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Statistical Mechanics of One-Dimensional Systems. I

——*Phase Transition of a van der Waals Gas*——

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The model of one-dimensional gas is proposed in which the particles have hard cores and pair potentials $-2a/L$, $a(>0)$ being a constant and L the length of the gas. The partition function for this model is exactly calculated and yields van der Waals' equation of state, involving an unstable portion of the isotherm. The grand partition function and the isothermal-isobaric partition function for this model are exactly obtained and a phase transition is deduced. Comparison of this model with the Husimi-Temperley model of a lattice system is made. The first five (volume-dependent) cluster integrals for this model are calculated.

§ 1. Introduction

——*A Model of One-Dimensional Gas*——

The condensation phenomenon of the usual three-dimensional gas is explained[1)~6)] in terms of the cluster integrals, which are effective mathematical expressions for the intermolecular forces of the usual type. On the other hand, one-dimensional gases with intermolecular forces of finite range exhibit no phase transition,[7),8)] owing to the essentially weak coupling of particles in the one-dimensional structure.

Kac, Uhlenbeck and Hemmer[9)] (KUH) have shown that the one-dimensional gas of particles with hard cores and with attractions given by the potential $-a\gamma e^{-\gamma R}$ with $\gamma\to+0$ ($a[>0]$ being a constant and R the distance between a pair of particles) undergoes a phase transition.

In this paper we consider the one-dimensional gas of N particles in a vessel of length L for which the pair potential is given by

$$\phi(R_{ij})=\begin{cases}+\infty & \text{for} \quad R_{ij}<\sigma\,,\\ -2a/L & \text{for} \quad R_{ij}\geqq\sigma\,,\end{cases} \tag{1·1}$$

where R_{ij} is the distance between the i-th and j-th particles and $\sigma(>0)$ and $a(>0)$ are constants (see Fig. 1). Clearly σ represents the diameter of the hard core of a particle, and the attraction $(-2a/L)$ is of infinite

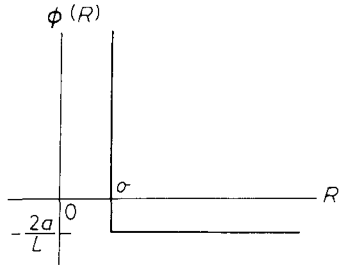

Fig. 1. Interparticle potential of a one-dimensional gas model.

range and is of infinitesimal strength in the limit $L\to\infty$. (If $a=0$, this model is reduced to Tonks' gas.[10])

Our model [(1·1)] is much simpler than that of KUH, and exactly obeys van der Waals' equation of state (§§ 2~4), just as the KUH model does. Thus our model offers a simple modern interpretation of the old concept of a van der Waals gas. For our model the partition function (§ 2), the grand partition function (§ 3) and the isothermal-isobaric partition function (§ 4) are exactly obtained, while the partition function for the KUH model has not been calculated. The partition function for our model involves an unstable portion of the isotherm (§ 2). The phase transition of our model is rigorously deduced both from the theory of grand canonical ensemble (§ 3) and from the theory of isothermal-isobaric ensemble (§ 4). Maxwell's equal-area rule is justified in our theory.

The mathematical proofs of some formulae in §§ 3 and 4 are given in Appendices A, B, C. The L-dependent (i.e., volume-dependent) cluster integrals $b_1, \cdots, b_5$ for our model for finite L and the limiting cluster integrals $b_1^{(0)}, \cdots, b_5^{(0)}$ for $L\to\infty$ are calculated in Appendix D.

§ 2. The partition function

The partition function for our model [(1·1)] is given by

$$Q(N, L, T)=\frac{1}{N!\Lambda^N}\int_0^L\int_0^L\cdots\int_0^L \exp\left\{-\frac{1}{kT}\sum_{i<j}\phi(|x_j-x_i|)\right\}dx_1 dx_2\cdots dx_N$$

$$=\Lambda^{-N}(N!)^{-1}\exp[(1/kT)\{N(N-1)/2\}(2a/L)]\cdot N!I_N(L), \qquad (2\cdot1)$$

with

$$\Lambda=h(2\pi mkT)^{-1/2}, \qquad (2\cdot2)$$

k being Boltzmann's constant, h Planck's constant, m the mass of a particle, T the temperature, and x_i the coordinate of the i-th particle ($i=1, 2, \cdots, N$); and here

$$I_N(L)=\int_{(N-1)\sigma}^{L}dx_N\int_{(N-2)\sigma}^{x_N-\sigma}dx_{N-1}\cdots\int_{2\sigma}^{x_4-\sigma}dx_3\int_{\sigma}^{x_3-\sigma}dx_2\int_0^{x_2-\sigma}dx_1$$

$$=H_N(x_{N+1})\Big|_{x_{N+1}=L-\sigma}, \qquad (2\cdot3)$$

where

$$H_j(x_{j+1})=\int_{(j-1)\sigma}^{x_{j+1}-\sigma}H_{j-1}(x_j)dx_j \;(j\geqq 2),\quad H_1(x_2)=\int_0^{x_2-\sigma}dx_1=x_2-\sigma, \qquad (2\cdot4)$$

whence $H_j(x_{j+1})=(x_{j+1}-j\sigma)^j/j!$ [since this holds for $j=1$ and is true for $j=n$ if true for $j=n-1$ $(n \geqq 2)$]. Therefore from (2·3) we have

$$I_N(L)=(L+\sigma-N\sigma)^N/N!\,. \tag{2·5}$$

Consequently from (2·1) we obtain

$$Q(N,L,T)=\Lambda^{-N}(N!)^{-1}(L+\sigma-N\sigma)^N \exp\{N(N-1)a/kTL\}. \tag{2·6}$$

From this the Helmholtz free energy F_N of the system is calculated as

$$\begin{aligned} F_N &= -kT \ln Q(N,L,T) \\ &= kT\{N \ln \Lambda + \ln(N!) - N \ln(L+\sigma-N\sigma)\} - N(N-1)a/L\,. \end{aligned} \tag{2·7}$$

Hence the pressure p_N of the system is given by

$$p_N = -(\partial F_N/\partial L)_{N,T} = NkT/(L+\sigma-N\sigma) - N(N-1)a/L^2\,. \tag{2·8}$$

Now by Stirling's theorem we have for every positive integer n

$$\ln n! = n \ln n - n + (1/2)\ln n + \gamma(n), \tag{2·9}$$

where

$$0<\gamma(n)<K_1 \qquad (\text{for every } n), \tag{2·10}$$

$K_1(>0)$ being an absolute constant. Denote by l the specific volume (length) or the volume (length) per particle, $l=L/N$, of the system. Then from (2·7), (2·9) [with $n=N$] and (2·10) we obtain the Helmholtz free energy per particle of the infinite system:

$$\begin{aligned} f_\infty &= \lim(N\to\infty,\ L\to\infty,\ L/N=l \text{ fixed})F_N/N \\ &= kT\{\ln \Lambda - 1 - \ln(l-\sigma)\} - a/l\,. \end{aligned} \tag{2·11}$$

From (2·8) the pressure of the infinite system is derived:

$$p_\infty = \lim(N\to\infty,\ L\to\infty,\ L/N=l \text{ fixed})\,p_N = kT/(l-\sigma) - a/l^2\,. \tag{2·12}$$

This is identical with van der Waals' equation of state.[11] Thus our model [(1·1)] represents a van der Waals gas. The equation of state (2·12) calculated from the *exact* partition function (2·6) has an unstable portion.

On the other hand, Van Hove's theorem[12] states that if a system (of volume V) consists of N particles with hard cores and with interparticle forces of short range, then the *exact* partition function for the system, in the limit $N\to\infty$, $V\to\infty$, with $V/N=v$ fixed, leads to the pressure monotonically decreasing with v (thus the isotherm has no unstable portion). But the interparticle forces for our model are of long range and thus do not satisfy the condition of Van Hove's theorem; hence it is possible that our model may have an unstable portion of the isotherm. (In particular, since the interparticle potential for our model depends on L, the derivative of the potential energy with respect to L contributes to the pressure.)

§ 3. The grand partition function

3.1. *Expression of the pressure in terms of the largest value of the function* $\Psi(\nu)$

The grand partition function for the system is given by

$$\Xi(L, z, T)=1+\sum_{N=1}^{[L/\sigma]} Q(N, L, T)(\Lambda z)^N \tag{3·1}$$

($[L/\sigma]$ denoting the largest integer not exceeding L/σ), where z is the activity of the system; Λz = absolute activity. Denote by P the pressure of the infinite system in the grand canonical ensemble. Then

$$P/kT[\equiv W, \text{say}]=\lim_{L\to\infty}(1/L)\ln \Xi(L, z, T). \tag{3·2}$$

Now put $N=\nu L$ and

$$\psi(\nu, L, z, T)=(1/L)\ln\{Q(\nu L, L, T)(\Lambda z)^{\nu L}\}, \tag{3·3}$$

where (for a given L) ν takes positive values such that νL is a positive integer not exceeding L/σ [thus, if $L=2.5$ and $\sigma=0.6$, then $\nu=0.4, 0.8, 1.2, 1.6$]. Then from (3·1) we have for every $L(>0)$, $z(>0)$ and $T(>0)$

$$\psi(\tilde{\nu}_L, L, z, T)\leqq(1/L)\ln \Xi(L, z, T)\leqq(1/L)\ln[L/\sigma]+\psi(\tilde{\nu}_L, L, z, T), \tag{3·4}$$

where $\tilde{\nu}_L$ is one of the values of ν for which $\psi(\nu, L, z, T)$ takes the largest value for given L, z, T. It follows from (3·2) and (3·4) that

$$W[\equiv P/kT]=\lim_{L\to\infty} \psi(\tilde{\nu}_L, L, z, T). \tag{3·5}$$

From (3·3), (2·6) and (2·9) [with $n=\nu L$] we obtain

$$\begin{aligned}\psi(\nu, L, z, T)&[\equiv\psi(\nu, L, y), \text{say}]\\ &=y\nu+\nu-\nu\ln\nu+\nu\ln(1-\sigma\nu+\sigma/L)\\ &\quad+\alpha(\nu^2-\nu/L)-(1/2L)\ln(\nu L)-\gamma(\nu L)/L\,,\end{aligned} \tag{3·6}$$

