

On the van der Waals Theory of the Vapor-Liquid Equilibrium.

I. Discussion of a One-Dimensional Model

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For a one-dimensional fluid model where the pair interaction potential between the molecules consists of a hard core and an exponential attraction, Kac has shown that the partition function can be determined exactly in the thermodynamic limit. In Sec. II this calculation is reviewed and further discussed. In Sec. III, we show that in the so-called van der Waals limit when the range of the attractive force goes to infinity while its strength becomes proportionally weaker, a phase transition appears which is described exactly by the van der Waals equation plus the Maxwell equal-area rule. In Sec. IV the approach to the van der Waals limit is discussed by an appropriate perturbation method applied to the basic integral equation. The perturbation parameter is the ratio of the size of the hard core to the range of the attractive force. It is seen that the phase transition persists in any order of the perturbation. The two-phase equilibrium is characterized by the fact that in this range of density, the maximum eigenvalue of the integral equation is doubly degenerate and that the corresponding two eigenfunctions do not overlap. In Sec. V we comment on the relevance of our results for the three-dimensional problem.

I. INTRODUCTION

IN this series of papers we intend to present a new discussion of the old theory of van der Waals¹ of the continuity of the gaseous and liquid states of matter. It is well known that the great merit of this theory lies in the fact that it gave the first qualitative kinetic interpretation of condensation phenomena and of the existence of a critical point. On the other hand, it has proved very difficult to make the theory more rigorous and as a result the modern theory² of the equation of state of a nonideal gas, has followed more the idea of Kamerlingh Onnes to represent all properties of the gas as power series in the density—the so-called virial expansion. In this way one can take successively into account the interaction of the molecules in pairs, triples, quadruples, etc., and one can derive precise expressions for the successive deviations from the ideal gas laws in terms of the intermolecular potential. Many attempts,³ thus far unsuccessful,

¹ J. D. van der Waals, Dissertation Leiden, 1873. This was expanded in the book: *Die Kontinuität des gasförmigen und flüssigen Zustandes* (Johann A. Barth, Leipzig, Germany, 1899), 2 volumes. Compare also the monograph by J. P. Kuenen, *Die Zustandsgleichung* (Vieweg, Braunschweig, 1907).

² Due mainly to J. E. Mayer. A summary is given in the book by J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chaps. 13 and 14. For a recent account see the monograph by G. E. Uhlenbeck and G. W. Ford in *Studies in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Vol. 1, Part B.

³ These also go back to J. E. Mayer; (see reference 2, Chap. 14). For a more recent discussion, see K. Ikeda, *Progr. of Theoret. Phys.* (Kyoto) **19**, 653 (1958), and **26**, 173 (1961). Much of the motivation came from the analogy with the Bose-Einstein condensation, which was pointed out by B. Kahn and G. E. Uhlenbeck [*Physica* **5**, 399 (1938)]. However, we now believe that this analogy is superficial and that there is no real connection between the Bose-Einstein condensation and ordinary condensation phenomena.

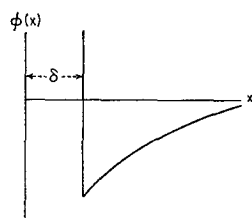


FIG. 1. Interaction potential $\varphi(x)$.

have been made to construct a rigorous theory of condensation phenomena from such expansions. In fact we believe that such a construction is very difficult, if not impossible,⁴ and it therefore seems worthwhile to try to reformulate in a more rigorous way, the basic ideas of van der Waals.

We have attempted to do this starting always from a one-dimensional gas model, first proposed by M. Kac,⁵ for which all calculations can be carried out exactly. The model consists of N particles moving on a line of length L and interacting in pairs through a potential $\varphi(x)$ which consists of a hard core of length δ and an exponential attraction (see Fig. 1.) For this model it is possible to give an exact discussion of the partition function in the *thermodynamic limit* $L \rightarrow \infty$, $N \rightarrow \infty$, $l = L/N$ finite. As shown already by Kac, the problem in this limit can be reduced to the discussion of a linear integral equation with a positive definite, Hilbert-Schmidt kernel of which the maximum eigenvalue determines the

⁴ The difficulties become especially clear in the formulation of the condensation problem according to C. N. Yang and T. D. Lee, *Phys. Rev.* **87**, 404 (1952). Compare also the discussion by G. E. Uhlenbeck and G. W. Ford in Chapter 3 of the book *Lectures in Statistical Mechanics* (Proceedings of the Summer Seminar, Boulder, Colorado, 1960, published by the American Mathematical Society, Providence, Rhode Island, 1963.)

⁵ M. Kac, *Phys. Fluids* **2**, 8 (1959).

thermodynamic potential (Gibbs free energy) of the system. These results will be recapitulated in Sec. II.

For finite γ , that is for a finite range of the attractive force, the system does *not* show a phase transition in agreement with all previously known results⁶ for one-dimensional systems. However, if one sets $\alpha = \alpha_0\gamma$, and then lets $\gamma \rightarrow 0$, (i.e., for a weak but very long-range force) so that the integral

$$\int_0^\infty dx \varphi_{\text{attr.}}(x)$$

is finite (we will call this the *van der Waals limit*), a phase transition appears which is described exactly by the van der Waals equation

$$p = kT/(l - \delta) - \alpha_0/l^2, \quad (1)$$

together with the well known Maxwell rule.⁷ This will be shown in detail in Sec. III.

In Sec. IV, all the eigenfunctions and eigenvalues of the Kac integral equation are found in this limit by a perturbation procedure with $\gamma\delta$ as the expansion parameter. The phase transition appears as a double degeneracy of the maximum eigenvalue, and the phase transition *persists* when the perturbation calculation is carried further to any finite power of $\gamma\delta$. One should also note that this entire development breaks down near the critical point. For the critical region, a separate discussion is required which will be given in Part III of this series of papers.

In the last section, we will comment on the relevance of our results for the three-dimensional problem, and on the relation to the usual derivation of the van der Waals equation.

II. THE KAC INTEGRAL EQUATION

The partition function for our one-dimensional gas is given by

$$\begin{aligned} Z(L, T, N) &= \frac{1}{\Lambda^N} \cdot \frac{1}{N!} \int_0^L \cdots \int_0^L dt_1 \cdots dt_N \\ &\quad \times \exp \left[-\frac{1}{kT} \sum_{i < j} \varphi(|t_i - t_j|) \right] \\ &= \frac{1}{\Lambda^N} \cdot \frac{1}{N!} \int_0^L \cdots \int_0^L dt_1 \cdots dt_N \end{aligned}$$

⁶ That there is no phase transition for a one-dimensional system with only nearest-neighbor interaction, was shown first by F. Gursey, Proc. Cambridge Phil. Soc. **46**, 182 (1950). This was generalized (with the same result) to the case where each molecule interacts with a finite number of neighbors by L. Van Hove, Physica **16**, 137 (1950). Compare also the discussion given by A. Munster in his book *Statistische Thermodynamik* (Springer-Verlag, Berlin, Germany, 1956), Secs. 7.7 and 8.8, where one also finds further references.

