives

$$X(\bar{z}, T) = \sum_{l=1}^{\infty} g_l \bar{z}^l \tag{19}$$

which gives, for $\bar{z} \leqslant 1$,

$$p/kT = \sum_{l=1}^{\infty} g_l \bar{z}^l, \qquad 1/v = \sum_{l=1}^{\infty} l g_l \bar{z}^l \tag{20}$$

This case is dealt with only to show that we get the already known result consistent with (5).

Case 2. $z/z_0 = \bar{z} \geqslant 1$. Let us choose the contour C in (17) to be a circle of radius $1/\bar{z}$ and put in (17) $\bar{\zeta} = (1/\bar{z})\, e^{i\theta}$, $-\pi \leqslant \theta \leqslant \pi$. We have

$$Z_{\mathrm{gr}}(V, T, \bar{z}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1 - (\bar{z}^2 e^{-i\theta})^{\bar{N}+1}}{1 - \bar{z}^2 e^{-i\theta}} \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l e^{il\theta}\right] d\theta \quad (21)$$

Since the $\bar{b}_l$ are positive for all l (the case when a finite number of b_l are not positive definite can be obtained by a straightforward generalization). We can prove from (21) (see Appendix A for the proof) using

$$\lim_{V\to\infty} (1/V) \log \bar{N} = \lim_{V\to\infty} (1/V) \log V = 0, \qquad \lim_{\bar{N}\to\infty} [(\sin \bar{N}\theta)/\theta] = \delta(\theta) \quad (22)$$

that

$$X(\bar{z}, T) = 2 \log \bar{z} + \sum_{l=1}^{\infty} g_l(1/\bar{z})^l \quad (23)$$

which gives for $\bar{z} \geqslant 1$

$$p/kT = 2 \log \bar{z} + \sum_{l=1}^{\infty} g_l(1/\bar{z})^l, \qquad 1/v = 2 - \sum_{l=1}^{\infty} l g_l(1/\bar{z})^l \quad (24)$$

From (20) and (24), we see that for stable interactions with hard cores, the pressure p is a continuous function of $\bar{z}$ [as previously established by Ruelle for the case considered here (Ref. 7, p. 58)], but $1/v$ has a discontinuity at $z = 1$. The isotherms for temperature $T < T_c$ will be given by (with $g_l = \bar{b}_l z_0^l$)

$$p/kT = \sum_{l=1}^{\infty} g_l \bar{z}^l, \qquad 1/v = \sum_{l=1}^{\infty} l g_l \bar{z}^l \qquad \text{for} \quad \bar{z} < 1 \quad (25)$$

$$p/kT = \sum_{l=1}^{\infty} g_l, \qquad \left[\sum_{l=1}^{\infty} l g_l\right]^{-1} \geqslant v \geqslant \left[2 - \sum_{l=1}^{\infty} l g_l\right]^{-1} \qquad \text{for} \quad \bar{z} = 1 \quad (26)$$

$$p/kT = 2 \log \bar{z} + \sum_{l=1}^{\infty} g_l(1/\bar{z})^l, \qquad 1/v = 2 - \sum_{l=1}^{\infty} l g_l(1/\bar{z})^l \qquad \text{for} \quad \bar{z} > 1 \quad (27)$$

(26) is a consequence of (i) Van Hove's theorem,[8] which states that pressure p obtained from (1) is a monotonic function of v and (ii) the fact that at $v = v_c^{(1)}$ and $v_c^{(2)}$ (see Fig. 1), the pressure p is the same. A typical isotherm from (25)–(27) is shown in Fig. 1. The curve to the right of B corresponds to the fugacity $\bar{z} < 1$, the flat portion AB corresponds to $\bar{z} = 1$, and the

