Extension of the Condensation Theory of Yang and Lee to the Pressure Ensemble

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Phase transitions which occur at or lead to a specific volume larger than the minimum specific volume can be described by roots of the Laplace transform $C_N(s)$ of the canonical partition function approaching real positive values of the pressure (kTs) in the limit of infinite number of particles. The formulation in the pressure ensemble has the advantage that the real values of the variables considered have the immediate physical meaning even for a finite number of particles.

For a special model (molecules whose incompressible cores are oriented cubes), a phase transition leading to the minimum specific volume at constant pressure is shown to be impossible.

I. INTRODUCTION

IN their theory of condensation, Yang and Lee[1] have stated the function-theoretical properties of the grand partition function $\mathcal{Q}_V(y)$ considered as a function of the complex fugacity y, which lead to phase transitions such as condensation. The grand partition function is defined as

$$\mathcal{Q}_V(y)=\sum_{N=0}^{M(V)} y^N Q_N(V), \tag{1}$$

where N is the number of particles in a fixed volume V, $M(V)$ is the largest number of particles that can fit in V, and $Q_N(V)$ is the canonical partition function defined as

$$Q_N(V)=\frac{1}{N!}\int_V\cdots\int e^{-\beta U}\prod_{j=1}^{N} d\tau_j,$$

where $\beta=1/kT$, U is the potential energy of the N particles and $d\tau_j$ is the volume element of the jth particle. In the grand canonical ensemble the pressure and density are given by

$$\beta\langle\bar{p}_\infty\rangle=\lim_{V\to\infty}\frac{1}{V}\ln\mathcal{Q}_V(y), \tag{2}$$

$$\bar{\rho}=\lim_{V\to\infty} y\frac{\partial}{\partial y}\left[\frac{1}{V}\ln\mathcal{Q}_V(y)\right]. \tag{3}$$

Yang[2] has pointed out that the quantity $(kT/V)\times\ln\mathcal{Q}_V(y)$ is actually a doubly averaged pressure, once over the distribution of the number of particles in V and once over the volume from 0 to V. In the canonical ensemble the pressure is given by

$$\beta p=(\partial/\partial V)\ln Q_N(V). \tag{4}$$

The average pressure in the grand canonical ensemble is obtained by averaging over the distribution of the number of particles in V i.e.,

$$\beta\bar{p}\equiv\sum_{N=0}^{M(V)} W(N)\beta p=\frac{\partial}{\partial V}\ln\mathcal{Q}_V(y), \tag{5}$$

where $W(N)$ is the probability of finding N particles in a volume V in a grand canonical ensemble of fugacity y, and $W(N)$ is given by

$$W(N)=y^N Q_N(V)/\mathcal{Q}_V(y). \tag{5a}$$

The pressure used by Yang and Lee is therefore obtained as a second average over all volumes from zero to the actual volume V:

$$\beta\langle\bar{p}\rangle\equiv\frac{1}{V}\int_0^V \beta\bar{p}dV'=\frac{1}{V}\ln\mathcal{Q}_V(y). \tag{6}$$

The quantity $\beta\langle\bar{p}\rangle$ has no immediate physical meaning for finite V but is used by Yang and Lee as the pressure only in the limit of infinite V. While there is little doubt that the two definitions $\langle\bar{p}\rangle$ and $\bar{p}$ become equivalent in the limit, a rigorous proof of this equivalence has not yet been given and would have to be based on the limit properties of the *canonical* partition function.

Some limit properties of the canonical partition function are known from the work of van Hove[3] and are more difficult to prove than the corresponding limit properties of the grand partition function. Since some of the advantage of the use of the grand canonical ensemble is therefore lost if one requires a proof of the equivalence of the two pressures in the limit, it seemed to us of interest to attempt to rigorize a variant of the Yang-Lee theory suggested by one of use,[4] which operates with a canonical ensemble from the beginning. We use a canonical ensemble whose elements are replicas of the system of interest together with a mechanical system used as a pressure gauge; that is, a pressure ensemble. We believe it to be an advantage of our variant that it deals directly with the expectation value of the specific volume as a function of the pressure, and that these quantities are physically

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[1] C. N. Yang and T. D. Lee, Phys. Rev. 87, 404 (1952).

[2] C. N. Yang, "Special Problems of Statistical Mechanics, I," mimeographed lecture notes, Seattle, 1952 (unpublished), p. 31.

[3] L. van Hove, Physica 15, 951 (1949).

[4] A. J. F. Siegert, Phys. Rev. 96, 243 (1954).

meaningful for a finite number of particles as well as in the limit. The latter advantage is academic as long as one deals only with equilibrium states, but may become of interest if one wants to deal with the nonequilibrium states such as overheated liquid and undercooled vapor which can appear with nonvanishing probability only in finite systems.

