Distribution of Zeros and the Equation of State

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§1. As was pointed out by Yang and Lee,[1] the distribution of zeros z_1, $z_2, \ldots, z_M$ of the grand partition function

$$\Xi_\Omega(z) = 1 + \sum_{N=1}^{M} Z_N(\Omega, T) z^N = \Pi_{j=1}^{M}(1 - z/z_j) \quad [Z_N\text{: partition function}] \qquad (1)$$

for a system of interacting particles in the complex z (activity) plane in the limit of Ω (volume) $\to \infty$ is connected with the equation of state [$p = p(\rho)$, p: pressure, ρ: density] and condensation; $p/kT = \lim[\Omega\to\infty](1/\Omega) \cdot \cdot \ln\Xi_\Omega(z)$, $\rho = (1/kT) z\, dp/dz$. It is one of the interesting problems of statistical mechanics to obtain the distribution of zeros for a given systems. However, for continuous gases such calculations are difficult because of the complicated character of their partition functions. Hemmer and Hauge[2] et al. have attempted to obtain the distribution of zeros for some continuous gases, starting from the equation of state.

§2. In this lecture, we first derive equations of state from some examples of distribution of zeros. We assume that in the limit of $\Omega \to \infty$ the zeros are distributed on the circle of radius a with centre at the origin; the distribution function for zeros is denoted by $g(\theta)$ [θ being the argument of a point on the circle] and we have $g(-\theta) = g(\theta)$ and $2\int_0^\pi g(\theta)d\theta = c \equiv \lim[\Omega\to\infty](M/\Omega)$. Example (i): $g(\theta) = (c/4\pi)(2 - \cos\theta)$. Example (ii): $g(\theta) = (c/8\pi)\{3 + (\pi - \theta)\sin\theta - 2\cos\theta\}$ $(0 \leq \theta \leq \pi)$. Example (iii): $g(\theta) = c\lambda/\alpha$ $(0 \leq \theta \leq \alpha)$, $= 0$ $(\alpha < \theta < \beta)$, $= c(\pi - \beta)^{-1}(1/2 - \lambda)$ $(\beta \leq \theta \leq \pi)$, where $0 < \alpha < \beta < \pi$ and $0 < 2\lambda \leq [1 + \{(\pi - \beta)/\alpha\}\tan(\beta/2)/\tan(\alpha/2)]^{-1}$. In these examples, the density ρ as a function of z is given by (3.10), (3.12), (3.15) of reference 3, respectively, and $\rho(z)$ (and its analytical continuation) is shown in Fig. 1 (i), (ii), (iii), respectively. The equation of state is expressed by OP-P'L. In (ii), the condensation point P is an "analytical" singularity (•);[4,5]

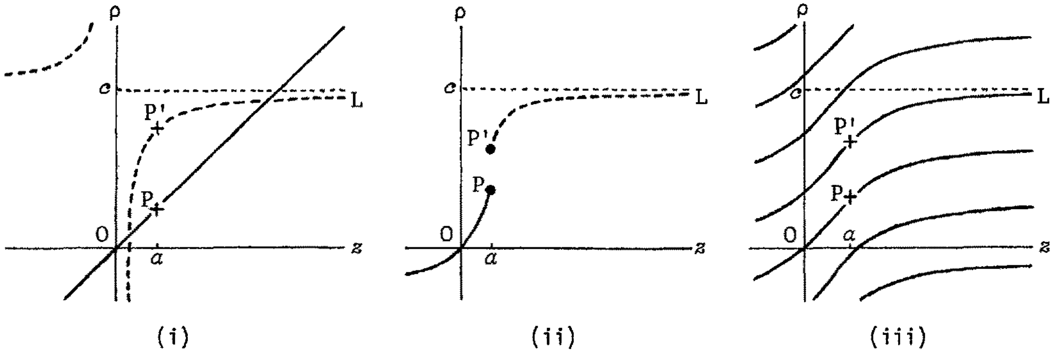

FIG. 1

in (i) and (iii), P is a "non-analytical" singularity (+).[4,5] In (i) and (ii), the function representing gas and the function representing liquid are different analytic functions (—— and ----); in (iii), they are different branches of one and the same analytic function. Thus, by giving some examples of distribution of zeros, we can see various types[5] of analytical behaviour of the functions describing condensation; (i), (ii), (iii) belong, respectively, to types (d), (c), (b) defined in reference 5.