where $y\equiv\ln z[=g/kT-\ln\Lambda$, with g the chemical potential] and

$$\alpha\equiv a/kT\,. \tag{3·7}$$

Putting $L_n=n/\nu$ $(n=1, 2, 3, \cdots)$, we have from (3·6) and (2·10)

$$\lim_{n\to\infty} \psi(\nu, L_n, y) = y\nu + \nu - \nu \ln \nu + \nu \ln(1-\sigma\nu) + a\nu^2 [\equiv \Psi(\nu, y), \text{ say}] \tag{3·8}$$

for every ν $(0<\nu<1/\sigma)$ and every y $(-\infty<y<+\infty)$. Now let $\bar{\nu}[=\bar{\nu}(y)]$ be one of the values of ν $(0<\nu<1/\sigma)$ for which $\Psi(\nu, y)$ takes the largest value for a given y. Then we can prove [see Appendix A] that

$$W[\equiv P/kT] = \Psi(\bar{\nu}, y). \tag{3·9}$$

3.2. *Behaviour of the function* $\Psi(\nu)$; *the extremal points*

From (3·8) we have

$$(\partial/\partial\nu)\Psi(\nu, y) = y - \chi(\nu), \tag{3·10}$$

where

$$\chi(\nu) \equiv \ln \nu - \ln(1-\sigma\nu) + \sigma\nu/(1-\sigma\nu) - 2a\nu\,, \tag{3·11}$$

whence $\chi(\nu)\to-\infty$ (as $\nu\to+0$), $\chi(\nu)\to+\infty$ (as $\nu\to1/\sigma-0$) and we have

$$\chi'(\nu) = \zeta(\nu)/\nu(1-\sigma\nu)^2\,, \tag{3·12}$$

with

$$\zeta(\nu) = 1 - 2a\nu(1-\sigma\nu)^2\,. \tag{3·13}$$

From (3·13)

$$\zeta'(\nu) = 2a(3\sigma\nu-1)(1-\sigma\nu). \tag{3·14}$$

Hence $\zeta'(\nu)=0$ at $\nu=1/3\sigma$, $1/\sigma$; and from (3·13) we have [by (3·7)]

$$\zeta(0) = \zeta(1/\sigma) = 1, \qquad \zeta(1/3\sigma) = 1 - a/a_c = 1 - T_c/T\,, \tag{3·15}$$

where

$$a_c \equiv 27\sigma/8 \equiv a/kT_c, \qquad T_c \equiv 8a/27k\sigma\,. \tag{3·16}$$

$\zeta(1/3\sigma)$ is the smallest value of $\zeta(\nu)$ for $0<\nu<1/\sigma$. Thus, if $T>T_c$ [whence $\zeta(1/3\sigma)>0$ by (3·15)], then $\zeta(\nu)>0$ [and so $\chi'(\nu)>0$ by (3·12)] for $0<\nu<1/\sigma$; if $T=T_c$, then $\zeta(1/3\sigma)=0$, $\chi'(1/3\sigma)=\chi''(1/3\sigma)=0$ [i.e., $1/3\sigma$ is an inflexion point] and $\chi'(\nu)>0$ for $0<\nu<1/\sigma$ $(\nu\neq1/3\sigma)$; if $T<T_c$ [whence $\zeta(1/3\sigma)<0$], $\zeta(\nu)=0$ has two real roots [say $\nu^\dagger$, $\nu^\ddagger(>\nu^\dagger)$] for $0<\nu<1/\sigma$, hence [by (3·12)] $\chi(\nu)$ has a maximum at $\nu=\nu^\dagger$ and a minimum at $\nu=\nu^\ddagger$ [see Fig. 2].

Now denote by ν_e the ν giving the extremal values of the function $\Psi(\nu, y)$ of ν (for a fixed y). Then $(\partial/\partial\nu)\Psi(\nu, y)|_{\nu=\nu_e}=0$; thus by (3·10)

$$\chi(\nu_e) = y\,. \tag{3·17}$$

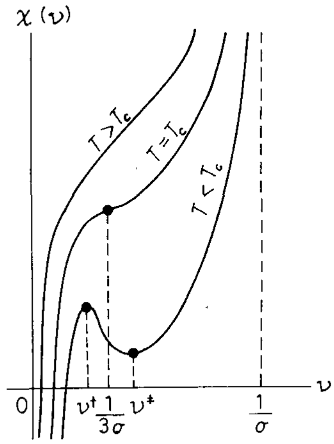

Fig. 2. Behaviour of the function $\chi(\nu)$ [(3·11)] (schematic).

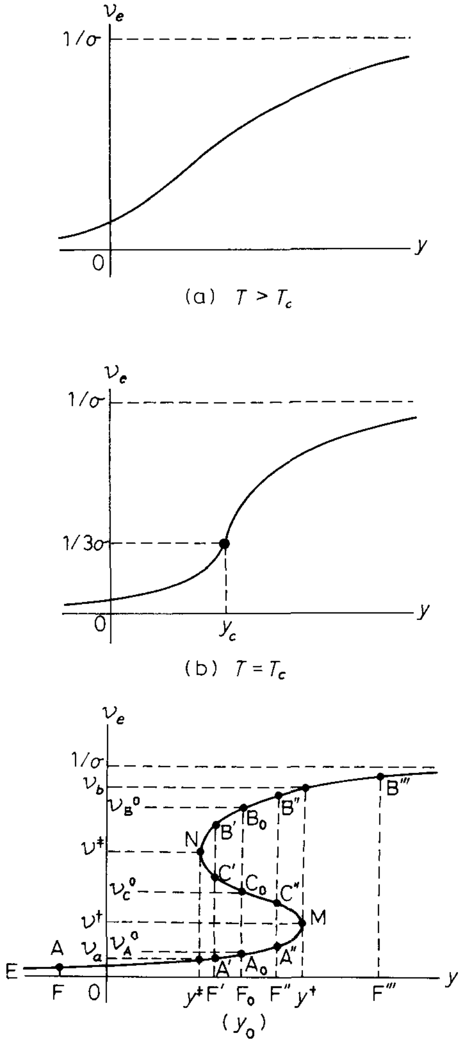

Fig. 3. Behaviour of ν_e [(3·17)] as a function of y (schematic).

We regard $\nu_e[=\nu_e(y)]$ as a (many-valued) function of $y\ (-\infty<y<+\infty)$. In view of Fig.2 and (3·17), the behaviour of ν_e as a function of y is schematically given by Fig. 3. If $T\geqq T_c$, the function $\nu_e(y)$ is single-valued, and if $T<T_c$, it is many-valued.

From (3·8) [with $\nu=\nu_e$] we obtain, using (3·17) and (3·11),

$$\Psi(\nu_e, y)=\nu_e/(1-\sigma\nu_e)-a\nu_e^2\ . \tag{3·18}$$

Hence

$$d\Psi(\nu_e, y)/d\nu_e=\zeta(\nu_e)/(1-\sigma\nu_e)^2\ , \tag{3·19}$$

with ζ given by (3·13). By (3·17), (3·19) and (3·12) [with $\nu=\nu_e$], we have

$$d\Psi(\nu_e, y)/dy=\{d\Psi(\nu_e, y)/d\nu_e\}\{\chi'(\nu_e)\}^{-1}=\nu_e\ . \tag{3·20}$$

Hence

$$\Psi(\nu_e, y)=\int_{-\infty}^{y}\nu_e dy\ , \tag{3·21}$$

since, if $y\to-\infty$, then $\nu_e\to+0$ [cf. Fig. 3], whence $\Psi(\nu_e, y)\to+0$ by (3·18).

Thus we have obtained a formula for the extremal values of the function $\Psi(\nu, y)$ of ν for various values of y.

3.3. *Pressure as a function of $y(\equiv \ln z)$ for $T \geqq T_c$; the critical point*

If $T \geqq T_c$, then [by (3·10) and Fig. 2], for any given y, we have $(\partial/\partial\nu)\Psi(\nu, y) > 0$ for $\nu < \nu_e$ and $(\partial/\partial\nu)\Psi(\nu, y) < 0$ for $\nu > \nu_e$; thus, for any fixed y, $\Psi(\nu_e, y)$

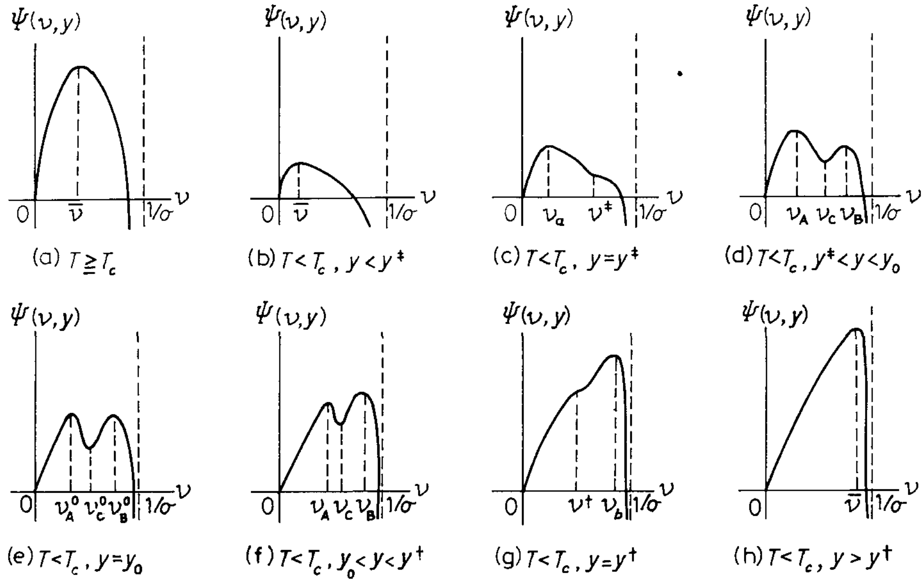

Fig. 4. Behaviour of $\Psi(\nu, y)$ [(3·8)] as a function of ν (schematic).

is the largest value, so that $\nu_e = \bar{\nu}$. [See Fig. 4(a); note that $\Psi(\nu, y) \to +0$ (as $\nu \to +0$) and $\Psi(\nu, y) \to -\infty$ (as $\nu \to 1/\sigma - 0$) from (3·8)]. Consequently, in virtue of (3·17) [with $\nu_e = \bar{\nu}$] and (3·11), we obtain

$$y = \ln \bar{\nu} - \ln(1 - \sigma\bar{\nu}) + \sigma\bar{\nu}/(1 - \sigma\bar{\nu}) - 2\alpha\bar{\nu}\,. \tag{3·22}$$

From (3·18) [with $\nu_e = \bar{\nu}$] and (3·9) we have

$$W = \bar{\nu}/(1 - \sigma\bar{\nu}) - \alpha\bar{\nu}^2\,. \tag{3·23}$$

Equations (3·22) and (3·23) give the function $W(y)[=\Psi(\bar{\nu}(y), y)]$ with $\bar{\nu}$ as a parameter.