II. PRESSURE ENSEMBLE

If a substance together with a mechanical system of potential energy pV is in thermodynamic equilibrium with a heat bath, the probability that the substance has a volume between V and $V+dV$ is

$$W(V)dV=\frac{1}{C_N(s)}e^{-sV}Q_N(V)dV, \tag{7}$$

where $s=\beta p$ and

$$C_N(s)=\int_0^\infty e^{-sV}Q_N(V)dV. \tag{8}$$

This can be realized, for example, with a gas in a vertical cylinder which is closed at the bottom and has a floating piston on top and a vacuum above the piston. The gas is then under a fixed force per unit area p. The average volume per particle is given by

$$\bar{v}_N(s)=-\frac{1}{N}\frac{\partial}{\partial s}\ln C_N(s). \tag{9}$$

For finite N the only singularities of $\bar{v}_N(s)$ in the open right half plane are the poles corresponding to roots of $C_N(s)$. These must occur at complex values of s. The real part of $\bar{v}_N(s)$ can be visualized as an electrostatic potential. Singularities of this potential can for finite N in the open right half-plane arise only from dipole lines perpendicular to the s plane located at roots of $C_N(s)$. We expect, therefore, that phase transitions can be described by the closing in of roots of $C_N(s)$ onto the real axis in the s plane in the limit $N\rightarrow\infty$. If, for instance, the dipole lines close in such as to form a dipole layer, a discontinuity of the specific volume occurs.

To make rigorous this formulation, we must prove that the limit $\lim_{N\rightarrow\infty}\bar{v}_N(s)$ exists and is an analytic function in those regions of the complex s plane that are free of roots of $C_N(s)$ and contain a segment of the positive real axis bounded away from the origin.

III. LIMIT OF INFINITE NUMBER OF PARTICLES

The proof falls naturally into two parts. By means of some minor extensions of van Hove's result and assumptions, we show that $\lim_{N\rightarrow\infty}(1/N)\ln C_N(s)$ exists on a certain interval $t_1\leqslant s\leqslant t_2$ of the real positive s axis. This part contains the physical features of the problem since the limit shown to exist is essentially the Gibbs free energy per particle in the limit of large number of particles, and the proof proceeds from van Hove's results which are based on assumptions concerning the intermolecular forces. The other part of the proof extends the existence of the limit to any region of the complex plane which is contained in the strip $t_1\leqslant \mathrm{Re}s\leqslant t_2$ and remains free of roots of $C_N(s)$ in the limit. Using the fact that $C_N(s)$ as a Laplace transform is analytic and regular for $\mathrm{Re}s>0$ and the Vitali convergence theorem,[5] we show that inside of such regions $c(s)\equiv\lim_{N\rightarrow\infty}(1/N)\ln C_N(s)$ exists and is analytic and that limits of derivatives such as $\lim_{N\rightarrow\infty}\bar{v}_N(s)$ are obtained as derivatives of the limit function $c(s)$.

In Sec. III-*A* we carry through the second part of the proof, postponing the first part of Sec. III-*B*.

A.—Vitali convergence theorem applied to our case states: If the sequence of functions $[C_N(s)]^{1/N}$ has the following properties:

(*a*) $[C_N(s)]^{1/N}$ regular in a region $\mathfrak{D}$.
(*b*) $[C_N(s)]^{1/N}$ tend to a limit as $N\rightarrow\infty$ at a set of points having a limit point inside of $\mathfrak{D}$, and
(*c*) $|C_N(s)|^{1/N}\leqslant M$ for every N and s in $\mathfrak{D}$,

then the sequence tends *uniformly* to a limit in any region bounded by a contour interior to $\mathfrak{D}$, the limit being an analytic function of s.

$C_N(s)$ exists for $\mathrm{Re}s>0$ and, being a Laplace transform, is analytic and regular there. The existence follows from the fact that $Q_N(V)=K^NV^N/N!$ where K is independent of N and V. Let then $\mathfrak{D}$ be a region which contains a segment of the real axis and which is entirely contained in the strip $t_1\leqslant s\leqslant t_2$ where t_1, t_2 are real and positive. Let further $\mathfrak{D}$ be chosen such that any roots of $C_N(s)$ are outside of $\mathfrak{D}$ for any N. Then condition (*a*) is satisfied. Condition (*b*) will be shown to be satisfied in Sec. III-*B*. Condition (*c*) is satisfied since

$$|C_N(s)|\leqslant C_N(\mathrm{Re}s)\leqslant C_N(t_1)\leqslant K^N/t_1^{N+1}$$

and, therefore, $|C_N(s)|^{1/N}\leqslant K/t_1^{1+1/N}$. We can certainly choose $t_1<1$ and have therefore

$$|C_N(s)|^{1/N}\leqslant K/t_1^2 \text{ in } \mathfrak{D}.$$

According to the Vitali theorem, therefore,

$$\lim_{N\rightarrow\infty}[C_N(s)]^{1/N}$$

and, therefore also

$$\lim_{N\rightarrow\infty}(1/N)\ln C_N(s)$$

exists and is analytic and regular in any region entirely contained in $\mathfrak{D}$. Any phase transition which occurs for $t_1<s<t_2$ must therefore be ascribed to roots of $C_N(s)$ which approach the real axis arbitrarily close in the limit $N\rightarrow\infty$.