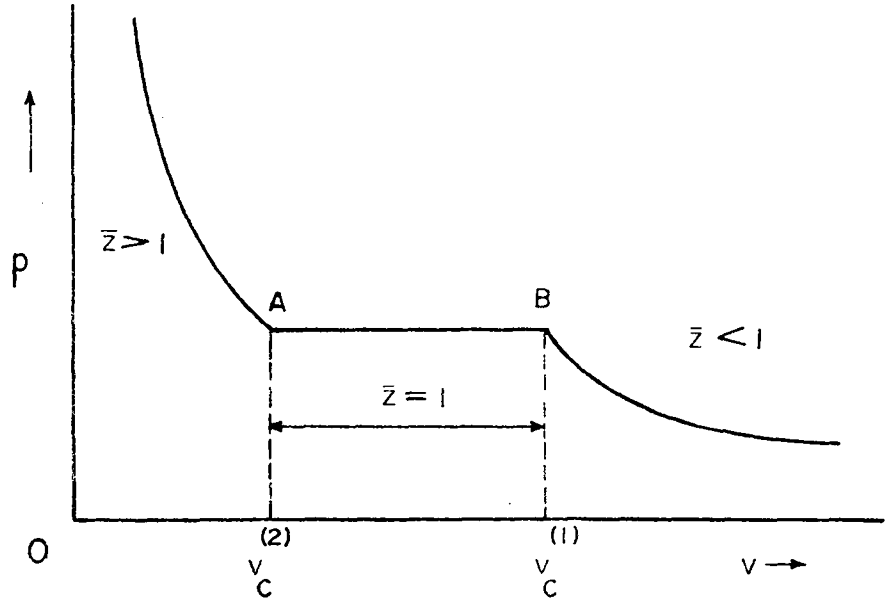

Fig. 1. Pressure as a function of specific volume at constant temperature $T < T_c$.

curve to the left of A corresponds to $\bar{z} > 1$. The vapor and the liquid specific volumes are given by

$$v_c^{(1)} = \left[\sum_{l=1}^{\infty} l g_l\right]^{-1} \quad \text{and} \quad v_c^{(2)} = \left[2 - \sum_{l=1}^{\infty} l g_l\right]^{-1} \tag{28}$$

The critical temperature T_c is given by

$$v_c^{(1)}(T_c) = v_c^{(2)}(T_c)$$

or

$$\sum_{l=1}^{\infty} l g_l(T_c) = 2 - \sum_{l=1}^{\infty} l g_l(T_c)$$

i.e.,

$$\sum_{l=1}^{\infty} l g_l(T_c) = 1 \tag{29}$$

The interval AB in Fig. 1 for a temperature $T < T_c$ is given by

$$v_c^{(1)} - v_c^{(2)} = \frac{1}{\sum_{l=1}^{\infty} l g_l} - \frac{1}{2 - \sum_{l=1}^{\infty} l g_l} = \frac{2(1 - \sum_{l=1}^{\infty} l g_l)}{(\sum_{l=1}^{\infty} l g_l)(2 - \sum_{l=1}^{\infty} l g_l)} \tag{30}$$

Thus we have a first-order phase transition. For temperature $T > T_c$, infinitely many b_l (presumably) alternate in sign and hence the series $\sum_{l=1}^{\infty} b_l \zeta^l$ ceases to have a singularity on the positive real axis in the complex ζ-plane. In that case, the isotherms for the whole range of z are given by relations (5).

3. DISCUSSION

The above considerations are model-independent and are valid for any potential $\sum_{i>j} \phi(\mathbf{r}_{ij})$ which is stable[7] and has hard cores. Ruelle (Ref. 7, Section 4.3.1) has shown that (i) if there exists a $B \geqslant 0$ such that

$$\sum_{i>j} \phi(r_{ij}) \geqslant -nB \qquad \text{for all} \quad n \geqslant 0 \tag{31}$$

(stability condition) the series $X(z, T) = \sum_{l=1}^{\infty} b_l(T) z^l$ is convergent at least up to

$$z < e^{-2\beta B-1}[C(\beta)]^{-1} \tag{32}$$

where

$$C(\beta) = \int d\kappa \mid e^{-\beta\phi(\kappa)} - 1 \mid \tag{33}$$

This means that the grand partition function does not have a zero on the positive real axis in the region (32). By Lee and Yang's[4] theorem (which gives the necessary condition for phase transition to occur), there is no phase transition in (32). The region (32) defines the gas region.[7] This also means that there is no phase transition at high temperature, since for small β, the region (32) extends to the whole of the positive z axis (see Ref. 7, Section 5.2 for proof).

Both the Mayer and Lee–Yang theories give a satisfactory necessary condition for phase transition to occur. Lee and Yang's theory is more of an abstract mathematical formulation for a necessary condition for phase transition.[1] Any theory based on Mayer's cluster expansion is the most promising one. But such a theory must give the details of the isotherm for the whole range of density, i.e., from the gas to the liquid state. Mayer's attempt to prescribe how the isotherm would look at the liquid state was unsuccessful. We shall not go into the details of the Mayers's theory of condensation, for which we refer to their book.[3] We stress that the purpose of this article, it is to show the potentiality of the Mayer cluster expansion to give a complete theory of phase transition. The above discussion is by no means complete. One should in fact discuss some specific potentials and examine whether the above conditions are really satisfied.[3] Our aim here, however, is to encourage a new line of approach on the basis of the most rigorous existing equilibrium theory of a many-particle system.