If $T > T_c$, $W(y)$ is regular and $dW/dy > 0$ for $-\infty < y < +\infty$ [see Fig. 5(a)], since $\nu_e = \bar{\nu} > 0$ in (3·20) and $\bar{\nu}(y)[=\nu_e(y)]$ is regular. Thus no phase transition occurs.

If $T = T_c$, then $dW/dy > 0$ for $-\infty < y < +\infty$ [by (3·20) with $\nu_e = \bar{\nu}$] and $W(y)$ is regular except at $y = \chi(1/3\sigma) = -7/4 - \ln(2\sigma)[\equiv y_c$, say]; and

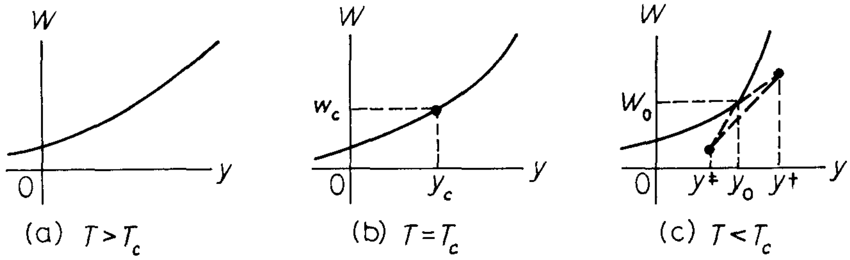

Fig. 5. Behaviour of the function $W(y)$ [(3·22) & (3·23)] (schematic).

$$\lim(y\to y_c\pm 0)\,d^2W/dy^2=+\infty \qquad (T=T_c), \tag{3·24}$$

since by (3·20), (3·17) and (3·12) we have $d^2\Psi(\nu_e, y)/dy^2=d\nu_e/dy=\{\chi'(\nu_e)\}^{-1}=\nu_e(1-\sigma\nu_e)^2/\zeta(\nu_e)$ and by (3·15) we have $\zeta(\nu_e)=0$ for $\nu_e=1/3\sigma$ and $\zeta(\nu_e)>0$ for $\nu_e\neq 1/3\sigma$. Hence $W(y)$ has an "analytical"[4] singularity at $y=y_c$ [see Fig. 5(b)]; from (3·23) [with $\bar{\nu}=1/3\sigma$] we have $W(y_c)=1/8\sigma[\equiv w_c$, say]. T_c is the critical temperature, and y_c, w_c give the critical point.

3.4. *Pressure as a function of $y(\equiv \ln z)$ for $T<T_c$; the phase transition*

When $T<T_c$, we put $y^{\dagger}\equiv\chi(\nu^{\dagger})$ and $y^{\ddagger}\equiv\chi(\nu^{\ddagger})$. Then, if $y<y^{\ddagger}$ or if $y>y^{\dagger}$, the function $\nu_e(y)$ is single-valued and [by (3·10) and Fig. 2] $(\partial/\partial\nu)\Psi(\nu, y)\gtrless 0$ according as $\nu\lessgtr\nu_e$, hence, for a given y, $\Psi(\nu_e, y)$ is the largest value, so that $\nu_e=\bar{\nu}$ [see Fig. 4(b), (h)].

If $y=y^{\ddagger}$ [or if $y=y^{\dagger}$], $\nu_e(y)$ is double-valued, the values being $\nu^{\ddagger}$ and $\nu_a(<\nu^{\ddagger})$ [or $\nu^{\dagger}$ and $\nu_b(>\nu^{\dagger})$]. Here ν_a [or ν_b] is a maximum point and $\nu^{\ddagger}$ [or $\nu^{\dagger}$] an inflexion point of the function $\Psi(\nu, y)$ of ν [note that $(\partial^2/\partial\nu^2)\Psi(\nu, y)=-\chi'(\nu)=0$ at $\nu=\nu^{\ddagger}, \nu^{\dagger}$]. Thus, $\nu_a=\bar{\nu}$ if $y=y^{\ddagger}$, and $\nu_b=\bar{\nu}$ if $y=y^{\dagger}$ [see Fig. 4(c), (g)].

If $y^{\ddagger}<y<y^{\dagger}$, $\nu_e(y)$ is triple-valued. Let the three values of $\nu_e(y)$ be ν_A, ν_C, ν_B ($\nu_A<\nu_C<\nu_B$) for a given y. Then from (3·10) and Fig. 2 it follows that $(\partial/\partial\nu)\Psi(\nu, y)$ is >0 (for $0<\nu<\nu_A$), <0 (for $\nu_A<\nu<\nu_C$), >0 (for $\nu_C<\nu<\nu_B$), and <0 (for $\nu_B<\nu<1/\sigma$); thus the function $\Psi(\nu, y)$ of ν has a maximum at $\nu=\nu_A$, a minimum at $\nu=\nu_C$, and a maximum at $\nu=\nu_B$.

We now discuss the behaviour of $\Psi(\nu_e(y), y)$ as a many-valued function of y for a given $T(<T_c)$, using (3·21) and Fig. 3(c), where E represents the point at $-\infty$ on the y-axis and on the curve expressing $\nu_e(y)$, and where M, N denote the points $(y^{\dagger}, \nu^{\dagger})$, $(y^{\ddagger}, \nu^{\ddagger})$ on the curve, respectively. Clearly there is one and only one value y_0 of y ($y^{\ddagger}<y_0<y^{\dagger}$) such that the points A_0, C_0, B_0 (on the curve) with abscissa y_0 [and with ordinates $\nu_A{}^0$, $\nu_C{}^0(>\nu_A{}^0)$, $\nu_B{}^0(>\nu_C{}^0)$ respectively] satisfy

$$[MC_0A_0M]_{ar}=[NC_0B_0N]_{ar}\,, \tag{3·25}$$

[$]_{ar}$ denoting the area of the domain indicated in [ ]. If $y<y^{\ddagger}$ [or if $y>y^{\dagger}$], then, taking that point A [or B‴] on the curve which has the abscissa y, we have from (3·21) and Fig. 3(c)

$$\Psi(\mathrm{A})=[\mathrm{EFAE}]_{\mathrm{ar}}, \qquad \Psi(\mathrm{B}''')=[\mathrm{EF}'''\mathrm{B}'''\mathrm{NME}]_{\mathrm{ar}}, \tag{3·26}$$

$\Psi(\mathrm{A})$, $\Psi(\mathrm{B}''')$ being the values of $\Psi(\nu_e, y)$ at A, B‴ respectively, and F, F‴ the feet of the perpendiculars from A, B‴ to the y-axis, respectively. Thus the function $\Psi(\nu_e(y), y)$ is single-valued. If $y^+<y<y_0$ [or if $y_0<y<y^\dagger$], we can take three points A′, C′, B′ [or A″, C″, B″] on the curve which have the same abscissa y (if $y=y^+$, then C′, B′ coincide with N, and if $y=y^\dagger$, then A″, C″ coincide with M). Thus $\Psi(\nu_e(y), y)$ is many-valued, and from (3·21) and Fig. 3(c) we have

$$\Psi(\mathrm{A}')=[\mathrm{EF}'\mathrm{A}'\mathrm{E}]_{\mathrm{ar}}, \tag{3·27a}$$

$$\Psi(\mathrm{B}')=[\mathrm{EF}'\mathrm{A}'\mathrm{E}]_{\mathrm{ar}}-[\mathrm{MC}'\mathrm{A}'\mathrm{M}]_{\mathrm{ar}}+[\mathrm{NC}'\mathrm{B}'\mathrm{N}]_{\mathrm{ar}}, \tag{3·27b}$$

$$\Psi(\mathrm{A}'')=[\mathrm{EF}''\mathrm{A}''\mathrm{E}]_{\mathrm{ar}}, \tag{3·28a}$$

$$\Psi(\mathrm{B}'')=[\mathrm{EF}''\mathrm{A}''\mathrm{E}]_{\mathrm{ar}}-[\mathrm{MC}''\mathrm{A}''\mathrm{M}]_{\mathrm{ar}}+[\mathrm{NC}''\mathrm{B}''\mathrm{N}]_{\mathrm{ar}}, \tag{3·28b}$$

$$\Psi(\mathrm{A}_0)=[\mathrm{EF}_0\mathrm{A}_0\mathrm{E}]_{\mathrm{ar}}, \tag{3·29a}$$

$$\Psi(\mathrm{B}_0)=[\mathrm{EF}_0\mathrm{A}_0\mathrm{E}]_{\mathrm{ar}}-[\mathrm{MC}_0\mathrm{A}_0\mathrm{M}]_{\mathrm{ar}}+[\mathrm{NC}_0\mathrm{B}_0\mathrm{N}]_{\mathrm{ar}}, \tag{3·29b}$$

F′, F″, F_0 being the feet of the perpendiculars from A′, A″, A_0 to the y-axis, respectively. From (3·25) and (3·27)~(3·29) it follows that

$$\Psi(\mathrm{A}')>\Psi(\mathrm{B}'), \quad \text{i.e.,} \quad \Psi(\nu_\mathrm{A}, y)>\Psi(\nu_\mathrm{B}, y) \quad \text{for } y^+<y<y_0, \tag{3·30}$$

$$\Psi(\mathrm{A}'')<\Psi(\mathrm{B}''), \quad \text{i.e.,} \quad \Psi(\nu_\mathrm{A}, y)<\Psi(\nu_\mathrm{B}, y) \quad \text{for } y_0<y<y^\dagger, \tag{3·31}$$

$$\Psi(\mathrm{A}_0)=\Psi(\mathrm{B}_0), \quad \text{i.e.,} \quad \Psi(\nu_\mathrm{A}^0, y_0)=\Psi(\nu_\mathrm{B}^0, y_0)[\equiv W_0, \text{ say}]. \tag{3·32}$$

Consequently, $\bar{\nu}=\nu_\mathrm{A}$ for $y^+<y<y_0$, $\bar{\nu}$ is double-valued ($\bar{\nu}=\nu_\mathrm{A}^0, \nu_\mathrm{B}^0$) for $y=y_0$, and $\bar{\nu}=\nu_\mathrm{B}$ for $y_0<y<y^\dagger$. [See Fig. 4(d)~(f).]