B.—This part of the proof is primarily based on some of van Hove's results for the canonical partition function for a system of N particles in a domain D of volume $V(D)$, in the usual limit. These results are based on

[5] E. C. Titchmarsh, *Theory of Functions* (Clarendon Press, Oxford, 1939), second edition, p. 168.

certain assumptions concerning (1) the intermolecular forces and (2) the way in which the limit of infinite domain and infinite N is taken. We make the same assumptions concerning the intermolecular forces, i.e., essentially impenetrable cores of the molecules and finite range and magnitude of the attractive part of the potential.[6]

Concerning the limit, van Hove assumes that the volume and the number of particles approach infinity in such a way that the volume per particle approaches a finite number,[7] and further that for each cubic lattice the number N_S of cubes which contain points on the surface of D satisfies $\lim_{N\to\infty} N_S/N=0$.[8]

We have imposed two additional regularity restrictions on D, namely that (1) $N_S(D)/N_S(D')\leqslant 1$ if $V(D)<V(D')$, where $V(D)$ is the volume of the domain D, and that (2)

$$N_S(D)/V(D)\geqslant N_S(D')/V(D') \text{ if } V(D)<V(D').$$

The meaning of these two additional assumptions is roughly that in the approach to the limit the surface area of D must not decrease and the surface-to-volume ratio not increase with increasing volume. These two restrictions are imposed for both the processes we consider, i.e., increase of the volume with increase of N (passage to the thermodynamic limit) and change of volume with fixed N (change in v). We also assume that in the passage to the thermodynamic limit $V(D)/N=V(D')/N'=v$. This assumption, although not necessary, simplifies our equations.

With this assumptions van Hove obtained the following results for

$$f(N,D)\equiv\frac{1}{N}\ln Q_N(D).$$

(1) $\lim_{N\to\infty} f(N,D)=f(v)$ exists and is a function of v only for $v>v_{\min}$, where $v_{\min}$ is the smallest specific volume obtainable.

(2) $f(v)$ is a nondecreasing function.

(3) df/dv exists almost everywhere.[9]

(4) df/dv is a nonincreasing function.

We have shown in Appendix I that with our additional assumption $f(N,D)$ approaches its limit *uniformly* in any closed interval $v_1\leqslant v\leqslant v_2$, where v_1 and v_2 are restricted by

$$v_{\min}<v_1<v_2<\infty, \qquad (10)$$

and otherwise arbitrary. In this range of values v we thus have

$$|f(v)-f(N,D)|<\epsilon_N,$$

where ϵ_N does not depend on v and can be made arbitrarily small for sufficiently large N.

We have then

$$\frac{1}{N}\ln C_N(s)\begin{cases}\leqslant\dfrac{1}{N}\ln\left(e^{N\epsilon_N}\displaystyle\int_{v_1}^{v_2}e^{N(-sv+f(v))}dv\right)\\[2ex] \qquad +\dfrac{1}{N}\ln\left[1+\dfrac{I_0^{v_1}}{I_{v_1}^{v_2}}+\dfrac{I_{v_2}^{\infty}}{I_{v_1}^{v_2}}\right]+\dfrac{1}{N}\ln N\\[2ex] \geqslant\dfrac{1}{N}\ln\left(e^{-N\epsilon_N}\displaystyle\int_{v_1}^{v_2}e^{N(-sv+f(v))}dv\right)+\dfrac{1}{N}\ln N,\end{cases} \qquad (11)$$

with

$$I_a^b\equiv\int_a^b e^{N(-sv+f(N,D))}dv.$$

The term $(1/N)\ln\int_{v_1}^{v_2}e^{N(-sv+f(v))}dv$ approaches, for $N\to\infty$ the largest value of $-sv+f(v)$.[10] Thus $\lim_{N\to\infty}\times(1/N)\ln C_N(s)$ exists if the terms $I_0^{v_1}/I_{v_1}^{v_2}$ and $I_{v_2}^{\infty}/I_{v_1}^{v_2}$ are of order $e^{O(N)}$, with $O(N)$ defined by $\lim_{N\to\infty}O(N)/N=0$.

We consider first the term $I_{v_2}^{\infty}/I_{v_1}^{v_2}$, and find an upper bound for $I_{v_2}^{\infty}$, and a lower bound for $I_{v_1}^{v_2}$, and then show that for a given s a value of v_1 and v_2 obeying the inequality (10) can be found such that the ratio of these two terms approaches zero as $N\to\infty$.

Using the inequality $Q_N(D)\leqslant K^N V(D)^N/N!$, we get, for $s\geqslant t_1>0$,

$$I_{v_2}^{\infty}\leqslant\frac{K^N N^N}{N!}\int_{v_2}^{\infty}e^{-sNv}v^N dv =\frac{K^N e^{-sNv_2}}{Ns^{N+1}}\sum_{k=0}^{N}\frac{(v_2 sN)^k}{k!}. \qquad (12)$$

If we choose $v_2 s>1$, the last term in the sum is the largest. Replacing the sum by $(N+1)$ times the last term, we have

$$I_{v_2}^{\infty}\leqslant\frac{K^N e^{-sNv_2}}{Ns^{N+1}}\frac{(v_2 sN)^N(N+1)}{N!}. \qquad (13)$$