⁷ Also called the equal-area rule. See Maxwell, *Collected Works*, Dover reprint, Vol. II, p. 425.

$$\times \exp \left[\nu \sum_{i < j} e^{-\gamma|t_i - t_j|} \right] \prod_{i < j} S(|t_i - t_j|), \quad (2)$$

with $\Lambda^2 = h^2/2\pi mkT$, $\nu = \alpha/kT$, and where the stepfunction $S(x)$ is defined by

$$S(x) = \begin{cases} 0 & \text{for } |x| < \delta \\ 1 & \text{for } |x| > \delta. \end{cases}$$

Since the integrand is symmetric in t_1, t_2, \dots, t_N , and because the hard cores impose a linear order of the molecules in L , one can write (2) in the form

$$\begin{aligned} Z(L, T, N) &= \frac{e^{-\frac{1}{2}N\nu}}{\Lambda^N} \int_{0 < t_1 < t_2 < \dots < t_N < L} dt_1 \cdots dt_N \\ &\quad \times \exp \left[\frac{\nu}{2} \sum_{i=1}^N \sum_{j=1}^N e^{-\gamma|t_i - t_j|} \right] \cdot \prod_{i=1}^{N-1} S(|t_{i+1} - t_i|). \quad (3) \end{aligned}$$

Also the attractive part of the integrand can be ordered by making use of the identity

$$\begin{aligned} &\exp \left[\frac{\nu}{2} \sum_{i,j=1}^N \exp(-\gamma|t_i - t_j|) \right] \\ &= \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} dx_1 \cdots dx_N \\ &\quad \times \exp [\nu^{\frac{1}{2}}(x_1 + x_2 + \cdots + x_N)] \\ &\quad \cdot W(x_i) \prod_{i=1}^N P(x_i | x_{i+1}, t_{i+1} - t_i), \quad (4) \end{aligned}$$

where

$$\begin{aligned} W(x) &= \frac{1}{(2\pi)^{\frac{1}{2}}} \exp \left[-\frac{1}{2}x^2 \right], \\ P(x | y, t) &= \{ [2\pi(1 - e^{-2\gamma t})]^{\frac{1}{2}} \}^{-1} \\ &\quad \times \exp \left[-(y - xe^{-\gamma t})^2 / 2(1 - e^{-2\gamma t}) \right]. \end{aligned} \quad (5)$$

The motivation and the proof of the identity (4) follows from the observation that $\exp(-\gamma|t_i - t_j|)$ is the covariance of a one-dimensional, Gaussian Markoff process (the so-called *O-U* process), but of course one can also prove (4) directly. By substituting (4) into (3) and by making a Laplace transformation in L , the integrals over the t_i can be separated in pairs since clearly

$$\int_0^\infty e^{-sL} Z(L, T, N) dL$$

is of the form

$$\begin{aligned} &\int_0^\infty dL e^{-sL} \int_0^L dt_1 \int_{t_1}^L dt_2 \\ &\quad \times \int_{t_2}^L dt_3 \cdots \int_{t_{N-1}}^L dt_N \prod_{i=1}^{N-1} F_i(t_{i+1} - t_i) \end{aligned}$$

$$= \int_0^\infty dt_1 \int_{t_1}^\infty dt_2 \cdots \int_{t_{N-1}}^\infty dt_N \times \int_{t_N}^\infty dL e^{-sL} \prod_{i=1}^{N-1} F_i(t_{i+1} - t_i). \tag{6}$$

Setting

$$t_1 = \tau_1, \\ t_2 = \tau_1 + \tau_2, \dots, t_N = \tau_1 + \tau_2 + \dots + \tau_N, \\ L = \tau_1 + \tau_2 + \dots + \tau_N + \tau_{N+1},$$

one easily shows that (6) becomes

$$\frac{1}{s^2} \prod_{i=1}^{N-1} \int_0^\infty d\tau e^{-s\tau} F_i(\tau),$$

so that by putting in the appropriate form for the $F_i(z)$, one obtains (suppressing the temperature T from now on)

$$\int_0^\infty dL e^{-sL} Z(L, N) = \frac{1}{\Lambda^N} \frac{e^{-N\nu/2}}{s^2} \int_{-\infty}^{+\infty} dx_1 \cdots dx_N \times \exp[\nu^{\frac{1}{2}}(x_1 + \dots + x_N)] W(x_1) \prod_{i=1}^{N-1} p_s(x_i | x_{i+1}) \tag{7}$$

with

$$p_s(x | y) = \int_s^\infty d\tau e^{-s\tau} P(x | y, \tau). \tag{8}$$

The ordering of the x_i in successive pairs suggests the introduction of the kernel

$$K_s(x, y) = \frac{W(x)p_s(x | y)}{[W(x)W(y)]^{\frac{1}{2}}} \exp[(\nu^{\frac{1}{2}}/2)(x + y)] \tag{9}$$

and the corresponding Kac integral equation

$$\int_{-\infty}^{+\infty} dy K_s(x, y) \psi(y) = \lambda \psi(x). \tag{10}$$

It is easy to see that $K_s(x, y)$ is symmetric and in addition one can show (for the proof, see Kac⁵):

(a) $K_s(x, y)$ is positive definite, which means that

$$\iint K_s(x, y) \psi(x) \psi(y) dx dy$$

is always positive, whenever $\psi(x)$ is not identically 0;

(b) $K_s(x, y)$ is a Hilbert-Schmidt kernel, which means that

$$\iint K_s^2(x, y) dx dy < \infty.$$

From these facts, one can conclude that Eq. (10)

has a discrete set of positive eigenvalues $\lambda_i(s)$ starting from a maximum eigenvalue $\lambda_0(s)$ and converging to zero as $i \rightarrow \infty$, that the corresponding eigenfunctions $\psi_i(x, s)$ form a complete orthonormal set, and that the kernel $K_s(x, y)$ can be expanded in the convergent series

$$K_s(x, y) = \sum_i \lambda_i(s) \psi_i(x, s) \psi_i(y, s). \tag{11}$$

Writing Eq. (7) in the form

$$\int_0^\infty dL e^{-sL} Z(L, N) = \frac{e^{-\frac{1}{2}N\nu}}{\Lambda^N s^2} \int_{-\infty}^{+\infty} dx_1 \cdots dx_N \exp\left[\frac{\nu^{\frac{1}{2}}}{2}(x_1 + x_N)\right] \times [W(x_1)W(x_N)]^{\frac{1}{2}} \prod_{i=1}^N K_s(x_i, x_{i+1}),$$

and using Eq. (11), one can integrate over x_2, x_3, \dots, x_{N-1} and obtain

$$\int_0^\infty dL e^{-sL} Z(L, N) = \frac{e^{-\frac{1}{2}N\nu}}{\Lambda^N s^2} \sum_{i=0}^\infty \lambda_i^{N-1}(s) A_i^2 \tag{12}$$

with

$$A_i = \int_{-\infty}^{+\infty} dx \psi_i(x, s) W^{\frac{1}{2}}(x) e^{\frac{1}{2}\nu x}. \tag{13}$$