If $y<y_0$ or $y>y_0$, then, putting $\nu_e=\bar{\nu}$ in (3·17) [with (3·11)] and (3·18), we deduce [by (3·9)] (3·22) and (3·23) (for $0<\bar{\nu}<\nu_\mathrm{A}^0$, $\nu_\mathrm{B}^0<\bar{\nu}<1/\sigma$), which give the function $W(y)$ with $\bar{\nu}$ as a parameter. If $y=y_0$, then, though $\bar{\nu}$ is double-valued, both values ν_A^0, ν_B^0 give the same value of y and of W through (3·22) and (3·23) [see (3·32)]. Thus we obtain the function $W(y)$ ($-\infty<y<+\infty$). The solid line in Fig. 5(c) shows $W(y)$; the whole line (including the broken line) represents the many-valued function $\Psi(\nu_e(y), y)$ [the broken line corresponds to the analytical continuation of $W(y)$]. $W(y)$ is regular (and $dW/dy>0$) except at $y=y_0$, and has a "non-analytical"[4] singularity at $y=y_0$, where W is continuous but dW/dy is discontinuous; we have from (3·20) [with $\nu_e=\bar{\nu}$] and (3·9)

$$\lim(y\to y_0-0)\,dW/dy=\nu_\mathrm{A}^0, \quad \lim(y\to y_0+0)\,dW/dy=\nu_\mathrm{B}^0. \tag{3·33}$$

Thus the system for fixed $T(<T_c)$ exhibits a phase transition at $y=y_0$.

3.5. *The number density*

So far we have used $\bar{\nu}$ as a parameter in the parametric representation of $W(y)$ [(3·22), (3·23)]. But we can consider $\bar{\nu}$ [i.e., the ν making $\Psi(\nu, y)$ *largest*] to be the number density realized in the infinite system at equilibrium. From the theory of grand canonical ensemble, the *average* number density ρ of the infinite system is given by

$$\rho=\lim_{L\to\infty}(z/L)(\partial/\partial z)\ln \Xi(L, z, T)=dW/d\ln z=dW/dy \tag{3·34}$$

[see (3·2)]. Hence by (3·20) [with $\nu_e=\bar{\nu}$] and (3·9) we obtain

$$\bar{\nu}=\rho\,. \tag{3·35}$$

In view of this, we have from (3·22) and (3·23)

$$y[\equiv\ln z]=\ln\rho-\ln(1-\sigma\rho)+\sigma\rho/(1-\sigma\rho)-2\alpha\rho\,, \tag{3·36}$$

$$W[\equiv P/kT]=\rho/(1-\sigma\rho)-\alpha\rho^2\,. \tag{3·37}$$

If $T>T_c$, the functions $y(\rho)$ and $W(\rho)$ are regular and $dy/d\rho>0$, $dW/d\rho>0$ for $0<\rho<1/\sigma$ [by Fig. 3(a), (3·19) (with $\nu_e=\bar{\nu}=\rho$) and (3·15)].

If $T=T_c$, $y(\rho)$ and $W(\rho)$ are regular for $0<\rho<1/\sigma$ and $dy/d\rho>0$, $dW/d\rho>0$ except at $\rho=1/3\sigma$, where $dy/d\rho=dW/d\rho=d^2y/d\rho^2=d^2W/d\rho^2=0$ [see (3·12), (3·19), (3·15); note that $\chi''(1/3\sigma)=0$ and $d^2\Psi(\nu_e, y)/d\nu_e^2|_{\nu_e=1/3\sigma}=0$].

If $T<T_c$, $y(\rho)$ and $W(\rho)$ are regular (and $dy/d\rho>0$, $dW/d\rho>0$) for $0<\rho<\nu_A^0$ and for $\nu_B^0<\rho<1/\sigma$, and have "non-analytical" [4] singularities at $\rho=\nu_A^0$ and $\rho=\nu_B^0$. The values of ρ such that $\nu_A^0<\rho<\nu_B^0$ do not exist, since, for the infinite system in the grand canonical ensemble, the average density ρ [(3·34)] at $y=y_0$ has no values other than the two values (3·33), and $\bar{\nu}$ (considered to be the $\nu[=N/L]$ realized in equilibrium) has, at $y=y_0$, only two values (ν_A^0, ν_B^0). [See Figs. 6 and 7.]

Equation (3·37) is identical with van der Waals' equation of state, except that

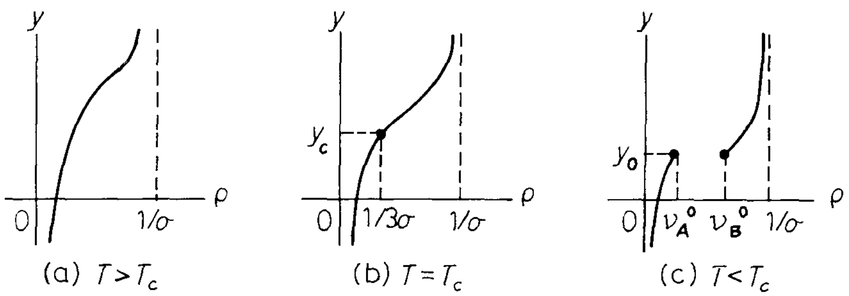

Fig. 6. Behaviour of the function $y(\rho)$ [(3·36)] (schematic).

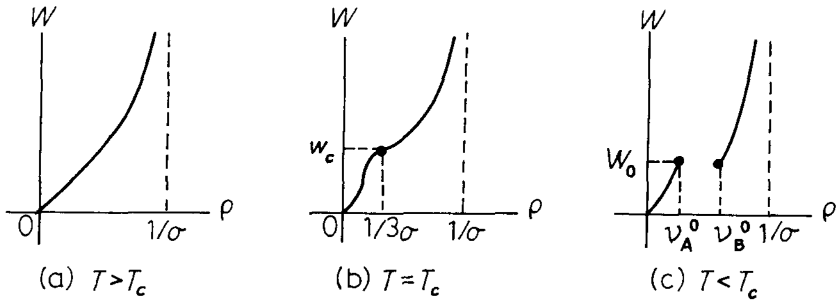

Fig. 7. Behaviour of the function $W(\rho)$ [(3·37)] (schematic).

for $T<T_c$ the former holds only when $0<\rho\leqq\nu_A{}^0$ or $\nu_B{}^0\leqq\rho<1/\sigma$. The densities of transition $\rho=\nu_A{}^0$, $\nu_B{}^0$ coincide with those determined by Maxwell's construction from van der Waals' equation.

§ 4. The isothermal-isobaric partition function

4.1. *Expression of the activity in terms of the largest value of the function* $\Phi(\lambda)$

The condensation of the usual gas in the isothermal-isobaric ensemble has been discussed in Ref. 13). We shall use this ensemble to treat our model. The isothermal-isobaric partition function is

$$R(N,p,T)=\int_{(N-1)\sigma}^{\infty}Q(N,L,T)\exp(-pL/kT)dL\,, \tag{4·1}$$

with p the pressure of the system. Let Z be the activity of the infinite system in the isothermal-isobaric ensemble. Then

$$\ln Z[\equiv Y,\text{say}]=-\lim_{N\to\infty}(1/N)\ln\{\Lambda^N R(N,p,T)\}. \tag{4·2}$$

Now put $L=\lambda N$ and

$$\varphi(\lambda,N,p,T)=(1/N)\ln\{\Lambda^N Q(N,\lambda N,T)\}-p\lambda/kT\,. \tag{4·3}$$

Then, from (4·1),

$$\Lambda^N R(N,p,T)=N\int_{\sigma-\sigma/N}^{\infty}\exp\{N\varphi(\lambda,N,p,T)\}d\lambda\,. \tag{4·4}$$

In virtue of (4·3), (2·6), (2·9) and (3·7), we have for $\lambda>\sigma-\sigma/N$

$$\varphi(\lambda,N,p,T)[\equiv\varphi(\lambda,N,w),\text{say}]$$
$$=-w\lambda+1+\ln(\lambda-\sigma+\sigma/N)+(1-1/N)a/\lambda$$

$$-(1/2N)\ln N-\gamma(N)/N \qquad [\text{with } w\equiv p/kT]. \tag{4·5}$$

Let $\tilde{\lambda}_N$ be one of the values of λ for which $\varphi(\lambda, N, w)$ takes the largest value for given N and w. Then we obtain [see Appendix B]

$$Y[\equiv\ln Z]=-\lim_{N\to\infty}\varphi(\tilde{\lambda}_N, N, w). \tag{4·6}$$

From (4·5) and (2·10) we have for every $\lambda(>\sigma)$ and every $w(>0)$

$$\lim_{N\to\infty}\varphi(\lambda, N, w)=-w\lambda+1+\ln(\lambda-\sigma)+a/\lambda[\equiv\Phi(\lambda, w),\text{ say}]. \tag{4·7}$$

Then, letting $\bar{\lambda}[=\bar{\lambda}(w)]$ be one of the values of $\lambda(>\sigma)$ for which $\Phi(\lambda, w)$ takes the largest value for a given w, we obtain [see Appendix C]

$$Y[\equiv\ln Z]=-\Phi(\bar{\lambda}, w). \tag{4·8}$$

4.2. *Behaviour of the function $\Phi(\lambda)$; the extremal points*

From (4·7) we have

$$(\partial/\partial\lambda)\Phi(\lambda, w)=-w+\theta(\lambda), \tag{4·9}$$

where

$$\theta(\lambda)\equiv 1/(\lambda-\sigma)-a/\lambda^2, \tag{4·10}$$

whence $\theta(\lambda)\to+\infty$ (as $\lambda\to\sigma+0$), $\theta(\lambda)\to+0$ (as $\lambda\to+\infty$) and we have

$$\theta'(\lambda)=\eta(\lambda)/(\lambda-\sigma)^2, \tag{4·11}$$

with

$$\eta(\lambda)=(2a/\lambda^3)(\lambda-\sigma)^2-1. \tag{4·12}$$

From (4·12)

$$\eta'(\lambda)=(2a/\lambda^4)(\lambda-\sigma)(3\sigma-\lambda). \tag{4·13}$$

Hence $\eta'(\lambda)=0$ at $\lambda=\sigma$, 3σ; and from (4·12) we have [by (3·7)]

$$\eta(\sigma)=\eta(+\infty)=-1, \qquad \eta(3\sigma)=a/a_c-1=T_c/T-1, \tag{4·14}$$

with a_c, T_c given by (3·16). $\eta(3\sigma)$ is the largest value of $\eta(\lambda)$ for $\sigma<\lambda<+\infty$. Thus, if $T>T_c$, then [by (4·14)] $\eta(\lambda)<0$ [and so $\theta'(\lambda)<0$ by (4·11)] for $\lambda>\sigma$; if $T=T_c$, then $\eta(3\sigma)=0$, $\theta'(3\sigma)=\theta''(3\sigma)=0$ [i.e., 3σ is an inflexion point] and $\theta'(\lambda)<0$ for $\lambda>\sigma(\lambda\neq 3\sigma)$; if $T<T_c$, then $\eta(\lambda)=0$ has two real roots [say $\lambda^\dagger$, $\lambda^\ddagger(<\lambda^\dagger)$] for $\lambda>\sigma$, hence [by (4·11)] $\theta(\lambda)$ has a maximum at $\lambda=\lambda^\dagger$ and a minimum at $\lambda=\lambda^\ddagger$ [see Fig. 8].