To obtain a lower bound for $I_{v_1}^{v_2}$, we use the fact that

$$Q_N(D)\geqslant\begin{cases}[V(D)-N\alpha]^N/N! & v\geqslant\alpha\\ 0 & \text{for } v\leqslant\alpha,\end{cases}$$

where α is the volume of a sphere of radius d_3, where d_3 is the maximum range of the forces.[11] If we choose $v_1\leqslant\alpha$, we have

$$I_{v_1}^{v_2}\geqslant\int_{\alpha}^{v_2}e^{-sNv}\frac{N^N(v-\alpha)^N}{N!}dv =\frac{e^{-\alpha sN}}{Ns^{N+1}}\left[1-e^{-sNv'}\sum_{l=0}^{N}\frac{(v'sN)^l}{l!}\right], \qquad (14)$$

[6] The precise statement is given in reference 3, Sec. 2 (*a*), first half of (*b*), (*c*), and second half of (*e*). Van Hove actually replaces assumption (*e*) second half by a less restrictive assumption in Sec. 6, but we have disregarded this refinement.

[7] See reference 3, p. 954, assumption (*d*).

[8] See reference 3, p. 954, assumption (*e*), first half.

[9] This actually follows already from (2) by a theorem of Lebesgue. See F. Riesz and B. Nagy, *Leçons d'analyse Fonctionnelle* (Académie des Sciences de Hongrie, Akademiai Kiodo, Budapest, 1952).

[10] A. Zygmund, *Trigonometrical Series, Monografje Mathematyczne* (M. Garasinski, Warszawa, Lwow, 1935), Vol. 5, p. 66.

[11] See reference 3, Sec. 2 (*e*).

with $v'\equiv v_2-\alpha$. If we now choose $v's>1$ the last term in the sum is again the largest, so we have

$$I_{v_1}{}^{v_2}\geqslant\frac{e^{-\alpha sN}}{Ns^{N+1}}\left[1-e^{-sNv'}\frac{(v'sN)^N(N+1)}{N!}\right].\quad(15)$$

We therefore have for an upper bound of $I_{v_2}{}^\infty/I_{v_1}{}^{v_2}$

$$\frac{I_{v_2}{}^\infty}{I_{v_1}{}^{v_2}}\leqslant\frac{\exp\{N(-sv_2+\alpha s+\ln K+\ln(v_2s)+1+O(1))\}}{1-\exp\{N(-sv'+\ln(v's)+1+O(1))\}},$$

where $\lim_{N\to\infty}O(1)=0$. Since we have already chosen $v_1\leqslant\alpha$ and $v_2>\alpha+s^{-1}$, we now need only to choose v_2 sufficiently large to assure $\lim_{N\to\infty}(I_{v_2}{}^\infty/I_{v_1}{}^{v_2})=0$.

We next consider the term $I_0{}^{v_1}/I_{v_1}{}^{v_2}$ in the inequality (11). The behavior of this term for large s depends very sensitively on the behavior of $f(v)$ in the neighborhood of $v_{\min}$. The results of van Hove are not sufficient to prove that $I_0{}^{v_1}/I_{v_1}{}^{v_2}$ is of order $e^{[O(N)]}$ for every value of s that leads to a state of the system different from that of minimum volume. In particular, the following possibility is not excluded by van Hove's results: $\lim_{v\to v_{\min}}f(v)=f_M$ (a finite number) and there exists a $\delta>0$ such that $f'(v)$ exists and is a constant ($=p_{\max}$) for $v_{\min}<v<v_{\min}+\delta$. This is physically a condensation phenomenon at pressure $p_{\max}$ in which the system is condensed into its minimum volume.[12] We cannot prove that this particular phase transition, if it exists, arises from roots of $C_N(s)$. We can prove, however, that all other phase transitions can be described in terms of the approach of roots of $C_N(s)$ to the real axis in the limit $N\to\infty$.

To prove the above results, we obtain an upper bound for $I_0{}^{v_1}$ and a lower bound for $I_{v_1}{}^{v_2}$. It can be shown (Appendix II) that

$$f(N,D)\leqslant f(v_1)+\epsilon_N'(v_1)\ \text{for}\ v_{\min}<v\leqslant v_1,\quad(16)$$

where $\lim_{N\to\infty}\epsilon_N'(v_1)=0$. Then

$$I_0{}^{v_1}\leqslant e^{N[f(v_1)+\epsilon_N'(v_1)]}\times\int_{v_{\min}}^{v_1}e^{-sNv}dv<\frac{\exp\{N(f(v_1)+\epsilon_N'(v_1)-sv_{\min})\}}{sN}.\quad(17)$$

From the uniform convergence of $f(N,D)$ in the interval $[v_1,v_2]$ we get

$$I_{v_1}{}^{v_2}\geqslant e^{-N\epsilon_N}\int_{v_1}^{v_2}e^{N(-sv+f(v))}dv.\quad(18)$$