If one now forms the grand partition function

$$G(L, z) = \sum_{N=1}^\infty Z(L, N) (\Lambda z)^N, \tag{14}$$

it follows from Eq. (12), that

$$\int_0^\infty dL e^{-sL} G(L, z) = \frac{ze^{-\frac{1}{2}\nu}}{s^2} \sum_i \frac{A_i^2}{1 - \lambda_i z e^{-\frac{1}{2}\nu}}, \tag{15}$$

provided $z < e^{\frac{1}{2}\nu}/\lambda_0(s)$. It is clear therefore that the abscissa of convergence of the Laplace transform of $G(L, z)$ is that value of s , for which

$$z = e^{\frac{1}{2}\nu}/\lambda_0(s). \tag{16}$$

Since on the other hand this abscissa is also

$$\lim_{L \rightarrow \infty} \frac{1}{L} \ln G(L, z), \tag{17}$$

which has the thermodynamic meaning of p/kT , it follows that the relation between z and the pressure of the gas is given by

$$\lambda_0(p/kT) = e^{\frac{1}{2}\nu}/z. \tag{18}$$

Furthermore, since the thermodynamic meaning of z is the fugacity, which is related to the chemical potential (Gibbs free energy per particle) $\mu(p, T)$ by

$$\mu = kT \ln (\Lambda z), \tag{19}$$

the equation of state follows from

$$l = (\partial\mu/\partial p)_T = -\lambda'_0(s)/\lambda_0(s), \quad s = p/kT, \tag{20}$$

where the prime denotes differentiation after s .

The following statements can be proved concerning the maximum eigenvalue $\lambda_0(s)$ and the eigenvalue spectrum $\lambda_i(s)$ (see Appendix 1):

(a) All eigenvalues are monotonically decreasing functions of s and approach zero for $s \rightarrow \infty$.

(b) The maximum eigenvalue $\lambda_0(s)$ goes to infinity for $s \rightarrow 0$. For no value of s can it be degenerate, and it is an analytic function of s for all real $s > 0$. Finally there is the inequality

$$\lambda'_0(s)^2 - \lambda_0(s)\lambda''_0(s) < 0, \tag{21}$$

which implies that $\lambda''_0(s)$ is always positive.

(c) All other eigenvalues are finite for $s = 0$.

It seems very likely that the curves $\lambda_i(s)$, $i > 0$ will also not cross each other, in which case the spectrum as a function of s may look as shown in Fig. 2.

One can conclude that for any value of z there is an *unique* value s fulfilling Eq. (16), and from Eqs. (20) and (21) it then follows that l is a monotonically decreasing and analytic function of $s = p/kT$ for all positive values of s . There is therefore *no* phase transition. Note that the theory gives directly [see Eqs. (18) and (19)], the Gibbs free energy as a function of the pressure, and that therefore one obtains the specific volume l as a function of the pressure instead of the pressure as a function of l as in the Mayer theory. The connection with the virial expansion of the equation of state is therefore quite complicated. One can show that the maximum eigenvalue $\lambda_0(s)$ can be expanded in the form

$$\lambda_0(s) = e^{3\gamma}(s^{-1} + a_0 + a_1s + a_2s^2 + \dots). \tag{22}$$

The coefficients a_i can be calculated successively and they are related to the Mayer cluster integrals b_i . One finds

$$a_0 = b_2; \quad a_1 = b_3 - b_2^2; \tag{23}$$

and so on. For the proof we refer again to Appendix I. From Eqs. (22) and (23) one can then verify that the equation of state (20) is, for small pressures, simply the inversion of the usual virial expansion

$$pl/kT = 1 + B/l + C/l^2 + \dots,$$

with $B = -b_2$, $C = -2b_3 + 4b_2^2$, etc. We have been unable to find a simple "graphological" characterization of the coefficients a_i .

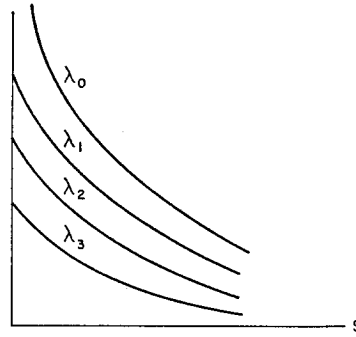


FIG. 2. Eigenvalue spectrum as a function of s .

III. THE VAN DER WAALS LIMIT

We will now study what happens to the maximum eigenvalue $\lambda_0(s)$, if one puts $\alpha = \alpha_0\gamma$ and then goes to the limit $\gamma \rightarrow 0$. To do this, we investigate the moments $\sum_i \lambda_i^n(s)$ of the distribution of the eigenvalues $\lambda_i(s)$. One has

$$\begin{aligned} \sum_i \lambda_i^n &= \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} dx_1 \dots dx_n \\ &\times K_s(x_1, x_2)K_s(x_2, x_3) \dots K_s(x_n, x_1) \\ &= \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} dx_1 \dots dx_n \\ &\times \exp [-(\nu_0\gamma)^{\frac{1}{2}}(x_1 + x_2 \dots + x_n)] \\ &\times \int_{\delta}^{\infty} \dots \int_{\delta}^{\infty} d\tau_1 \dots d\tau_n \\ &\times \exp [-s(\tau_1 + \dots + \tau_n)] \prod_{i=1}^n P(x_i | x_{i+1}, \tau_i), \end{aligned}$$

where $\nu_0 = \alpha_0/kT$ and $x_{n+1} \equiv x_1$. The integrals over the x_i can be carried out and one can then investigate the limit $\gamma \rightarrow 0$. Some of the details are given in Appendix II. The result is the following theorem. For $\gamma \rightarrow 0$,

$$\begin{aligned} \lim_{\gamma \rightarrow 0} \gamma \sum_i \lambda_i^n &= \frac{1}{2\pi} \iint_{-\infty}^{+\infty} d\xi d\eta \\ &\times \left(\exp [\eta(2\nu_0)^{\frac{1}{2}}] \int_{\delta}^{\infty} d\tau \exp [-s\tau - \frac{1}{2}(\xi^2 + \eta^2)\tau] \right)^n. \end{aligned} \tag{24}$$