If λ_e denotes the λ giving the extremal values of the function $\Phi(\lambda, w)$ of λ (for a fixed w), then $(\partial/\partial\lambda)\Phi(\lambda, w)|_{\lambda=\lambda_e}=0$; so by (4·9)

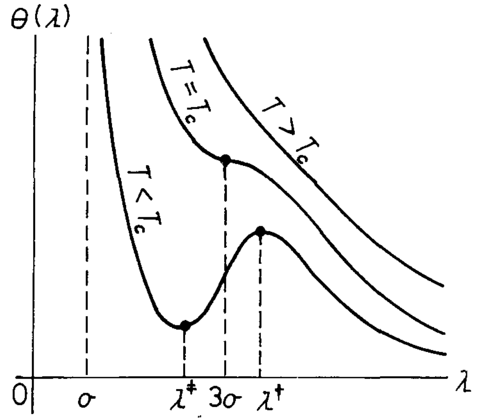

Fig. 8. Behaviour of the function $\theta(\lambda)$ [(4·10)] (schematic).

$$\theta(\lambda_e)=w\ . \qquad (4\cdot15)$$

By using Fig. 8 and (4·15), the function $\lambda_e(w)$ $(w>0)$ is schematically shown in Fig. 9; $\lambda_e(w)$ is single-valued if $T \geqq T_c$, and is many-valued if $T<T_c$.

From (4·7) [with $\lambda=\lambda_e$] we have, by (4·15) and (4·10),

$$\Phi(\lambda_e,\ w)=\ln(\lambda_e-\sigma)-\sigma/(\lambda_e-\sigma)+2\alpha/\lambda_e\ . \qquad (4\cdot16)$$

Hence

$$d\Phi(\lambda_e,\ w)/d\lambda_e=-\eta(\lambda_e)\lambda_e/(\lambda_e-\sigma)^2\ . \qquad (4\cdot17)$$

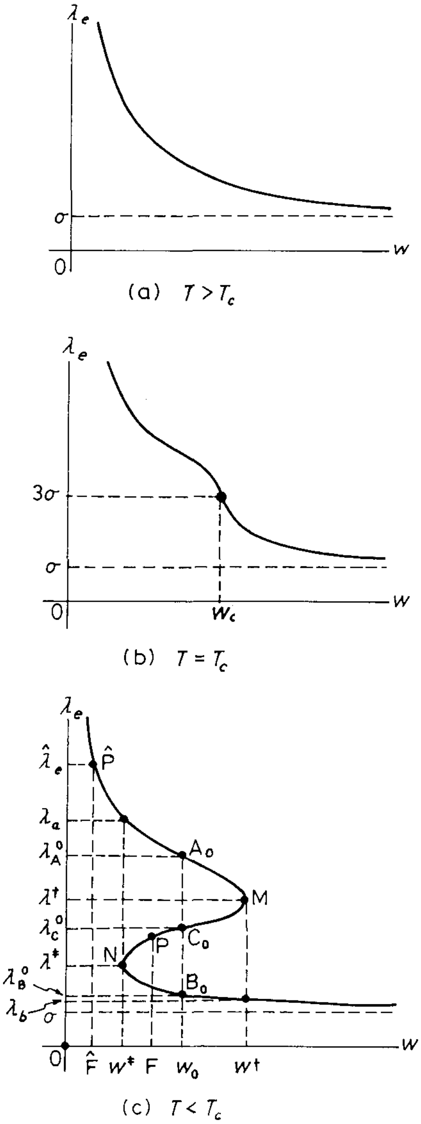

Fig. 9. Behaviour of λ_e [(4·15)] as a function of w (schematic).

Using (4·15), (4·17) and (4·11) [with $\lambda=\lambda_e$], we have

$$d\Phi(\lambda_e,\ w)/dw=\{d\Phi(\lambda_e,\ w)/d\lambda_e\}\{\theta'(\lambda_e)\}^{-1}=-\lambda_e\ . \qquad (4\cdot18)$$

Thus

$$\Phi(\hat{\lambda}_e,\ \hat{w})-\Phi(\lambda_e,\ w)=\int_{\hat{w}}^{w}\lambda_e dw\ , \qquad (4\cdot19)$$

where $\hat{\lambda}_e$ is the value of $\lambda_e(w)$ when w takes a value $\hat{w}$. Thus we have found a formula for the extremal values of the function $\Phi(\lambda, w)$ of λ for various values of w.

4.3. *Logarithm of activity as a function of $w(\equiv p/kT)$ for $T \geqq T_c$; the critical point*

If $T \geqq T_c$, it follows from (4·9) and Fig. 8 that, for any given $w(>0)$, $\Phi(\lambda_e, w)$ is the largest value; thus $\lambda_e = \bar{\lambda}$. [See Fig. 10(a); here $\Phi(\lambda, w) \to -\infty$ both for

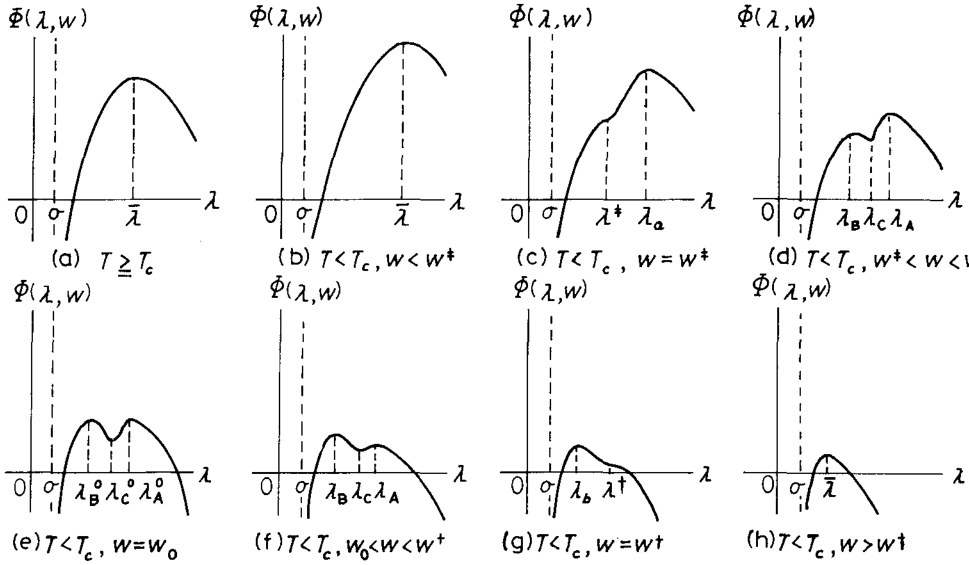

Fig. 10. Behaviour of $\Phi(\lambda, w)$ [(4·7)] as a function of λ (schematic).

$\lambda \to \sigma+0$ and for $\lambda \to +\infty$, by (4·7).] Hence, from (4·15) and (4·16) [with $\lambda_e = \bar{\lambda}$], we obtain, using (4·10) and (4·8),

$$w = 1/(\bar{\lambda}-\sigma) - a/\bar{\lambda}^2\,, \tag{4·20}$$

$$Y = -\ln(\bar{\lambda}-\sigma) + \sigma/(\bar{\lambda}-\sigma) - 2a/\bar{\lambda}; \tag{4·21}$$

these give the function $Y(w)[= -\Phi(\bar{\lambda}(w), w)]$ with $\bar{\lambda}$ as a parameter, and coincide with (3·23) and (3·22) if we set $w = W$, $Y = y$ and $\bar{\lambda} = 1/\bar{\nu}$.

If $T > T_c$, $Y(w)$ is regular and $dY/dw > 0$ for $w > 0$ [by (4·18) and (4·8)], hence no phase transition occurs [see Fig. 11(a)].

If $T = T_c$, then $dY/dw > 0$ for $w > 0$ and $Y(w)$ is regular except at $w = \theta(3\sigma) = 1/8\sigma [\equiv w_c]$; and

$$\lim(w \to w_c \pm 0)\, d^2Y/dw^2 = -\infty \qquad (T = T_c), \tag{4·22}$$

since by (4·18), (4·15) and (4·11) we have $-d^2\Phi(\lambda_e, w)/dw^2 = d\lambda_e/dw = \{\theta'(\lambda_e)\}^{-1}$

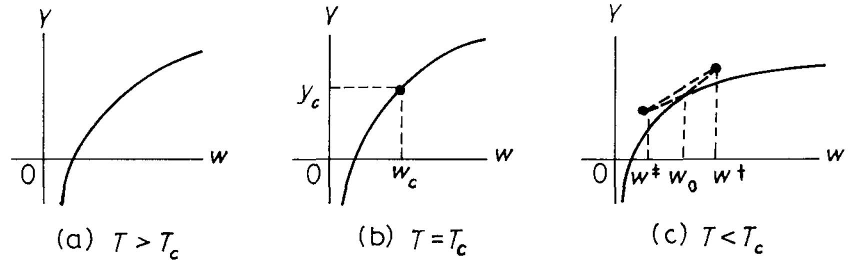

Fig. 11. Behaviour of the function $Y(w)$ [(4·20) & (4·21)] (schematic).