It was stated in Sec. III that

$$\frac{1}{N}\ln\int_{v_1}^{v_2}e^{N[-sv+f(v)]}dv$$

approaches as $N\to\infty$ the largest value of $-sv+f(v)$. Let $\mathcal{V}$ be the set of values of v for which $-sv+f(v)$ assumes its largest value in $[v_1,v_2]$. (There may be only one such value.) Let v_0 be some number in $\mathcal{V}$. Then

$$I_{v_1}{}^{v_2}\geqslant\exp\{N(-sv_0+f(v_0)-\epsilon_N''(v_1,v_2)-\epsilon_N)\},\quad(19)$$

where $\lim_{N\to\infty}\epsilon_N''(v_1,v_2)=0$, and, therefore,

$$I_0{}^{v_1}/I_{v_1}{}^{v_2}<\exp\{N(sv_0-sv_{\min}+f(v_1)-f(v_0)+O(1))\}.\quad(20)$$

If, for a given s, a value of v_1 can be found which obeys the inequality $v_1>v_{\min}$, and such that

$$s(v_0-v_{\min})+f(v_1)-f(v_0)\leqslant 0,$$

then the term $I_0{}^{v_1}/I_{v_1}{}^{v_2}$ does not contribute in the limit. It is clear that, if $\lim_{v\to v_{\min}}f(v)=-\infty$, such a value v_1 can always be found. To show under what circumstance this can be done if $\lim_{v\to v_{\min}}f(v)=f_M$, we compare $f(v)$ with the linear function $s(v-v_{\min})+b$ where b is an adjustable parameter. Van Hove has proven that $f(v)$ is a continuous, nondecreasing concave[13] function[14]; for a given s smaller than some $s_{\max}$ we can therefore find a b such that $s(v-v_{\min})+b$ intercepts $f(v)$ at least two points v_a' and v_c'; we have

$$f(v)\geqslant s(v-v_{\min})+b,\qquad v_a'\leqslant v\leqslant v_c',\quad(21)$$

$$f(v)<s(v-v_{\min})+b,\qquad v_{\min}<v<v_a'.\quad(22)$$

If we increase b until the equality sign holds in Eq. (21), then the new closed interval $[v_a,v_c]$ (which may degenerate into a point) is the set $\mathcal{V}$. We denote by $b_{\max}$ this value of b and we have

$$f(v)=s(v-v_{\min})+b_{\max},\qquad v_a\leqslant v\leqslant v_c,\quad(23)$$

$$f(v)<s(v-v_{\min})+b_{\max},\qquad v_{\min}<v<v_a.\quad(24)$$

We can now prove the conclusion stated in the beginning of this section. For a given s we obtain a value or set of values $\mathcal{V}$. There are two possibilities we must consider:

(*a*) The points of $\mathcal{V}$ have a lower bound different from $v_{\min}$. We can then pick a v^* in the open interval $v_{\min}<v^*<v_a$ and using v^* in Eq. (24) and v_0 in Eq. (23) we have

$$f(v^*)-f(v_0)+s(v_0-v^*)<0.\quad(25)$$

If we let v^* approach $v_{\min}$ the strict inequality in Eq.

[12] We believe that for a system of molecules which possess a finite impenetrable core, a finite range of attraction, and a bounded attractive poetential, $\lim_{v\to v_{\min}}f(v)=-\infty$ or, more precisely, there esists a δ such that $f(v_{\min}+\delta)<-M$ for arbitrary $M>0$. However, we have been able to prove this only for the special case that the impenetrable cores of the molecules are oriented cubes, and the attractive part of the potential is finite and of finite range (see Appendix III). For this case, $f(v)$ has as an upper bound:

$$f(v)\leqslant\ln(v-v_{\min})+C,$$

where C is independent of v.

[13] Van Hove uses the term convex, but concave seems to be the accepted terminology for a function whose values are never below any of its cords.

[14] The fact that continuity of $f'(v)$ has never been proven necessitates the following proof of two statements which are intuitively obvious.

(25) is preserved and

$$f_M - f(v_0) + s(v_0 - v_{\min}) < 0. \quad (26)$$

Therefore there exists a $v_1 > v_{\min}$ such that

$$f(v_1) - f(v_0) + s(v_0 - v_{\min}) = 0. \quad (27)$$

Thus the term $I_0^{v_1}/I_{v_1}^{v_2}$ does not contribute in the limit.

(*b*) Points of $\mathcal{V}$ come arbitrarily close to $v_{\min}$. In this case Eq. (24) does not apply and the inequality in Eq. (23) becomes $v_{\min} < v \leqslant v_c$. In this case the system undergoes a phase transition with constant pressure into the minimum volume. If we use, in Eq. (23), a value v_0^* and v_0 obeying the inequality $v_{\min} < v_0^* < v_0 < v_c$ we obtain by letting $v_0^* \to v_{\min}$

$$f_M - f(v_0) + s(v_0 - v_{\min}) = 0. \quad (28)$$

Therefore there exists no suitable v_1 and the term $I_0^{v_1}/I_{v_1}^{v_2}$ cannot be neglected in the limit.

We have thus the following results: all phase transitions arise from roots of $C_N(s)$ unless there is a phase transition which brings the system to its minimum volume at constant pressure. If a system has a phase transition of this type, we cannot prove that this particular phase transition arises from the closing in of roots of $C_N(s)$, but even for such a system, all other phase transitions arise from roots of $C_N(s)$. In the special case of molecules whose incompressible cores are oriented cubes, we can rule out the possibility of a phase transition of this type.