APPENDIX A

Referring to Eq. (21), let

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

$$= \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1 - (\bar{z}^2 e^{i\theta})^{\bar{N}+1}}{1 - \bar{z}^2 e^{i\theta}} \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l e^{-il\theta} \right] d\theta \qquad \text{(A.1)}$$

Therefore

$$I(\bar{N}) = \frac{1}{4\pi} \int_{-\pi}^{\pi} d\theta \left\{ \frac{1 - (\bar{z}^2 e^{-i\theta})^{\bar{N}+1}}{1 - \bar{z}^2 e^{-i\theta}} \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l e^{il\theta} \right] \right.$$

$$\left. + \frac{1 - (\bar{z}^2 e^{i\theta})^{\bar{N}+1}}{1 - \bar{z}^2 e^{i\theta}} \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l e^{-il\theta} \right] \right\}$$

$$= \frac{1}{4\pi} \int_{-\pi}^{\pi} d\theta \left\{ \frac{1 - (\bar{z}^2 e^{-i\theta})^{\bar{N}+1}}{1 - \bar{z}^2 e^{-i\theta}} \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l (\cos l\theta + i \sin l\theta) \right] \right.$$

$$\left. + \frac{1 - (\bar{z}^2 e^{i\theta})^{\bar{N}+1}}{1 - \bar{z}^2 e^{i\theta}} \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l (\cos l\theta - i \sin l\theta) \right] \right\} \qquad \text{(A.2)}$$

$$= \frac{1}{2\pi} \int d\theta \left(\left\{ \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \cos l\theta \right] \right\} \cos\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \sin l\theta \right] \right.$$

$$\left. \times \operatorname{Re} \frac{1 - (\bar{z}^2 e^{-i\theta})^{\bar{N}+1}}{1 - \bar{z}^2 e^{-i\theta}} \right)$$

$$+ \int d\theta \left(\left\{ \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \cos l\theta \right] \right\} \sin\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \sin l\theta \right] \right.$$

$$\left. \times \operatorname{Im} \frac{1 - (\bar{z}^2 e^{-i\theta})^{\bar{N}+1}}{1 - \bar{z}^2 e^{-i\theta}} \right) \qquad \text{(A.3)}$$

[3] Note that the following assumption has been made throughout in the above discussion: Let $z_0(V, T)$ be the radius of convergence of the series $\sum_{l=1}^{\infty} b_l(V, T) z^l$ and $z_0(T)$ the radius of convergence for $\sum_{l=1}^{\infty} \bar{b}_l(T) z^l$; then $\lim_{V\to\infty} z_0(V, T) = z_0(T)$. A comment should also be made about the existence of the limit $\lim_{V\to\infty} b_l(V, T) = \bar{b}_l(T)$. In fact, Ruelle's "temperedness" condition (Ref. 7, Section 3.1.1, p. 32) assures the existence of this limit. As remarked by Ruelle himself, "temperedness" is not the best possible condition for the proof of the existence of the thermodynamic limit. This is, however, satisfied by most of the realistic interactions.

Now, we have

$$\exp\left[V\sum_{l=1}^{\infty} g_l(1/\bar{z})^l \cos l\theta\right] \leqslant \exp\left[V\sum_{l=1}^{\infty} g_l(1/\bar{z})^l\right] \tag{A.4}$$

(thus $g_l > 0$ for all l) and

$$\operatorname{Re}\frac{1-(\bar{z}^2e^{-i\theta})^{\bar{N}+1}}{1-\bar{z}^2e^{-i\theta}} \leqslant \frac{1-(\bar{z}^2)^{\bar{N}+1}}{1-\bar{z}^2} \tag{A.5}$$

$$\operatorname{Im}\frac{1-(\bar{z}^2e^{-i\theta})^{\bar{N}+1}}{1-\bar{z}^2e^{-i\theta}} \leqslant \frac{1-(\bar{z}^2)^{\bar{N}+1}}{1-\bar{z}^2} \tag{A.6}$$

Therefore

$$I(\bar{N}) \leqslant 2\pi\frac{1-(\bar{z}^2)^{\bar{N}+1}}{1-\bar{z}^2}\exp\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\right]$$

$$= 2\pi\bar{z}^{2\bar{N}}\frac{1-(1/\bar{z}^2)^{\bar{N}+1}}{1-(1/\bar{z}^2)}\exp\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\right] \tag{A.7}$$