$=(\lambda_e-\sigma)^2/\eta(\lambda_e)$ and by (4·14) we have $\eta(\lambda_e)=0$ for $\lambda_e=3\sigma$ and $\eta(\lambda_e)<0$ for $\lambda_e \neq 3\sigma$. Thus $Y(w)$ has an "analytical"[4)] singularity at $w=w_c$ [see Fig. 11(b)]. T_c is the critical temperature; w_c and $y_c[=Y(w_c)=-7/4-\ln(2\sigma)$, by (4·21)] give the critical point.

4.4. *Logarithm of activity as a function of $w(\equiv p/kT)$ for $T<T_c$; the phase transition*

For $T<T_c$, put $w^{\dagger}\equiv\theta(\lambda^{\dagger})$, $w^{\ddagger}\equiv\theta(\lambda^{\ddagger})$. Then, if $w<w^{\ddagger}$ or if $w>w^{\dagger}$, the function $\lambda_e(w)$ is single-valued, and $\Phi(\lambda_e, w)$ is the largest value for a given w; thus $\lambda_e=\bar{\lambda}$ [see Fig. 10(b), (h)].

If $w=w^{\ddagger}$ [or if $w=w^{\dagger}$], $\lambda_e(w)$ is double-valued, the values being $\lambda^{\ddagger}$, $\lambda_a(>\lambda^{\ddagger})$ [or $\lambda^{\dagger}$, $\lambda_b(<\lambda^{\dagger})$]. Here λ_a [or λ_b] is a maximum point and $\lambda^{\ddagger}$ [or $\lambda^{\dagger}$] an inflexion point of the function $\Phi(\lambda, w)$ of λ [note that $(\partial^2/\partial\lambda^2)\Phi(\lambda, w)=\theta'(\lambda)=0$ at $\lambda=\lambda^{\ddagger}$, $\lambda^{\dagger}$]. Thus, $\lambda_a=\bar{\lambda}$ if $w=w^{\ddagger}$, and $\lambda_b=\bar{\lambda}$ if $w=w^{\dagger}$ [see Fig. 10(c), (g)].

If $w^{\ddagger}<w<w^{\dagger}$, then $\lambda_e(w)$ is triple-valued, and we let λ_A, λ_C, λ_B be the values of $\lambda_e(w)$ for a given w ($\lambda_A>\lambda_C>\lambda_B$). Then it follows that λ_A, λ_B are maximum points and λ_C a minimum point of the function $\Phi(\lambda, w)$ of λ. Now see Fig. 9(c), where M, N represent the points $(w^{\dagger}, \lambda^{\dagger})$, $(w^{\ddagger}, \lambda^{\ddagger})$ respectively, and $\hat{\mathrm{P}}$, P denote, respectively, the starting point $(\hat{w}, \hat{\lambda}_e)$ of integration in (4·19) and an arbitrary point (w, λ_e) on the curve [for convenience we let $\hat{w}<w^{\ddagger}$]. The integral (4·19) equals the area of the domain surrounded by the part of the curve from $\hat{\mathrm{P}}$ to P and the straight line segments PF, $\hat{\mathrm{P}}\hat{\mathrm{F}}$ and $\mathrm{F}\hat{\mathrm{F}}$, where F, $\hat{\mathrm{F}}$ are the feet of the perpendiculars from P, $\hat{\mathrm{P}}$ to the w-axis, respectively. (We agree that the area is negative if P lies to the left of $\hat{\mathrm{P}}$.) Thus there is one and only one pair of values of λ_e [say $\lambda_A{}^0$, $\lambda_B{}^0(<\lambda_A{}^0)$] giving the same value, say w_0, of w ($w^{\ddagger}<w_0<w^{\dagger}$) and the same value, say Y_0, of $-\Phi(\lambda_e, w)$. Let A_0, B_0 denote those points on the curve which correspond to $\lambda_A{}^0$, $\lambda_B{}^0$, respectively, and let C_0 be the point of intersection of the curve and the straight line A_0B_0, and $\lambda_C{}^0$ the ordinate of C_0. Then we have $[\mathrm{MC_0A_0M}]_{\mathrm{ar}}=[\mathrm{NC_0B_0N}]_{\mathrm{ar}}$. Therefore it follows that, if $w^{\ddagger}<w<w_0$, then $\Phi(\lambda_A, w)>\Phi(\lambda_B, w)$ [hence $\lambda_A=\bar{\lambda}$], and if $w_0<w<w^{\dagger}$, then $\Phi(\lambda_A, w)<\Phi(\lambda_B, w)$ [hence $\lambda_B=\bar{\lambda}$]. If $w=w_0$, then $\Phi(\lambda_A{}^0, w_0)=\Phi(\lambda_B{}^0, w_0)=-Y_0$, so that $\bar{\lambda}$ is double-valued ($\bar{\lambda}=\lambda_A{}^0, \lambda_B{}^0$). [See Fig. 10(d), (e), (f).]

If $w<w_0$ or $w>w_0$, then from (4·15) and (4·16) [with $\lambda_e=\bar{\lambda}$], using (4·10) and (4·8), we obtain (4·20) and (4·21) (for $\sigma<\bar{\lambda}<\lambda_B{}^0$, $\lambda_A{}^0<\bar{\lambda}<+\infty$), which give the function $Y(w)$ with $\bar{\lambda}$ as a parameter. If $w=w_0$, both values $\lambda_A{}^0$, $\lambda_B{}^0$ of $\bar{\lambda}$ give the same value of w and of Y, on using (4·20) and (4·21). Thus the function $Y(w)$ is obtained; it is schematically described by the solid line in Fig. 11(c) [where the whole line (including the broken line) represents $\Phi(\lambda_e(w), w)$]. $Y(w)$ is regular (and $dY/dw>0$) except at $w=w_0$, and has a "non-analytical"[4] singularity at $w=w_0$, where Y is continuous but dY/dw is discontinuous; we have, by (4·18) [with $\lambda_e=\bar{\lambda}$] and (4·8),

$$\lim(w\to w_0-0)dY/dw=\lambda_A{}^0, \qquad \lim(w\to w_0+0)dY/dw=\lambda_B{}^0 . \tag{4·23}$$

Thus the system with fixed $T(<T_c)$ shows a phase transition at $w=w_0$.

4.5. *The specific volume*

The quantity $\bar{\lambda}$, which serves as a parameter in the parametric representation [(4·20), (4·21)] of $Y(w)$, can be considered as the specific volume realized in the infinite system at equilibrium, since $\bar{\lambda}$ makes $\Phi(\lambda, w)$ *largest*. The *average* specific volume v of the infinite system in the isothermal-isobaric ensemble is given by

$$v=-\lim_{N\to\infty}(kT/N)(\partial/\partial p)\ln\{\Lambda^N R(N, p, T)\}=dY/dw , \tag{4·24}$$

on account of (4·2). Therefore, by (4·18) [with $\lambda_e=\bar{\lambda}$] and (4·8),

$$\bar{\lambda}=v . \tag{4·25}$$

Substituting this in (4·20) and (4·21), we obtain

$$w[\equiv p/kT]=1/(v-\sigma)-a/v^2 , \tag{4·26}$$

$$Y[\equiv \ln Z]=-\ln(v-\sigma)+\sigma/(v-\sigma)-2a/v . \tag{4·27}$$

If $T>T_c$, the functions $w(v)$ and $Y(v)$ are regular and $dw/dv<0$, $dY/dv<0$ for $v>\sigma$ [by Fig. 9(a), (4·17) (with $\lambda_e=\bar{\lambda}=v$) and (4·14)].

If $T=T_c$, $w(v)$ and $Y(v)$ are regular for $v>\sigma$ and $dw/dv<0$, $dY/dv<0$ except at $v=3\sigma$, where $dw/dv=dY/dv=d^2w/dv^2=d^2Y/dv^2=0$ [see (4·11), (4·17) and (4·14); note that $\theta''(3\sigma)=0$ and $d^2\Phi(\lambda_e, w)/d\lambda_e{}^2|_{\lambda_e=3\sigma}=0$].

If $T<T_c$, $w(v)$ and $Y(v)$ are regular (and $dw/dv<0$, $dY/dv<0$) for $v>\lambda_A{}^0$ and for $\sigma<v<\lambda_B{}^0$, and have "non-analytical"[4] singularities at $v=\lambda_A{}^0$ and $v=\lambda_B{}^0$. The values of v such that $\lambda_B{}^0<v<\lambda_A{}^0$ do not exist, since, for the infinite system in the isothermal-isobaric ensemble, v [(4·24)] at $w=w_0$ has only the two values (4·23), and $\bar{\lambda}$ (considered to be the $\lambda[=L/N]$ realized in equilibrium) at $w=w_0$ has the values $\lambda_A{}^0$, $\lambda_B{}^0$ only. [See Figs. 12 and 13.]

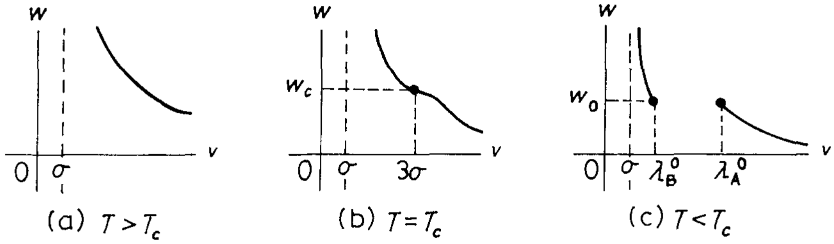

Fig. 12. Behaviour of the function $w(v)$ [(4·26)] (schematic).

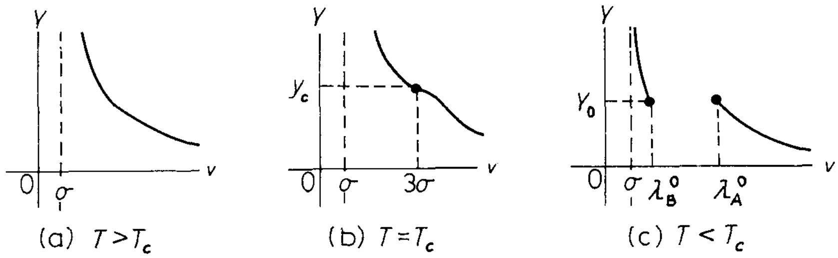

Fig. 13. Behaviour of the function $Y(v)$ [(4·27)] (schematic).