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APPENDIX I. PROOF OF UNIFORM CONVERGENCE OF $f(N,D)$

Van Hove has shown the following inequality to hold[15]:

$$\tilde{f}_d\left(\frac{V(\Gamma_1)-d^3}{N}\right) - \frac{\rho V(\Gamma_1)}{Nd} - \epsilon\left(1-\frac{d_3}{d}\right) \leqslant f(N,D)$$
$$\leqslant \tilde{f}_d\left(\frac{V(\Gamma_2)}{N}\right) + \frac{\rho V(\Gamma_2)}{Nd} + \epsilon\left(1-\frac{d_3}{d}\right) + \epsilon_1\left(\frac{V(\Gamma_2)}{Nd^3}\right), \quad \text{(IA-1)}$$

where $\epsilon(x)$ is a function which depends only on the intermolecular forces and approaches zero for $x \to 1$ and d_3 is the maximum range of the intermolecular forces. ρ depends only on the intermolecular forces and the temperature but is independent of the number of particles N and of the number of cubes N_S which contain the surface of D. Γ_1 is the domain formed by the cubes of a cubic lattice of length d entirely interior to D and $V(\Gamma_1)$ the volume of Γ_1. Γ_2 is the domain formed by Γ_1 and the cubes which contain boundary points of $D[V(\Gamma_2) = V(\Gamma_1) + N_S d^3]$. $\epsilon_1(x)$ is a monotonically increasing function and $\epsilon(0) = 0$. The graph of $\tilde{f}_d(v)$ is a concave polygonal contour which has for extreme sides a vertical line on the left and horizontal line on the right.[16]

We next prove that for a given arbitrary η, there exists an $N_0(\eta)$ such that $|f(N',D') - f(N,D)| < \eta$ for $N' \geqslant N \geqslant N_0(\eta)$ for all v in the closed interval $v_1 \leqslant v \leqslant v_2$ with $v_{\min} < v_1 < v_2 < \infty$ where $V(D)/N = V(D')/N' = v$, i.e., uniform convergence. Γ_1' and Γ_2' are defined for D' in the same way as Γ_1 and Γ_2 for D. As stated at the beginning of Sec. III-*A*, we restrict the limit process to sequences of domains such that $N_S'/N' \leqslant N_S/N$, in addition to van Hove's requirement $\lim_{N\to\infty} N_S/N = 0$. Applying Eq. (IA-1) to the domain D with N particles and D' with N' particles $[V(D)/N = V(D')/N' = v]$, we get

$$[f(N',D') - f(N,D)]$$
$$\times\begin{cases} \leqslant \tilde{f}_d\left(\dfrac{V(\Gamma_2')}{N'}\right) + \dfrac{\rho V(\Gamma_2')}{N'd} + 2\epsilon\left(1-\dfrac{d_3}{d}\right) \\ \quad + \epsilon_1\left(\dfrac{V(\Gamma_2')}{N'd^3}\right) - \tilde{f}_d\left(\dfrac{V(\Gamma_1)-d^3}{N}\right) + \dfrac{\rho V(\Gamma_1)}{Nd} \\ \geqslant \tilde{f}_d\left(\dfrac{V(\Gamma_1')-d^3}{N'}\right) - \dfrac{\rho V(\Gamma_1')}{N'd} - 2\epsilon\left(1-\dfrac{d_3}{d}\right) \\ \quad - \tilde{f}_d\left(\dfrac{V(\Gamma_2)}{N}\right) - \dfrac{\rho V(\Gamma_2)}{Nd} - \epsilon_1\left(\dfrac{V(\Gamma_2)}{Nd^3}\right). \end{cases} \quad \text{(IA-2)}$$

The following inequalities follow from the definition of Γ_1 and Γ_2 and are valid for both the primed and unprimed systems:

$$\frac{V(\Gamma_1)}{N} \leqslant v, \quad \frac{V(\Gamma_1)}{N} \geqslant v - \frac{N_S d^3}{N}, \quad \frac{V(\Gamma_2)}{N} \leqslant v + \frac{N_S d^3}{N}.$$

Using these relations in Eq. (IA-2) and using the properties of the foregoing functions we have

$$|f(N',D') - f(N,D)| \leqslant \tilde{f}_d\left(v + \frac{N_S d^3}{N}\right)$$
$$- \tilde{f}_d\left(v - \frac{(N_S+1)d^3}{N}\right) + 2\epsilon\left(1-\frac{d_3}{d}\right)$$
$$+ \frac{2\rho v}{d} + \frac{\rho N_S d^2}{N} + \epsilon_1\left(\frac{v}{d^3} + \frac{N_S}{N}\right). \quad \text{(IA-3)}$$

For fixed d and N, we will replace the terms on the right with the maximum value they assume in the interval $v_1 \leqslant v \leqslant v_2$, with $v_1 = V(D_1)/N$ and $v_2 = V(D_2)/N$. From our assumption in *A*, $N_S(D_2) \geqslant N_S(D_1)$. The term $\epsilon(1 - d_3/d)$ is independent of v. The terms $2\rho v/d$ and $\rho N_S d^2/N$ are obviously a maximum at v_2. The term

[15] See reference 3, Eq. (14).