§3. Next we show the non-uniqueness of the derivation of the distribution of zeros from a given equation of state. For example, if all zeros are at one point $-d$ on the negative real axis [case (i)], the equation of state (on the positive real axis) is given by $W(z)\,[\equiv p/kT] = c\ln\{(z+d)/d\}$ [from (1)]. The same equation of state is obtained, (ii) by distributing the zeros uniformly on a circle C with centre $-d$ and radius r_0, (iii) by distributing the zeros uniformly inside the circle C, or (iv) by distributing the zeros on the imaginary axis with distribution function $g(y) = cd/\pi(y^2+d^2)$. [In case (ii), W inside C is given by another analytic function $\tilde{W} = \text{const} = c\ln(r_0/d)$; in case (iii), W' inside C is not an analytic function; in case (iv), W when $\text{Re}\, z < 0$ is given by another analytic function $\tilde{W} = c\ln\{(d-z)/d\}$.] There are infinitely many possibilities of distribution of zeros leading to the same equation of state [e.g. Fig. 2]. To obtain a unique distribution of zeros, we make the following assumptions:[6]

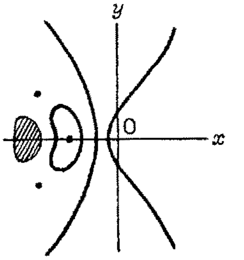

FIG. 2

(i) *The zeros are distributed on lines at most (not over domains).*

(ii) *The zeros are so distributed that one can make as far-reaching analytical continuation of $W(z)$ as possible from the positive real axis to the upper half and to the lower half of the complex z plane.*

According to these assumptions, case (i) will be realized for the given equation of state $W(z) = c\ln\{(z+d)/d\}$, since in this case the analytical continuation of $W(z)$ is the most far-reaching. The validity of these assumptions will be discussed in the future. For the present we can only say that they are based on a philosophical principle: "Nature likes economy."

§4. On the above assumptions, we derive the distribution of zeros for gases obeying Tonks' equation of state $[p = kT/(\rho^{-1} - b)]$ and van der Waals' equation of state $[(p + a\rho^2)(\rho^{-1} - b) = kT]$, i.e. for one-dimensional systems of hard rods with no attraction and with infinitesimal attraction of infinite range, which are the only examples of continuous gases for which the equation of state is exactly obtained.[7] We construct the Riemann surface of the function $W(z)\,[\equiv p/kT]$, and derive the "field plane" (i.e. the part of the Riemann surface covered by our analytical continuation), and from it we determine uniquely the line of zeros as "jumping line", across which we jump from one Riemann sheet to another and the real part of $W(z)$ is continuous. The distribution function

$$g(s) = (1/2\pi)(dV_R/ds - dV_L/ds) \qquad (2)$$

for zeros on the line is calculated, V_R and V_L denoting the values approached by the imaginary part of $W(z)$ from the right and left sides of the line, respectively (s is the length of an arc on the line). Note that a jumping line is different from a branch cut, across which the function is analytically (smoothly) continued from one sheet to another. The following figures show the Riemann surfaces [where E (i.e. $z = -1/e$), P_1, P_2, P_3 and O (i.e. $z = 0$) are branch points] and the field planes [where bold lines represent jumping lines (i.e. zero lines) and usual lines represent branch cuts]. (In Figs. 4a, 5a, 6a the infinitely many sheets concerning O are omitted.) In Fig. 4b, K is the point of intersection of the zero line and the positive real axis; thus K is the condensation point.

Riemann surface — Field plane

Tonks' equation

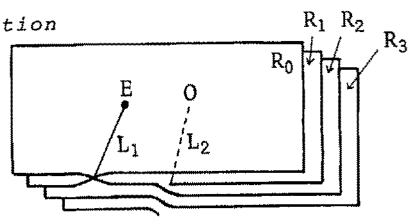

FIG. 3a

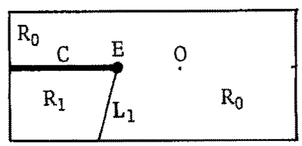

FIG. 3b

van der Waals' equation

$T < T_c$

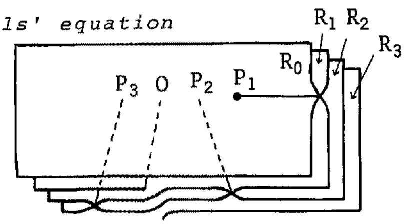

FIG. 4a

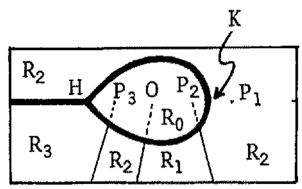

FIG. 4b

$T = T_c$

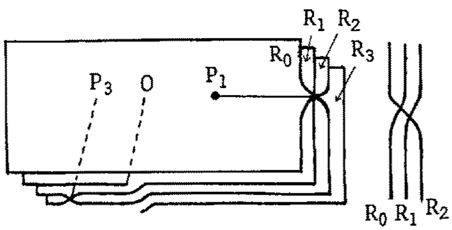

FIG. 5a

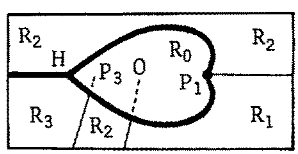

FIG. 5b

$T > T_c$

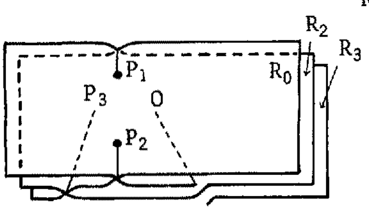

FIG. 6a

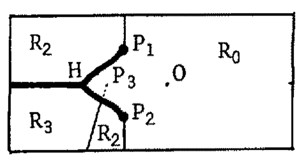

FIG. 6b

§5. For Tonks' equation (from which $z = We^{W}$, with $b = 1$) we confirm Hauge-Hemmer's results[2] by our method of argument (Figs. 3a, 3b). For van der Waals' equation, from which we have (on putting $\alpha \equiv a/b^2kT$)