Equation (4·26) is the same as van der Waals' equation of state, except that if $T<T_c$ then we have (4·26) only in the range $\sigma<v\leqq\lambda_B{}^0$, $\lambda_A{}^0\leqq v<+\infty$. The determination of w_0 in Fig. 9(c) is equivalent to Maxwell's construction.

§ 5. Concluding remarks

The partition function for our model yields van der Waals' equation of state, involving an unstable portion of the isotherm. But the grand partition function and the isothermal-isobaric partition function for our model lead to the isotherms constructed from van der Waals' equation of state by removing the unstable portions with the use of Maxwell's equal-area rule; thus our model undergoes condensation. The condensation point derived from the theory of *grand canonical ensemble* (g.c.e.) and that derived from the theory of *isothermal-isobaric ensemble* (t.b.e.) are the same, though the independent variable in g.c.e. is z(= activity) and that in t.b.e. is p(=pressure). In g.c.e. the number density is double-valued at the condensation point, while in t.b.e. the specific volume is double-valued at the condensation point.

From the analytical point of view, the condensation point is a "non-analytical" singularity of the pressure as a function of z (in g.c.e.) and of the activity as a function of p (in t.b.e.). The function for the liquid phase is the analytical continuation of the gaseous function. Thus the condensation belongs to type b according to the classification given by one of the present authors (Ikeda).[4),6),14)]

In particular, at the critical temperature, the transition is of type a. The distribution of zeros (on the complex z-plane) of the grand partition function for the van der Waals gas has been investigated in Ref. 15).

We now make a comparison of our model with the Husimi-Temperley (HT) model[16] of a lattice gas, in which more than one particle cannot occupy the same site and the interaction potential between a pair of particles on different sites is $-2a/M$ ($a[>0]$ being a constant and M the total number of sites). The *exact* partition function for the HT model leads to the equation of state:

$$p_\infty = -kT\ln(1-v^{-1}) - av^{-2} \qquad (v=M/N), \tag{5·1}$$

which has an unstable portion, just as in our model. Thus our model may be said to be the counterpart (in the continuous gas) of the HT model. The HT model may be a one-, two- or three-dimensional system; but its continuous-gas counterpart (our model) is restricted to a one-dimensional system, because the essential structure of a continuous gas is much more complicated than that of a lattice gas. The arguments given in §§ 3 and 4 of this paper on the condensation in g.c.e. and t.b.e. can be straightforwardly applied to the HT model.

Appendix A

——Proof of (3·9)——

The proof is given for any fixed $z(>0)$ and $T(>0)$; so we write $\psi(\nu, L)$, $\Psi(\nu)$ for $\psi(\nu, L, y)[\equiv\psi(\nu, L, z, T)]$, $\Psi(\nu, y)$ respectively.

It follows from (3·6) and (3·8) that

$$|\psi(\nu, L)-\Psi(\nu)|$$
$$\leqq (1/L)\{\sigma\nu/(1-\sigma\nu)+a\nu+(1/2)\ln(\nu L)+\gamma(\nu L)\} \tag{A·1}$$

for every pair ν, L such that $0<\nu<1/\sigma$ and νL is a positive integer [note that $0<\ln(1+x)<x$ for $x>0$]. Hence [by (2·10)], for any given $\epsilon>0$, there exists a real number $L_0(\epsilon;\mu)[>0]$, independent of ν, such that

$$|\psi(\nu, L)-\Psi(\nu)|<\epsilon \quad \text{if} \quad 0<\nu\leqq\mu, \quad L>L_0(\epsilon;\mu) \quad \text{and} \quad \nu L=\text{integer}, \tag{A·2}$$

where μ is any real number such that $0<\mu<1/\sigma$.

Now, assuming ν to be a continuous variable, we have from (3·6)

$$(\partial/\partial\nu)\psi(\nu, L) = y-\ln\nu+\ln(1-\sigma\nu+\sigma/L)$$
$$-\sigma\nu(1-\sigma\nu+\sigma/L)^{-1}+a(2\nu-1/L)-1/2\nu L-\gamma'(\nu L), \tag{A·3}$$

where $\gamma'(\nu L)$ is bounded. Consequently

$$\lim_{\substack{\nu\to 1/\sigma-0 \\ L\to+\infty}} (\partial/\partial\nu)\psi(\nu, L) = -\infty\,. \tag{A·4}$$

Thus there exist real numbers ν^* $(0<\nu^*<1/\sigma)$ and $L^*[>(1/\sigma-\nu^*)^{-1}]$ such that $(\partial/\partial\nu)\psi(\nu, L)<0$ for $\nu^*<\nu<1/\sigma$ and for $L>L^*$; so, by the definition of $\tilde{\nu}_L$,

$$0<\tilde{\nu}_L<\nu^*+1/L<\nu^*+1/L^*[\equiv\nu', \text{say}]<1/\sigma \quad \text{for } L>L^* . \tag{A·5}$$

Now put $L_m=m/\bar{\nu}$ $(m=1, 2, 3, \cdots)$, $\nu_0=\max\{\bar{\nu}, \nu'\}$ and $m_0(\epsilon)=\bar{\nu}\max\{L_0(\epsilon;\nu_0), L^*\}$ ($\max\{a, b\}$ denoting the larger of a and b). Then clearly $0<\bar{\nu}\leqq\nu_0$, and if $m>m_0(\epsilon)$, we have $L_m>L_0(\epsilon;\nu_0)$ and $L_m>L^*$, whence $0<\tilde{\nu}_{L_m}\leqq\nu_0$ by (A·5). Hence, from (A·2) (with $\mu=\nu_0$), we have for any given $\epsilon>0$

$$|\psi(\bar{\nu}, L_m)-\Psi(\bar{\nu})|<\epsilon \quad \text{and} \quad |\psi(\tilde{\nu}_{L_m}, L_m)-\Psi(\tilde{\nu}_{L_m})|<\epsilon \quad \text{for } m>m_0(\epsilon). \tag{A·6}$$

From the definitions of $\tilde{\nu}_L$ and $\bar{\nu}$ we have

$$\psi(\bar{\nu}, L_m)\leqq\psi(\tilde{\nu}_{L_m}, L_m) \quad \text{and} \quad \Psi(\bar{\nu})\geqq\Psi(\nu_{L_m}) \quad (\text{for every } m\geqq1). \tag{A·7}$$

Consequently, in virtue of (A·6), it follows that, for $m>m_0(\epsilon)$,

$$-\epsilon<\psi(\bar{\nu}, L_m)-\Psi(\bar{\nu})\leqq\psi(\tilde{\nu}_{L_m}, L_m)-\Psi(\bar{\nu})\leqq\psi(\tilde{\nu}_{L_m}, L_m)-\Psi(\tilde{\nu}_{L_m})<\epsilon. \tag{A·8}$$

Hence $\lim_{m\to\infty}\{\psi(\tilde{\nu}_{L_m}, L_m)-\Psi(\bar{\nu})\}=0$. Therefore $\lim_{L\to\infty}\psi(\tilde{\nu}_L, L)=\Psi(\bar{\nu})$, which, in view of (3·5), completes the proof of (3·9).

Appendix B

—— Proof of (4·6) ——

The proof is given for any fixed $p(>0)$ and $T(>0)$; accordingly we denote $\varphi(\lambda, N, w)[\equiv\varphi(\lambda, N, p, T)]$ by $\varphi(\lambda, N)$.

First we have from (4·5)

$$(\partial/\partial\lambda)\varphi(\lambda, N)=-w+(\lambda-\sigma+\sigma/N)^{-1}-(1-1/N)a/\lambda^2 . \tag{B·1}$$

$\lambda=\tilde{\lambda}_N$ gives an extremal value of the function $\varphi(\lambda, N)$ of λ; so by (B·1)

$$\tilde{\lambda}_N-\sigma+\sigma/N=\{w+(1-1/N)a/\tilde{\lambda}_N{}^2\}^{-1}>0 \quad (\text{for every } N\geqq1). \tag{B·2}$$

Thus $\tilde{\lambda}_N>\sigma-\sigma/N\geqq\sigma/2$ (for every $N\geqq2$); therefore from (B·2) we obtain

$$1/w>\tilde{\lambda}_N-\sigma+\sigma/N>(w+4a/\sigma^2)^{-1}[\equiv B, \text{say}] \quad (\text{for every } N\geqq2). \tag{B·3}$$

Hence

$$\sigma+1/w>\tilde{\lambda}_N>\sigma/2+B \qquad (\text{for every } N\geqq2). \tag{B·4}$$

Next it follows from (4·5) that, for every $N\geqq1$ and for $\lambda>\sigma-\sigma/N$,

$$\varphi(\lambda, N)-\varphi(\tilde{\lambda}_N, N)=-w(\lambda-\tilde{\lambda}_N)+\ln\{1+(\lambda-\tilde{\lambda}_N)/(\tilde{\lambda}_N-\sigma+\sigma/N)\}$$
$$-(1-1/N)a(\lambda-\tilde{\lambda}_N)/\lambda\tilde{\lambda}_N . \tag{B·5}$$

Hence, in view of the definition of $\tilde{\lambda}_N$, we have

$$\ln\{1+(\lambda-\tilde{\lambda}_N)/(\tilde{\lambda}_N-\sigma+\sigma/N)\}\leqq\varphi(\lambda,N)-\varphi(\tilde{\lambda}_N,N)\leqq 0$$
$$(\text{for } \sigma-\sigma/N<\lambda\leqq\tilde{\lambda}_N) \tag{B·6}$$

for every $N\geqq 1$. Now let $x=A$ be the largest root of the equation $\ln(1+x/B)=(w/2)x$; thus $A\geqq 0$. Then, in virtue of (B·3), we have for every $N\geqq 2$

$$\ln\{1+(\lambda-\tilde{\lambda}_N)/(\tilde{\lambda}_N-\sigma+\sigma/N)\}\leqq(w/2)(\lambda-\tilde{\lambda}_N)\quad(\text{for } \lambda\geqq\tilde{\lambda}_N+A). \tag{B·7}$$

With the use of (B·5), we have for every $N\geqq 1$

$$-(w+a/\tilde{\lambda}_N{}^2)(\lambda-\tilde{\lambda}_N)\leqq\varphi(\lambda,N)-\varphi(\tilde{\lambda}_N,N)\leqq 0\quad(\text{for } \tilde{\lambda}_N\leqq\lambda\leqq\tilde{\lambda}_N+A) \tag{B·8}$$