[16] See reference 3, Fig. 1.

ϵ_1 is also a maximum at v_2 since ϵ_1 is a monotonically increasing function.

Using first the concaveness of $\tilde{f}_d$, then the fact that it is nonincreasing, and the assumption $N_S(D) \leqslant N_S(D_2)$ we get

$$\tilde{f}_d\left(\frac{V(D)}{N}+\frac{N_S(D)d^3}{N}\right)-\tilde{f}_d\left(\frac{V(D)}{N}-\frac{[N_S(D)+1]d^3}{N}\right)$$
$$\leqslant \tilde{f}_d\left(\frac{V(D_1)}{N}+\frac{N_S(D)d^3}{N}\right)$$
$$-\tilde{f}_d\left(\frac{V(D_1)}{N}-\frac{[N_S(D)+1]d^3}{N}\right)$$
$$\leqslant \tilde{f}_d\left(\frac{V(D_1)}{N}+\frac{N_S(D_2)d^3}{N}\right)$$
$$-\tilde{f}_d\left(\frac{V(D_1)}{N}-\frac{[N_S(D_2)+1]d^3}{N}\right).$$

Using these results in Eq. (IA-3), we obtain

$$|f(N',D')-f(N,D)| \leqslant \tilde{f}_d\left(v_1+\frac{N_S(D_2)d^3}{N}\right)$$
$$-\tilde{f}_d\left(v_1-\frac{[N_S(D_2)+1]d^3}{N}\right)+2\epsilon(1-d_3/d)$$
$$+2\rho v_2/d+\rho N_S(D_2)d^2/N+\epsilon_1\left(\frac{v_2}{d^3}+\frac{N_S(D_2)}{N}\right). \quad \text{(IA-4)}$$

Equation (IA-4) is true for all v ($V(D')/N'=V(D)/N=v$) between v_1 and v_2 and, since the right-hand side is independent of v and can be made as small as we choose by first choosing d and then N sufficiently large, we have proved the uniform convergence of $f(N,D)$.

APPENDIX II. PROOF OF EQ. (16)

From Eq. (IA-1) and the inequalities following (IA-2), we have

$$f(N,D)\begin{cases} \leqslant \tilde{f}_d\left(v+\dfrac{N_S d^3}{N}\right)+\epsilon(1-d_3/d) \\ \quad +\epsilon_1\left(\dfrac{v}{d^3}+\dfrac{N_S}{N}\right)+\dfrac{\rho}{d}(N_S d^3/N)\equiv U_N(v) \\ \geqslant \tilde{f}_d\left(v-\dfrac{N_S+1}{N}d^3\right)-\rho v/d-\epsilon(1-d_3/d) \\ \qquad \equiv L_N(v), \end{cases} \quad \text{(IIA-1)}$$

where $V(D)/N=v$. From the properties of the function given in Appendix I, the right-hand side of the inequality is a nondecreasing function of v. Therefore,

$$f(N,D) \leqslant U_N(v_1) \quad \text{for} \quad V(D)/N=v\leqslant v_1.$$

If we go to the limit $N\rightarrow\infty$ with v fixed in Eq. (IIA-1), we have

$$L_\infty(v)\equiv\tilde{f}_d(v)-\rho v/d-\epsilon(1-d_3/d)\leqslant f(v). \quad \text{(IIA-2)}$$

We thus have

$$f(N,D)\leqslant[U_N(v_1)-L_\infty(v_1)]+L_\infty(v_1)$$
$$\leqslant f(v_1)+[U_N(v_1)-L_\infty(v_1)]. \quad \text{(IIA-3)}$$

The quantity $[U_N(v_1)-L_\infty(v_1)]$ can be made arbitrarily small by choosing d and N large enough. Therefore

$$f(N,D)\leqslant f(v_1)+\epsilon_N'(v_1) \quad \text{for} \quad V(D)/N=v\leqslant v_1, \quad \text{(IIA-4)}$$

with

$$\lim_{N\rightarrow\infty}\epsilon_N'(v_1)=0.$$

APPENDIX III

We can disregard the attractive forces and need to prove only that, for a gas of hard-oriented cubes, an upper bound for $f(v)$ is given by

$$f(v)\leqslant\ln(v-v_{\min})+C,$$

where C is independent of v. Consider $N(=N_0^3)$ [17] particles in a square cylinder of cross-sectional area $N_0^2a^2$ and length L. The centers of the particles are allowed to reach the surface of the container. The container of smallest length which can accommodate N_0^3 particles has a volume per particle $(N_0-1)N_0^2a^3/N_0^3$.

We divide the parallelepiped into N_0^2 square cylinders with a cross-sectional area a^2 and a length L. Neglecting interactions between the cells and counting a particle in the jth cell if it is inside or on one of two adjacent surfaces of the jth cell, we then have

$$Q_N(V)\leqslant\sum_{\{n_j\}}{}'\prod_{j=1}^{N_0^2}Q_{n_j},$$

with

$$Q_{n_j}=\frac{1}{n_j!}\int_a\cdots\int\prod_{K=1}^{n_j}d\sigma_K\int_L\cdots\int\prod_{K=1}^{n_j}dZ_Ke^{-\beta U'}, \quad \text{(IIIA-1)}$$

where U' is the interaction energy of the n_j particles in the cell. The sum is taken over the set of integers n_j such that

$$\sum_{j=1}^{N_0^2}n_j=N.$$

The potential energy U' is a function only of $Z_1, Z_2, \cdots Z_{n_j}$ and is equal to zero if for all pairs $|Z_i-Z_j|>a$ and infinite otherwise.