One now can reason heuristically as follows. Call

$$\begin{aligned} f(\xi, \eta) &= \exp [\eta(2\nu_0)^{\frac{1}{2}}] \int_{\delta}^{\infty} d\tau \\ &\times \exp [-s\tau - \frac{1}{2}(\xi^2 + \eta^2)\tau]; \end{aligned} \tag{25}$$

then since (24) holds for all n , one can expect that for any reasonable function $g(x)$,

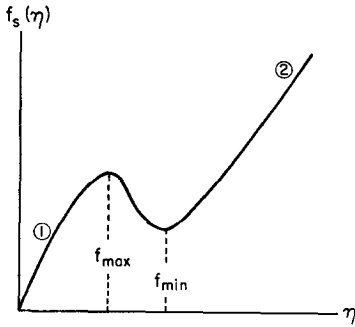


FIG. 3. The function $f_s(\eta)$ in the two-phase region.

$$\lim_{\gamma \rightarrow 0} \gamma \sum_i g(\lambda_i) = \frac{1}{2\pi} \iint_{-\infty}^{+\infty} d\xi d\eta g[f(\xi, \eta)]. \quad (26)$$

Take now for $g(x)$ the step function

$$g(x) = \begin{cases} 1 & \text{for } \alpha < x < \beta \\ 0 & \text{otherwise,} \end{cases}$$

and let $N_\gamma(\alpha, \beta)$ be the number of eigenvalues between α and β ; then one concludes from Eq. (26) that

$$\lim_{\gamma \rightarrow 0} \gamma N_\gamma(\alpha, \beta) = \frac{1}{2\pi}$$

$$\times [\text{Area in } (\xi, \eta) \text{ plane for which } \alpha < f(\xi, \eta) < \beta]. \quad (27)$$

Suppose that $f(\xi, \eta)$ has an absolute maximum $\omega(s)$, then it is clear that for $\gamma \rightarrow 0$, ω must be a limit point for the series of eigenvalues, because in any interval between $\omega - \epsilon$ and ω there must be in the limit $\gamma \rightarrow 0$, an infinite number of eigenvalues because the area $(\omega - \epsilon) < f(\xi, \eta) < \omega$ is finite. It seems therefore reasonable to expect that for $\gamma \rightarrow 0$, $\omega(s)$ is the maximum eigenvalue, or in other words that

$$\lim_{\gamma \rightarrow 0} \lambda_0(s, \gamma) = \omega(s) = \max_{(\xi, \eta)} f(\xi, \eta) = \max_{(\eta)} F(\eta), \quad (28)$$

with

$$F(\eta) \equiv f(0, \eta) = \exp[-\delta(s + \frac{1}{2}\eta^2) - \ln(s + \frac{1}{2}\eta^2) + \eta(2\nu_0)^{\frac{1}{2}}],$$

since the maximum of $f(\xi, \eta)$ will always occur for $\xi = 0$.

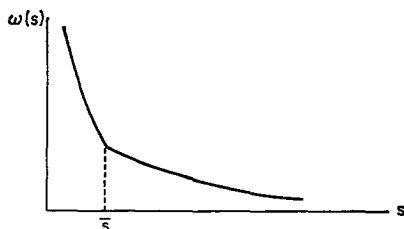


FIG. 4. The maximum eigenvalue, in the van der Waals limit, for a temperature below the critical.

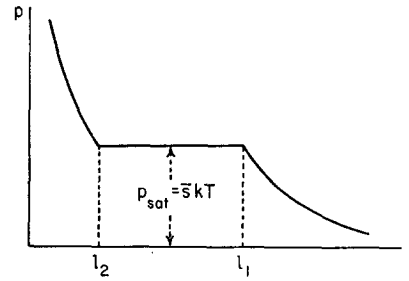


FIG. 5. Isotherm corresponding to Fig. 4.

Note that our argument from Eq. (27) does not really prove Eq. (28), since (27) does not exclude that a few discrete eigenvalues remain above $\omega(s)$ for $\gamma \rightarrow 0$. However, Eq. (28) is correct and the argument can be made completely rigorous. This is not done, because in the next section, the detailed investigation of the approach to the limit $\gamma \rightarrow 0$ implies a rigorous proof of Eq. (28).

To discuss Eq. (28) further, first note that the maximum will occur for that value $\eta(s)$ for which

$$f_s(\eta) \equiv \eta[\delta + 1/(s + \frac{1}{2}\eta^2)] = (2\nu_0)^{\frac{1}{2}}. \quad (29)$$

Since $df_s/d\eta = 0$ implies

$$s + \frac{1}{2}\eta^2 = (1/2\delta)[1 \pm (1 - 8s\delta)^{\frac{1}{2}}], \quad (30)$$

one must distinguish two cases.

(a) $8s\delta > 1$; $f_s(\eta)$ is then a monotonically increasing function of η , so that (29) has always one solution $\eta(s)$ corresponding to an unique maximum for $F(\eta)$. The equation of state follows from

$$l = -\omega'(s)/\omega(s) = +\delta + [1/(s + \frac{1}{2}\eta^2(s))] = +(2\nu_0)^{\frac{1}{2}}/\eta(s), \quad (31)$$

using (29). Putting $s = p/kT$ and $\eta(s) = (2\nu_0)^{\frac{1}{2}}/l$ in Eq. (29), one obtains the van der Waals equation

$$p = kT/(l - \delta) - \alpha_0/l^2.$$

(b) $8s\delta < 1$; $f_s(\eta)$ has then a maximum and a minimum (see Fig. 3), and one easily verifies that for $s = 1/8\delta$, $f_{\min} = f_{\max} = (\frac{3}{2})(3\delta)^{\frac{1}{2}}$, and that for decreasing s , f_{\min} and f_{\max} increase monotonically; f_{\min} remains finite, while f_{\max} goes to infinity for $s \rightarrow 0$.