[which is unnecessary if $A=0$]. By (B·5) and (B·7), we have for $N\geqq 2$

$$-(w+a/\tilde{\lambda}_N{}^2)(\lambda-\tilde{\lambda}_N)\leqq\varphi(\lambda,N)-\varphi(\tilde{\lambda}_N,N)\leqq-(w/2)(\lambda-\tilde{\lambda}_N-A)$$
$$(\text{for } \lambda\geqq\tilde{\lambda}_N+A). \tag{B·9}$$

Now we have

$$\int_{\sigma-\sigma/N}^{\tilde{\lambda}_N}\left\{1+\frac{\lambda-\tilde{\lambda}_N}{\tilde{\lambda}_N-\sigma+\sigma/N}\right\}^N d\lambda=\frac{\tilde{\lambda}_N-\sigma+\sigma/N}{N+1},$$

$$\int_c^\infty \exp\{-Nq(\lambda-c)\}\,d\lambda=\frac{1}{Nq}$$

[with $q=w+a/\tilde{\lambda}_N{}^2$, $w/2$ and $c=\tilde{\lambda}_N$, $\tilde{\lambda}_N+A$]. In virtue of these, on integrating $\exp N\{\varphi(\lambda,N)-\varphi(\tilde{\lambda}_N,N)\}$ over λ (from $\sigma-\sigma/N$ to ∞), it follows from (4·4), (B·6), (B·8) and (B·9) that

$$(\tilde{\lambda}_N-\sigma+\sigma/N)/(N+1)+1/N(w+a/\tilde{\lambda}_N{}^2)$$
$$\leqq N^{-1}\Lambda^N R(N,p,T)\exp\{-N\varphi(\tilde{\lambda}_N,N)\}\leqq\tilde{\lambda}_N-\sigma+\sigma/N+A+2/Nw \tag{B·10}$$

for every $N\geqq 2$. Hence, by (4·2) and (B·4), one proves (4·6).

Appendix C

—— *Proof of (4·8)* ——

The proof is given for any fixed $p(>0)$ and $T(>0)$; so we denote $\varphi(\lambda,N,w)$, $\Phi(\lambda,w)$ by $\varphi(\lambda,N)$, $\Phi(\lambda)$ respectively.

From (4·5) and (4·7) we have

$$|\varphi(\lambda,N)-\Phi(\lambda)|\leqq(1/N)\{\sigma/(\lambda-\sigma)+a/\lambda+(1/2)\ln N+\gamma(N)\} \tag{C·1}$$

for every $\lambda(>\sigma)$ and every $N(\geqq 1)$. Hence [by (2·10)], for any given $\epsilon>0$, there exists a positive integer $N_0(\epsilon;\mu)$, independent of λ, such that

$$|\varphi(\lambda, N)-\Phi(\lambda)|<\epsilon \quad \text{for } \lambda \geqq \mu \quad \text{for } N \geqq N_0(\epsilon;\mu), \tag{C·2}$$

where μ is any real number such that $\mu>\sigma$.

From (B·1) we have

$$\lim_{\substack{\lambda\to\sigma+0\\ N\to\infty}}(\partial/\partial\lambda)\varphi(\lambda, N)=+\infty\,. \tag{C·3}$$

Consequently, there exist $\lambda^*(>\sigma)$ and $N^*(\geqq 1)$ such that $(\partial/\partial\lambda)\varphi(\lambda, N)>0$ for $\sigma<\lambda<\lambda^*$ and for $N\geqq N^*$. Hence $\tilde{\lambda}_N\geqq\lambda^*$ for $N\geqq N^*$. Consequently, putting $\lambda_0=\min\{\bar{\lambda}, \lambda^*\}$ and $N_1(\epsilon)=\max\{N_0(\epsilon;\lambda_0), N^*\}$, we have $\bar{\lambda}\geqq\lambda_0$ and $\tilde{\lambda}_N\geqq\lambda_0$ for $N\geqq N_1(\epsilon)$; therefore, by (C·2) (with $\mu=\lambda_0$), we have for any given $\epsilon>0$

$$|\varphi(\bar{\lambda}, N)-\Phi(\bar{\lambda})|<\epsilon \quad \text{and} \quad |\varphi(\tilde{\lambda}_N, N)-\Phi(\tilde{\lambda}_N)|<\epsilon \quad \text{for } N\geqq N_1(\epsilon). \tag{C·4}$$

Hence (by the definitions of $\tilde{\lambda}_N$ and $\bar{\lambda}$) it follows that, for $N\geqq N_1(\epsilon)$,

$$-\epsilon<\varphi(\bar{\lambda}, N)-\Phi(\bar{\lambda})\leqq\varphi(\tilde{\lambda}_N, N)-\Phi(\bar{\lambda})\leqq\varphi(\tilde{\lambda}_N, N)-\Phi(\tilde{\lambda}_N)<\epsilon\,. \tag{C·5}$$

Thus $\lim_{N\to\infty}\varphi(\tilde{\lambda}_N, N)=\Phi(\bar{\lambda})$, which [in view of (4·6)] proves (4·8).

Appendix D

—— The Cluster Integrals ——

The (volume-dependent) cluster integrals b_j are defined so that

$$P^*/kT=L^{-1}\ln\Xi(z)=\sum_{j=1}^{\infty}b_j z^j \quad (P^*=\text{pressure of finite system}); \tag{D·1}$$

thus

$$b_j=(j!)^{-1}(\partial^j/\partial z^j)(L^{-1}\ln\Xi)|_{z=0}=(j!L)^{-1}(\partial^{j-1}/\partial z^{j-1})(\Xi'\Xi^{-1})|_{z=0}\,. \tag{D·2}$$

Hence, putting $\xi\equiv e^{2\alpha/L}$ [cf. (3·7)], we obtain from (3·1) and (2·6)

$$b_1=L^{-1}\Xi'\Xi^{-1}|_{z=0}=1,$$

$$b_2=(2L)^{-1}(\Xi''\Xi^{-1}-\Xi'^2\Xi^{-2})|_{z=0}$$

$$=L(\xi-1)/2-\sigma\xi+\sigma^2\xi/2L\,,$$

$$b_3=(6L)^{-1}(\Xi'''\Xi^{-1}-3\Xi''\Xi'\Xi^{-2}+2\Xi'^3\Xi^{-3})|_{z=0}$$

$$=L^2(\xi^3-3\xi+2)/6-\sigma L(\xi^3-\xi)+\sigma^2(4\xi^3-\xi)/2-4\sigma^3\xi^3/3L\,,$$

$$b_4=(24L)^{-1}(\Xi^{\mathrm{IV}}\Xi^{-1}-4\Xi'''\Xi'\Xi^{-2}-3\Xi''^2\Xi^{-2}$$

$$+12\Xi''\Xi'^2\Xi^{-3}-6\Xi'^4\Xi^{-4})|_{z=0}$$

$$=L^3(\xi^6-4\xi^3-3\xi^2+12\xi-6)/24-\sigma L^2(\xi^6-2\xi^3-\xi^2+2\xi)/2$$
$$+\sigma^2 L(9\xi^6-8\xi^3-3\xi^2+2\xi)/4$$
$$-\sigma^3(27\xi^6-8\xi^3-3\xi^2)/6+\sigma^4(27\xi^6-\xi^2)/8L\,,$$
$$b_5=(120L)^{-1}(\Xi^{\mathrm{V}}\Xi^{-1}-5\Xi^{\mathrm{IV}}\Xi'\Xi^{-2}-10\Xi'''\Xi''\Xi^{-2}+20\Xi'''\Xi'^2\Xi^{-3}$$
$$+30\Xi''^2\Xi'\Xi^{-3}-60\Xi''\Xi'^3\Xi^{-4}+24\Xi'^5\Xi^{-5})|_{z=0}$$
$$=L^4(\xi^{10}-5\xi^6-10\xi^4+20\xi^3+30\xi^2-60\xi+24)/120$$
$$-\sigma L^3(\xi^{10}-3\xi^6-4\xi^4+6\xi^3+6\xi^2-6\xi)/6$$
$$+\sigma^2 L^2(16\xi^{10}-27\xi^6-25\xi^4+24\xi^3+18\xi^2-6\xi)/12$$
$$-\sigma^3 L(32\xi^{10}-27\xi^6-19\xi^4+8\xi^3+6\xi^2)/6$$
$$+\sigma^4(256\xi^{10}-81\xi^6-56\xi^4+6\xi^2)/24-\sigma^5(128\xi^{10}-10\xi^4)/15L\,, \qquad \text{(D·3)}$$

since [by (3·1) and (2·6)] we have $\Xi|_{z=0}=1$ and

$$\Xi^{(n)}|_{z=0}\equiv(\partial^n\Xi/\partial z^n)|_{z=0}=n!\,\Lambda^n Q(n,L,T)$$
$$=(L+\sigma-n\sigma)^n\xi^{n(n-1)/2}$$

for every positive integer n.

For the infinite system, from (2·12) we have $\beta_1^{(0)}=2(a-\sigma)$, $\beta_s^{(0)}=-s^{-1}(s+1)\cdot\sigma^s$ ($s\geqq 2$), where $p_\infty/kT=l^{-1}\{1-\sum_{s=1}^{\infty}s(s+1)^{-1}\beta_s^{(0)}l^{-s}\}[=\sum_{j=1}^{\infty}b_j^{(0)}z^j]$. Hence

$$b_1^{(0)}=1,\quad b_2^{(0)}=a-\sigma,\quad b_3^{(0)}=2a^2-4\sigma a+3\sigma^2/2,$$
$$b_4^{(0)}=16a^3/3-16\sigma a^2+13\sigma^2 a-8\sigma^3/3\,,$$
$$b_5^{(0)}=50a^4/3-200\sigma a^3/3+85\sigma^2 a^2-118\sigma^3 a/3+125\sigma^4/24\,, \qquad \text{(D·4)}$$

since[1] $b_j^{(0)}=j^{-2}\sum_{\{n_s\}}\prod_{s=1}^{j-1}(s\beta_s^{(0)})^{n_s}/n_s!$ [where the sum extends over the sets of non-negative integers n_s such that $\sum_{s=1}^{j-1}sn_s=j-1$]. From (D·3) and (D·4) we can confirm $b_j^{(0)}=\lim_{L\to\infty}b_j$, using the fact that $\xi^m=\sum_{r=0}^{\infty}(r!)^{-1}(2ma/L)^r$ ($m=1,2,3,\cdots$).

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