The integral over the Z coordinates is thus the partition function of the gas of hard rods of length a on a

[17] By a more laborious derivation our result can be proven for numbers N which are not cubes of an integer.

line of length L, i.e.,

$$\frac{1}{n_j!}\int_L\cdots\int\prod_{K=1}^{n_j}dZ_Ke^{-\beta U'}=\frac{1}{n_j!}[L-(n_j-1)a]^{n_j}, \quad \text{(IIIA-2)}$$

and

$$Q_N(V)\leqslant\sum_{\{n_j\}}'\prod_{j=1}^{N_0^2}\frac{a^{2n_j}}{n_j!}[L-(n_j-1)a]^{n_j}. \quad \text{(IIIA-3)}$$

It is easily shown that the largest term in the sum is the term with all n_j equal (i.e., $n_j=N_0$ for all j). Then

$$Q_N(V)\leqslant\mathfrak{N}\left\{\frac{a^{2N_0}}{N_0!}[L-(N_0-1)a]^{N_0}\right\}^{N_0^2}, \quad \text{(IIIA-1)}$$

where $\mathfrak{N}$ is the number of terms in the sum and is equal to the number of ways of placing N_0^3 indistinguishable particles in N_0^2 boxes; therefore

$$Q_N(V)\leqslant\frac{[N_0^3+N_0^2-1]!}{N_0^3![N_0^2-1]!}\left\{\frac{a^{2N_0}}{N_0!}[L-(N_0-1)a]^{N_0}\right\}^{N_0^2}. \quad \text{(IIIA-5)}$$

With $L\equiv(N_0-1)l$, we then have

$$f(v)=\lim_{N_0\to\infty}\frac{1}{N_0^3}\ln Q_N(V)\leqslant\ln(la^2-a^3)+1 \quad \text{(IIIA-6)}$$

or

$$f(v)\leqslant\ln(v-v_{\min})+1. \quad \text{(IIIA-7)}$$

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Refinement of the Brillouin-Wigner Perturbation Method*

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New variational parameters are introduced into the wave function employed in the Brillouin-Wigner perturbation method, and determined to minimize the total energy. The original and modified procedures are illustrated by a numerical example.

THE variational perturbation method for bound states generated by the operator $H+V$ can be developed in terms of the complete set of functions ψ_l generated by the eigenvalue equation

$$H\psi_l=E_l\psi_l,\quad E_0\leqq E_l\leqq E_{l+1}\cdots. \quad (1)$$

The prescription[1–3]

$$\psi^{(n)}=\frac{1}{N}\bigg[\psi_0+\sum{}'\psi_a\frac{V_{a0}}{E-E_a}+\sum{}'\psi_b\frac{V_{ba}V_{a0}}{(E-E_b)(E-E_a)}+\cdots+\sum{}'\psi_l\frac{V_{lk}\cdots V_{a0}}{(E-E_l)(E-E_k)\cdots(E-E_a)}\bigg], \quad (2)$$

inserted into the variational integral for the energy,

$$E=(\psi|H+V|\psi)/(\psi|1|\psi), \quad (3)$$

yields

$$E=E_0+V_{00}+\epsilon_2+\epsilon_3+\cdots+\epsilon_{2n+1}, \quad (4)$$

in which

$$\epsilon_2=\sum_a{}'\frac{V_{0a}V_{a0}}{E-E_a},\qquad \epsilon_3=\sum_{a,b}{}'\frac{V_{0a}V_{ab}V_{b0}}{(E-E_a)(E-E_b)}, \quad (5)$$

and so on. Here E in the energy denominator is identified with the approximate value of the energy given by the variational integral. The prime on the summation symbols in Eqs. (2), (4), and (5) signifies that the value 0 is excluded; the variable indices range through the values 1, 2, $\cdots l$, $\cdots\infty$ independently. Because the indices are independent, repetitions occur; i.e., two or more indices may take on the same value in a single product of V matrix elements. The proof that $\epsilon_{2l}<0$ for $E<E_0$ is fairly immediate.

The Brillouin-Wigner perturbation procedure just described can be improved in accuracy and rapidity of convergence by a simple modification of the wave function which entails no additional complications in the actual calculations. The wave function of Eq. (2) is replaced by

$$\psi^{(n)}=\frac{1}{N}\bigg[\psi_0+G_1\sum{}'\psi_a\frac{V_{0a}}{E-E_a}+G_2\sum{}'\psi_b\frac{V_{ba}V_{a0}}{(E-E_b)(E-E_a)}+\cdots+G_n\sum{}'\psi_l\frac{V_{lk}\cdots V_{a0}}{(E-E_l)(E-E_k)\cdots(E-E_a)}\bigg]. \quad (6)$$

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