If now $(2\nu_0)^{\frac{1}{2}} < f_{\min}$, then again there is only one solution of Eq. (29) corresponding to an unique maximum of $F(\eta)$. This is also the case if $(2\nu_0)^{\frac{1}{2}} > f_{\max}$. However if $f_{\min} < (2\nu_0)^{\frac{1}{2}} < f_{\max}$, then Eq. (29) has three roots, the outer two corresponding to local maxima of $F(\eta)$ and the inner one to a local minimum. One must now decide which of the two maxima is the absolute maximum. Clearly if one varies ν_0 at fixed s , or if one varies s (keeping $8s\delta < 1$) at

fixed ν_0 , there must be a value $\bar{s}(\nu_0)$ for which the two maxima are equal. It is at this value that $\omega(s)$ changes its analytic behavior abruptly, since $\eta(s)$ will suddenly jump from the branch ① to the branch ② of the $f_s(\eta)$ curve (see Fig. 3). In fact it is easy to show that for $s = \bar{s}$, $\omega(s)$ has a discontinuity in slope, and since $l = -\omega'(s)/\omega(s)$ this corresponds to an isotherm with a horizontal piece (see Figs. 4 and 5). Furthermore, since (31) remains valid, both the liquid and the vapor part are still described by the van der Waals equation. Finally, the equality of the maxima of $F(\eta)$ for $s = \bar{s}$ or of the two values of $\omega(s)$ means the equality of the Gibbs free energy of the two phases for $s = \bar{s}$, which in turn is equivalent to the Maxwell rule.

The critical point is determined by $8s_c\delta = 1$ and $(2\nu_c)^\frac{1}{2} = f_{\min}(s_c) = f_{\max}(s_c) = (\frac{3}{2})(3\delta)^\frac{1}{2}$, and this leads to the well-known formula

$$\nu_c = 3\delta; \quad p_c = \alpha_0/27\delta^2; \quad kT_c = 8\alpha_0/27\delta. \quad (32)$$

IV. THE EIGENFUNCTIONS AND EIGENVALUES FOR SMALL γ

Clearly the reason that, for small γ , the eigenvalues $\lambda_n(s, \gamma)$ of the Kac equation crowd together near the value $\omega(s)$, must be related to the fact that for $\gamma \rightarrow 0$, $P(x | y, t)$ approaches the Dirac δ function $\delta(x - y)$. However if one assumes that for $\gamma \rightarrow 0$, the eigenfunctions $\psi_n(x, s, \gamma)$ would remain centered around $x = 0$, as in the usual eigenvalue problems, then it follows from Eq. (10) that for $\gamma \rightarrow 0$, the eigenvalues would cluster around e^{-s}/s which is the maximum eigenvalue for the gas of hard rods. This contradiction can only be removed if, for $\gamma \rightarrow 0$, the eigenfunctions are centered farther and farther away from the origin. This in fact is the clue for constructing a consistent successive-approximation method for the eigenfunctions and eigenvalues if γ is small.

In the basic integral equation (10), substitute

$$x = x' + \eta(2/\gamma)^\frac{1}{2}, \quad y = y' + \eta(2/\gamma)^\frac{1}{2}, \quad (33)$$

where $\eta \equiv \eta(s)$ is the value of η for which the function $F(\eta, s)$ defined by (28) has an absolute maximum. Think first of the one-phase region, so that $\eta(s)$ is unique. Let

$$h(x') \equiv \psi[x' + \eta(2/\gamma)^\frac{1}{2}]; \quad (34)$$

then Eq. (10) can be written in the form

$$\exp[\eta(2\nu_0)^\frac{1}{2}] \int_{-\infty}^{+\infty} dy' \int_s^{\infty} d\tau \left[\frac{W(x')}{W(y')} \right]^\frac{1}{2} P(x' | y', \tau) \times \exp \left[-s\tau - \frac{\eta^2}{\gamma} \tanh \left(\frac{\gamma\tau}{2} \right) + (x' + y') \frac{(\nu_0\gamma)^\frac{1}{2}}{2} \right]$$

$$- \frac{\eta}{2} \left(\frac{2}{\gamma} \right)^\frac{1}{2} \tanh \left(\frac{\gamma\tau}{2} \right) (x' + y') \Big] h(y') = \lambda h(x'). \quad (35)$$

Clearly now for $\gamma \rightarrow 0$, $P(x' | y', \tau) \rightarrow \delta(x' - y')$ if $h(x')$ is centered around $x' = 0$, the eigenvalues will approach

$$\exp[\eta(2\nu_0)^\frac{1}{2}] \int_s^{\infty} d\tau \exp \left[-s\tau - \frac{\eta^2\tau}{2} \right] = \omega(s),$$

as expected. One may say that by the substitution (33) one has "tamed" the integral equation for a perturbation expansion of the form

$$\lambda = \omega(s) \{ 1 + \mu^{(1)}\gamma + \mu^{(2)}\gamma^2 + \dots \}, \quad (36)$$

$$h(x') = h^{(0)}(x') + \gamma^\frac{1}{2}h^{(1)}(x') + \gamma h^{(2)}(x') + \dots$$

Since the algebra is involved, we simply indicate how this is done. In the left-hand side of Eq. (35), set

$$y' = x'e^{-\gamma\tau} + \zeta(1 - e^{-2\gamma\tau})^\frac{1}{2},$$

and develop the whole integrand in powers of $\gamma^\frac{1}{2}$. The integrals over ζ are Gaussian integrals and the integrals over τ can all be expressed in terms of $\omega(s)$ and its derivatives. Up to order $\gamma^\frac{1}{2}$, and except for a common factor $\omega(s)$, the left-hand side of (35) becomes

$$h(x') + \gamma l [h''(x') + h(x) (\frac{1}{2} - \frac{1}{2}x'^2 + \frac{1}{2}x'^2\nu_0(l - \delta)^2/l^3)] + [\gamma^\frac{1}{2}\nu_0^\frac{1}{2}(l - \delta)^2/l] [\frac{1}{4}x'^3h(x')(1 - 4\nu_0(l - \delta)/l^2) - \frac{1}{2}x'h(x') - h'(x') - x'h''(x')],$$

where (31) has been used to express $\eta(s)$ in terms of l . If one now introduces the expansions (36) on both sides of Eq. (35) and equates equal powers of $\gamma^\frac{1}{2}$, one obtains, in zeroth approximation,

$$\frac{d^2H^{(0)}}{dz^2} + \left[\frac{1}{B} \left(\frac{l}{2} - \mu^{(1)} \right) - \frac{z^2}{4} \right] H^{(0)}(z) = 0, \quad (37)$$

where we have set

$$B^2 = l^2 - 2\nu_0(l - \delta)^2/l, \quad x' = z(l/B)^\frac{1}{2}, \quad (38)$$

$$h^{(0)}(x') = H^{(0)}(z).$$

This is the equation for the Weber functions and hence one concludes that

$$\mu_n^{(1)} = \frac{1}{2}[l - (2n + 1)B], \quad (39)$$

$$H_n^{(0)}(z) = N_n D_n(z),$$

where N_n is the normalization factor $(B/2\pi l)^\frac{1}{2}(n!)^{-\frac{1}{2}}$. Note that the quantity B is related to the compressibility of the gas, since, from the van der Waals equation,

$$B^2 = [-l^2(l - \delta)^2/kT](\partial p/\partial l)_T. \quad (40)$$

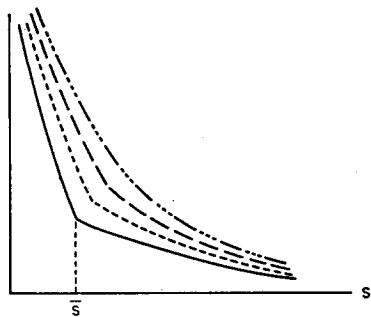


FIG. 6. ——— $\omega(s)$; - · - · - $\lambda(s, \gamma)$ (exact); - - - $\lambda(s, \gamma)$ to order $\gamma\delta$; — · — $\lambda(s, \gamma)$ to order $(\gamma\delta)^2$.