Again,

$$I(\bar{N}) = \bar{z}^{2\bar{N}}\frac{1}{2\pi}\left(\int d\theta\left\{\exp\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\cos l\theta\right]\right\}\right.$$

$$\times\cos\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\sin l\theta\right]\operatorname{Re}\left[\frac{1-(e^{i\theta}/\bar{z}^2)^{\bar{N}+1}}{1-(e^{i\theta}/\bar{z}^2)}\exp(-i\bar{N}\theta)\right]$$

$$+\int d\theta\left\{\exp\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\cos l\theta\right]\right\}\sin\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\sin l\theta\right]$$

$$\left.\times\operatorname{Im}\left[\frac{1-(e^{i\theta}/\bar{z}^2)^{\bar{N}+1}}{1-(e^{i\theta}/\bar{z}^2)}\exp(-i\bar{N}\theta)\right]\right) \tag{A.8}$$

It is clear that for large $\bar{N}$, the contribution to the integral on the left-hand side of (A.8) comes from small values of θ around $0 = 0$. Since $(\sin\bar{N}\theta)/\bar{N}\theta \leqslant 1$, we have

$$\bar{z}^{2\bar{N}}\frac{1}{2\pi\bar{N}}\left(\int_{-\pi}^{\pi} d\theta\frac{\sin\bar{N}\theta}{\theta}\left\{\exp\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\cos l\theta\right]\right\}\right.$$

$$\times\cos\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\sin l\theta\right]\operatorname{Re}\left[\frac{1-(e^{i\theta}/\bar{z}^2)^{\bar{N}+1}}{1-(e^{i\theta}/\bar{z}^2)}\exp(-i\bar{N}\theta)\right]$$

$$+\int_{-\pi}^{\pi} d\theta\frac{\sin\bar{N}\theta}{\theta}\left\{\exp\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\cos l\theta\right]\right\}\sin\left[V\sum_{l=1}^{\infty} g_l\left(\frac{1}{\bar{z}}\right)^l\sin l\theta\right]$$

$$\left.\times\operatorname{Im}\left[\frac{1-(e^{i\theta}/\bar{z}^2)^{\bar{N}+1}}{1-(e^{i\theta}/\bar{z}^2)}\exp(-i\bar{N}\theta)\right]\right)$$

$$\leqslant I(\bar{N}) \tag{A.9}$$

Thus we have from (A.7) and (A.8)

$$
\begin{aligned}
&2\log \bar{z} - \lim_{\bar{N}\to\infty} \frac{1}{\bar{N}} \log \bar{N} + \lim_{\bar{N}\to\infty} \frac{1}{\bar{N}} \log 2\pi \\
&\quad + \lim_{\bar{N}\to\infty} \frac{1}{\bar{N}} \log \Bigg(\int_{-\pi}^{\pi} d\theta \, \frac{\sin \bar{N}\theta}{\theta} \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \cos l\theta \right] \\
&\quad \times \operatorname{Re}\left[\frac{1-(e^{i\theta}/\bar{z}^2)^{\bar{N}+1}}{1-(e^{i\theta}/\bar{z}^2)} \exp(-i\bar{N}\theta) \right] \cos\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \sin l\theta \right] \\
&\quad + \int_{-\pi}^{\pi} d\theta \, \frac{\sin \bar{N}\theta}{\theta} \left\{ \exp\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l \cos l\theta \right] \right\} \sin\left[V \sum_{l=1}^{\infty} g_l \left(\frac{1}{|\bar{z}|}\right)^l \sin l\theta \right] \\
&\quad \times \operatorname{Im}\left[\frac{1-(e^{i\theta}/\bar{z}^2)^{\bar{N}+1}}{1-(e^{i\theta}/\bar{z}^2)} \exp(-i\bar{N}\theta) \right] \Bigg) \\
&\leqslant \lim_{\bar{N}\to\infty} \frac{1}{\bar{N}} \log I(\bar{N}) \leqslant 2\log \bar{z} + \sum_{l=1}^{\infty} g_l \left(\frac{1}{\bar{z}}\right)^l
\end{aligned}
\qquad (A.10)
$$

For the integrals on the left-hand side of (A.9), we shall suppose that the limit $\bar{N} \to \infty$ can be taken inside the integral sign and we shall further use that $\lim_{\bar{N}\to\infty}[(\sin \bar{N}\theta)/\theta] = \delta(\theta)$, so that the integrals are to be evaluated at $\theta = 0$. Rigorously speaking, this means that for large $\bar{N}$, the contribution to the integral comes from the neighborhood of $\theta = 0$. The range of the neighborhood becomes arbitrarily small as $\bar{N}$ increases indefinitely. This gives immediately

$$
X(\bar{z}, T) = \lim_{V\to\infty} (1/V) \log I(\bar{N}) = 2\log \bar{z} + \sum_{l=1}^{\infty} g_l (1/\bar{z})^l \qquad (\bar{z} > 1) \qquad (A.11)
$$

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