$$W = \rho/(1-\rho) - \alpha\rho^2, \quad z = \{\rho/(1-\rho)\}\exp\{\rho/(1-\rho) - 2\alpha\rho\} \quad (\text{with } b = 1), \tag{3}$$

we obtain[6] the equation for the zero line enclosing the origin at low temperatures (cf. Figs. 4a, 4b)

$$\begin{aligned} r = \alpha e^{-\alpha}[&1 - \alpha^{-1} + (-1/2 + \theta^2/2)\alpha^{-2} + (-5/6 + 3\theta^2/2)\alpha^{-3} \\ &+ (-43/24 + 21\theta^2/4 - \theta^4/8)\alpha^{-4} + (-529/120 + 229\theta^2/12 - 61\theta^4/24)\alpha^{-5} \\ &+ (-8501/720 + 1131\theta^2/16 - 363\theta^4/16 + \theta^6/16)\alpha^{-6} + O(\alpha^{-7}) \\ &+ \{\alpha - 1 + \theta^2\alpha^{-1} + (1/3 + 2\theta^2)\alpha^{-2} + (5/3 + 5\theta^2)\alpha^{-3}\}e^{-\alpha}\cos\theta + O(\alpha^{-4}e^{-\alpha})], \end{aligned} \tag{4}$$

and the distribution function for zeros on this line

$$\begin{aligned} g(\theta) = (2\pi)^{-1}\alpha^{-1}e^{\alpha}[&1 + (-2 - \theta^2/2)\alpha^{-2} + (-37/6 + \theta^2/2)\alpha^{-3} \\ &+ (-103/8 + 47\theta^2/4)\alpha^{-4} + (-2681/120 + 395\theta^2/6 - 241\theta^4/48)\alpha^{-5} \\ &+ (-29807/720 + 6973\theta^2/24 - 2027\theta^4/48 - 121\theta^6/32)\alpha^{-6} + O(\alpha^{-7}) \\ &+ \{-2\alpha + 7\alpha^{-1} + (79/2 - 2\theta^2)\alpha^{-2} + (501/8 - 47\theta^2 + 3\theta^4/2)\alpha^{-3}\}\cdot \\ &\cdot e^{-\alpha}\cos\theta + \{-\alpha^{-1} - 4\alpha^{-2} + (-33/2 + \theta^2)\alpha^{-3}\}\theta e^{-\alpha}\sin\theta + O(\alpha^{-4}e^{-\alpha})], \end{aligned} \tag{5}$$

and the distribution function for zeros on the part of the negative real axis between $-\infty$ and H at low temperatures

$$\begin{aligned} g(x) = -x^{-1}q^{-2}[&1 + 2q^{-1}\ln q - 3q^{-1} + 6\alpha q^{-2} + 3q^{-2}(\ln q)^2 + (-11q^{-2} + 24\alpha q^{-3})\ln q \\ &+ (6 - \pi^2)q^{-2} - 38\alpha q^{-3} + 40\alpha^2 q^{-4} + 4q^{-3}(\ln q)^3 + (-25q^{-3} + 60\alpha q^{-4})(\ln q)^2 \\ &+ \{(35 - 4\pi^2)q^{-3} - 214\alpha q^{-4} + 240\alpha^2 q^{-5}\}\ln q + (-10 + 25\pi^2/3)q^{-3} \\ &+ (138 - 20\pi^2)\alpha q^{-4} - 388\alpha^2 q^{-5} + 224\alpha^3 q^{-6} + O\{\alpha^{-4}(\ln\alpha)^4\}], \end{aligned} \tag{6}$$

with $q \equiv \ln(-x) + 2\alpha$. Calculations are also made[6] for the critical temperature T_c (cf. Figs. 5a, 5b) and for high temperatures (cf. Figs. 6a, 6b). From these calculations we may conclude that the existence of repulsions between particles leads to distribution of zeros on part of the negative real axis, whereas the existence of attractions causes distribution of zeros on a curve (open or closed) crossing the negative real axis, and brings about condensation when the curve is closed to cross the positive real axis; these features might hold for the general systems of interacting molecules.

References

1. C. N. Yang and T. D. Lee, Phys. Rev. 87 (1952), 404.
2. E. H. Hauge and P. C. Hemmer, Physica 29 (1963), 1338.
   P. C. Hemmer and E. H. Hauge, Phys. Rev. 133 (1964), A1010.
3. K. Ikeda, *Modern Developments in Thermodynamics*, B. Gal-Or, ed. (Wiley, 1974), p. 311.
4. K. Ikeda, *Proceedings of the International Conference of Theoretical Physics, Kyoto and Tokyo* (1953), p. 544.
5. K. Ikeda, Prog. Theor. Phys. 16 (1956), 341.
6. K. Ikeda, Prog. Theor. Phys. 52 (1974), 54, 415, 840; 53 (1975), 66.
7. M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4 (1963), 216.