In the one-phase region $\partial p/\partial l$ is always negative, and therefore B can be taken positive. The maximum eigenvalue corresponds therefore to $n = 0$, and is given up to first order by

$$\lambda_0(s, \gamma) = \omega(s)[1 + \frac{1}{2}\gamma(l - B)]. \quad (41)$$

This proves the statement in Sec. III, that the maximum eigenvalue is $\omega(s)$ in the van der Waals limit.

In first approximation one obtains

$$\begin{aligned} \frac{d^2 H_n^{(1)}}{dz^2} + (n + \frac{1}{2} - \frac{1}{2}z^2)H_n^{(1)} &= \frac{\nu_0^{\frac{1}{2}}(l - \delta)^2}{l^{\frac{1}{2}}B^{\frac{1}{2}}} \frac{dH_n^{(0)}}{dz} \\ &+ \frac{\nu_0^{\frac{1}{2}}(l - \delta)^2}{l^{\frac{1}{2}}B^{\frac{1}{2}}} \left(\frac{l}{2B} - n - \frac{1}{2} \right) z H_n^{(0)} \\ &- \frac{\nu_0^{\frac{1}{2}}(l - \delta)^3(l - 3\delta)}{6l^{\frac{5}{2}}B^{\frac{5}{2}}} z^3 H_n^{(0)}. \end{aligned} \quad (42)$$

It can be easily verified that the right-hand side is orthogonal to $H_n^{(0)}$, so that (42) has an unique solution. For the explicit form of the solution and also for the second approximation, which will be needed in Part II of this series of papers, we refer to Appendix III.

Let us now consider the *two-phase region*.

It is clear that in this case the argument must be revised, since the $\eta(s)$ in the shift (33) is no longer unique. In fact, since $F(\eta, s)$ has now two equal maxima, there are *two* values of $\eta(s)$ corresponding to the volumes l_1 and l_2 of the saturated vapor and liquid phase (see Fig. 5). For each of these two

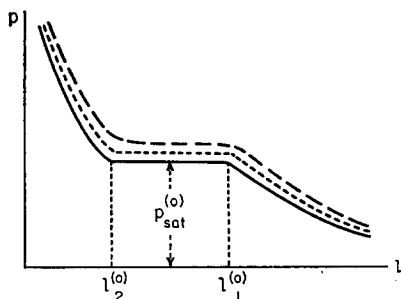


FIG. 7. ——— The van der Waals isotherm ($\gamma = 0$); - - - The exact isotherm; ····· The isotherm to order $\gamma\delta$.

values one can make the shift (33), and repeat the the argument. Clearly in both cases one will get the *same* zeroth-order eigenvalue $\omega(s)$, but one will get *another* eigenfunction, since the quantity l/B will be different at l_1 and l_2 . One must say therefore that for $l_2 < l < l_1$, i.e. in the two-phase region, the maximum eigenvalue in the van der Waals limit is *doubly degenerate*, and in lowest order, the eigenfunction will have the form [since $D_0(z) = \exp(-\frac{1}{4}z^2)$],

$$\begin{aligned} \psi_0(x, s) &= \alpha_1 \left(\frac{B_1}{2\pi l_1} \right)^{\frac{1}{2}} \exp \left[-\frac{B_1}{4l_1} \left(x - \eta_1 \left[\frac{2}{\gamma} \right]^{\frac{1}{2}} \right)^2 \right] \\ &+ \alpha_2 \left(\frac{B_2}{2\pi l_2} \right)^{\frac{1}{2}} \exp \left[-\frac{B_2}{4l_2} \left(x - \eta_2 \left[\frac{2}{\gamma} \right]^{\frac{1}{2}} \right)^2 \right], \end{aligned} \quad (43)$$

where $\eta_1(\bar{s}) = (2\nu_0)^{\frac{1}{2}}/l_1$ and $\eta_2(\bar{s}) = (2\nu_0)^{\frac{1}{2}}/l_2$.

The question now arises as to the appropriate linear combination corresponding to a specific length $l = \xi_1 l_1 + \xi_2 l_2$, (where ξ_1, ξ_2 are the mole fractions of the vapor and liquid phase), so that $\xi_1 + \xi_2 = 1$. We show that the answer is given by

$$\xi_1 = \alpha_1^2 \quad \xi_2 = \alpha_2^2. \quad (44)$$

To prove this, note first that for small γ , the *two Gaussian functions in (43) do not overlap*. Hence from the normalization of $\psi(x, \bar{s})$, one obtains $\alpha_1^2 + \alpha_2^2 = 1$. Furthermore, for any finite γ , it follows from the Kac equation that

$$\begin{aligned} \lambda_0(s, \gamma) &= \iint dx dy K_s(x, y) \\ &\times \psi_0(x, s, \gamma) \psi_0(y, s, \gamma), \end{aligned} \quad (45)$$

$$\begin{aligned} \lambda_0'(s, \gamma) &= -\lambda_0(s, \gamma)l = \iint dx dy \frac{\partial K_s}{\partial s} \\ &\times \psi_0(x, s, \gamma) \psi_0(y, s, \gamma) \end{aligned}$$

[since the differentiation of the eigenfunctions after s gives zero because the normalization of $\psi_0(x, s, \gamma)$ implies

$$\int \psi_0(x, s, \gamma) \frac{\partial}{\partial s} \psi_0(x, s, \gamma) dx = 0].$$

Now take $s = \bar{s}$, and let $\gamma \rightarrow 0$. Since for each of the two functions in Eq. (43) one has an equation like (45) with the same s and the same $\lambda_0(s) = \omega(s)$, but with l successively l_1 and l_2 , and since one can again neglect the overlap of the two functions, it follows from Eq. (45) that for $\gamma \rightarrow 0$,

$$l = \alpha_1^2 l_1 + \alpha_2^2 l_2,$$

which proves Eq. (44).

We conclude this section with the following two remarks.

(a) It is clear that the entire development breaks down near the critical point because at that point, $B \rightarrow 0$ and $l_1 \cong l_2$. The overlap of the two eigenfunctions in the two-phase region can therefore no longer be neglected. In the critical region, one has to "tame" the integral equation in a different way, which will be explained in the third part of this series.

(b) It follows from Eq. (41) that up to first order in γ , $\lambda_0(s, \gamma)$ still shows a discontinuity in slope, and one can be convinced that the discontinuity remains if the perturbation calculation is continued up to any finite order in γ . For finite γ , $\lambda_0(s, \gamma)$ is an analytic function of s for $s > 0$. This means that for small γ , the successive-approximation method which we have developed, approximates the analytic function $\lambda_0(s, \gamma)$ by a series of functions which have a discontinuity in slope in the region of s , where the slope of $\lambda_0(s, \gamma)$ varies very quickly (see Fig. 6). This implies that the phase transition persists up to any finite order in γ , although the equation of state is then of course different from the van der Waals equation. In fact it is not difficult to show from Eq. (41), that, up to first order in γ , the equation of state in the one-phase region is given by

$$p_{\text{sat}} = \frac{kT}{l - \delta} - \frac{\alpha_0}{l^2} + \frac{\gamma}{2} \left\{ kT - \frac{l}{B} \left[kT - \frac{\alpha_0(l^2 - \delta^2)}{l^3} \right] \right\}.$$

The saturated vapor pressure and the densities of the saturated vapor and liquid also change accordingly. One finds

$$p_{\text{sat}} = p_{\text{sat}}^{(0)} + \gamma \frac{kT}{2} \left(\frac{B_1 - B_2}{l_1 - l_2} - 1 \right)$$

$$l_i = l_i^{(0)} + \frac{\gamma}{2} (l_i - \delta)^2 \left(\frac{l_i}{B} \right)^2$$

$$\times \left[\frac{B_1 - B_2}{l_1 - l_2} - \frac{l_i}{B_i} \left(1 - \frac{\alpha_0(l_i^2 - \delta^2)}{kT l_i^3} \right) \right]$$

with $i = 1, 2$.

V. CONCLUDING REMARKS

To judge the relevance of our results for the three-dimensional case, let us first recall the usual derivation⁸ of the van der Waals equation from the partition function. One can argue as follows: If the range

⁸ This derivation goes back to L. S. Ornstein, Dissertation Leiden 1908. Van der Waals himself, and then later also Lorentz [Collected Papers (Martinus Nyhoff, The Hague, Netherlands, 1935), Vol. 6, p. 40], started from the virial theorem of Clausius. We will come back to this in Part II in this series of papers.

of the attractive force is very large so that there are many molecules in the action sphere of each molecule, then the potential energy of the attractive forces should for almost all configurations of the molecules, be equal to the average value

$$\Phi_{\text{attr}} = -CN^2/2V, \tag{46}$$

where

$$C = - \int dr \varphi_{\text{attr}}(r).$$

Equation (46) follows because on the average, the potential energy of one molecule will be proportional to the number density N/V and is in fact equal to $-CN/V$. The factor two in (46) is of course needed because each molecule interacts with all other molecules. For long-range attractive forces it seems reasonable therefore to approximate the partition function by

$$Z(V, T, N) = \frac{1}{\Lambda^{3N}} \frac{1}{N!} \exp [CN^2/2kTV] \times \int_V \cdots \int_V dr_1 \cdots dr_N \prod_{i < j} S(|r_i - r_j|), \tag{47}$$

where $S(x)$ is the same step function as used in Sec. II. Now if V is very large compared to the total proper volume Nv_0 , $v_0 = \frac{4}{3}\pi r_0^3$ of the molecules, then clearly the integral approaches V^N , while if V is of the same order as Nv_0 the integral will become strongly zero about as $(V - Nv_0)^N$. Approximation of the integral by the "interpolation" formula $(V - b)^N$ with $b \cong Nv_0$, then leads immediately to the van der Waals equation

$$(p + a/V^2)(V - b) = RT, \tag{48}$$

with $a = \frac{1}{2}CN^2$.

This derivation has been criticized mainly for two reasons:

1. A correct evaluation of the partition function in the thermodynamic limit should always give a stable isotherm for which $\partial p / \partial v \leq 0$. This has been proved rigorously by Van Hove⁹ for an intermolecular force of finite range and with a hard core. Since there is an unstable part in the van der Waals equation below the critical temperature, the equation is in conflict with this theorem.

2. The approximation $(V - b)^N$ for the repulsive

⁹ L. Van Hove, Physica 15, 951 (1949). Recently Dr. N. G. van Kampen has pointed out a gap in Van Hove's argument. Apparently the theorem can be proved even under less restrictive conditions by a different method. See a recent paper by D. Ruelle, which will appear in the Helv. Phys. Acta. (to be published).

part of the partition function must be very rough. Even if b is fixed so that the correct second virial coefficient (which makes $b = 4Nv_0$) is obtained, the higher virial coefficients which can be computed exactly, do *not* agree with the van der Waals' values.

Let us now return to our one-dimensional system. Note that by the same reasoning as used above, one would obtain

$$Z(L, T, N) = \frac{1}{\Lambda^N} \frac{1}{N!} \exp \left[\frac{\alpha_0 N^2}{kTL} \right] \\ \times \int_L \cdots \int_L dt_1 \cdots dt_N \prod_{i < j} S(|t_i - t_j|), \quad (49)$$

since C becomes $2\alpha_0$, with the factor two because of the two sides of the attractive force $-\alpha_0 \gamma \exp[-\gamma|t|]$. The *great difference* between Eqs. (47) and (49) is that the integral in Eq. (49) can be carried out *exactly* because of the linear order which the hard cores impose. The result is $(L - N\delta)^N$. For a gas of hard rods of length δ , the equation of state as noted by Tonks¹⁰ has precisely the van der Waals form

$$p = kT/(l - \delta). \quad (50)$$

The second objection against the van der Waals equation disappears in one dimension, and it is therefore *no* wonder that for our model in the van der Waals limit, Eq. (48) with $b = N\delta$, $a = \alpha_0 N^2$ is obtained exactly. The only question which remains is the conflict of the form (49) for Z with the Van Hove theorem. From the point of view of the development in Secs. II and III, it is clear that this conflict is due to the fact that in the derivation given above, the thermodynamic and the van der Waals limits have been coupled together, while they should be taken separately and in the proper order. Since we go *first* to the thermodynamic limit for a finite range of the attractive force, and *then* allow the range to go to infinity, we do not conflict with the Van Hove theorem, and we always obtain the stable isotherm¹¹). It seems to us therefore, that the first objection against the van der Waals equation is *not* as serious as we have been led to believe.

To summarize this discussion, we conclude with the following statements.

(a) It seems a good idea, following the example of van der Waals, to try to separate the effects of the repulsive and the attractive forces on the equation

¹⁰ L. Tonks, Phys. Rev. 50, 955 (1936).

¹¹ For our model, the Van Hove theorem is expressed by the inequality (21) for the maximum eigenvalue $\lambda_0(s, \gamma)$, which holds for any value of γ . The isotherm is monotonically decreasing for any γ , and therefore also in the limit $\gamma = 0$, $\partial p/\partial l \leq 0$.

of state, and to develop all thermodynamic functions in the ratio

$$\rho = \frac{\text{range of repulsive force}}{\text{range of attractive force}}. \quad (51)$$

One expects that for $\rho \ll 1$ one will get a van der Waals-like equation of state which would lead to the condensation phenomena and the existence of a critical point. The thermodynamic equilibrium conditions will follow automatically by going first to the thermodynamic limit.

(b) *Only in one dimension* does one obtain in the limit $\rho \rightarrow 0$, *exactly* the van der Waals equation of state for hard-core repulsion. This should be independent of the precise form of the attractive force. We have been able to confirm this by generalizing the Kac model to the case where the attractive force is of the form

$$\varphi_{\text{attr}}(x) = - \sum_{i=1}^m \alpha_i \gamma \exp[-\gamma \sigma_i x]. \quad (52)$$

The calculation of the partition function can be reduced as in Sec. II to an integral equation in m variables and the behavior of the maximum eigenvalue in the limit $\gamma \rightarrow 0$ may be considered in the same way as in Sec. III: the *same* equation (28) is obtained, except that $2v_0$ is replaced by

$$\frac{1}{kT} \sum_{i=1}^m \frac{2\alpha_i}{\sigma_i} = - \frac{2}{kT} \int_0^\infty \varphi_{\text{attr}}(x) dx. \quad (53)$$

Thus, again the van der Waals equation is obtained and the van der Waals a is again proportional to the area of the attractive potential.

(c) In *three* dimensions, the equation of state of a gas of hard spheres is certainly *not* $p = kT(v - b)$, although qualitatively the behavior may be similar. Even for very long-range attractive forces one can only hope to get a van der Waals-like equation of state. In a sense, the problem of the gas of hard spheres becomes the central problem. Whether such a gas would show a phase transition for densities near close packing (the so-called Kirkwood transition), is a famous open question. We believe that there are strong indications for the existence of such a transition and that this transition might be an idealization (or caricature!) of the fluid-solid transition. Clearly, in one dimension [see Eq. (50)], such a transition does *not* exist, and we believe therefore that even with long-range forces, to enforce co-operation, *one phase transition at most* can occur in one dimension.

Finally, we would like to mention two questions

which we have so far been unable to answer in a satisfactory way.

1. What is the relation of our theory with the Yang-Lee theory of condensation? From the existence of a hard core, it follows that the grand partition function $G(L, z)$ must be a polynomial of degree $M = L/\delta$ in z with positive coefficients. Setting

$$G(L, z) = \exp [L\chi(L, z)],$$

one can write

$$\chi(L, z) = \frac{1}{L} \sum_{i=1}^M \ln \left(1 - \frac{z}{z_i} \right),$$

where the z_i are the zero's of $G(L, z)$, none of which can be on the positive real axis. One can interpret $\chi(L, z)$ as the complex logarithmic potential of M point charges of strength $1/L$ situated at the points z_i . In the limit $L \rightarrow \infty$, the strength of the charges becomes smaller and smaller while the number M increases. Suppose now that in the limit $L \rightarrow \infty$, a number of the charges concentrate in a single layer which crosses the positive real axis, say at $z = z_0$. The limit function

$$\bar{\chi}(z) = \lim_{L \rightarrow \infty} \chi(L, z),$$

which surely exists, will then for positive and real z , consist of two analytic pieces, one for $z < z_0$ and the other for $z > z_0$. At z_0 these two pieces will be continuous but the first derivative will have a discontinuity. Since $\bar{\chi}(z) = p/kT$ one would therefore obtain a curve as in Fig. 4 (with abscissa and ordinates interchanged), and condensation would occur. It is clear that something like this must happen for our model in the van der Waals limit. It must be that for finite γ , the single layer will *not* cross the positive real axis but leave a gap, say, of order γ . For finite γ , $\bar{\chi}(z)$ will then be analytic for all real and positive z , but in the van der Waals limit when the gap closes, condensation occurs. However, we have been unable to substantiate this picture, because it is difficult to discuss the behavior of the eigenvalues of the Kac equation for complex values of s .

2. What is the relation of our theory with the Ursell-Mayer theory? We have already mentioned the problem of the "graphological" interpretation of the coefficients a_i in the expansion of $\lambda_0(s)$ [see Eq. (22)], but there are also other questions. For instance it should be possible to introduce Mayer f functions both for the repulsive and for the attractive parts of the intermolecular potential, which would lead to graphs with two types of lines. The

question is then, which simplifications occur if the attractive force is long range, and whether one can learn from the one-dimensional model how to characterize better the van der Waals-like equation in three dimensions.

APPENDIX 1

For the proof of statement (a) see Kac (reference 5, p. 11). There one also finds the proof that

$$\lambda_0(s) \geq e^{s^2} \int_0^\infty d\tau \exp [-s\tau + \nu e^{-\gamma\tau}], \quad (A.1)$$

and since for $s = 0$ the integral diverges, $\lambda_0(s) \rightarrow \infty$ for $s \rightarrow 0$. Furthermore, since the right hand side of (A.1) can be shown to correspond to the "nearest-neighbor" approximation, one should expect that for small s (i.e. small pressure), $\lambda_0(s)$ becomes equal to it, which implies that for $s \rightarrow 0$, $\lambda_0(s) \sim e^{s^2}/s$, and this will be confirmed later when we derive the expansion (22).

The statement that $\lambda_0(s)$ cannot be degenerate for any value of s , follows from the fact that the kernel $K_s(x, y)$ is positive for all x, y and for $s > 0$. Since

$$\lambda_0(s) \geq \frac{\iint dx dy \varphi(x) K_s(x, y) \varphi(y)}{\int dx \varphi^2(x)} \quad (A.2)$$

for any function $\varphi(x)$, and since the maximum is reached when $\varphi(x) = \psi_0(x)$, $K_s(x, y) > 0$ implies that $\psi_0(x)$ must have the same sign for all x , and we may assume therefore $\psi_0(x) \geq 0$. Furthermore, $\psi_0(x)$ cannot be zero, unless for some particular value of x , say x_0 , $K_s(x_0, y) \equiv 0$ in y , which is excluded by $K_s > 0$. Now suppose that for some value of s , $\lambda_0(s)$ was degenerate and corresponded to the two eigenfunctions $\psi_0^{(1)}(x)$ and $\psi_0^{(2)}(x)$. Taking $\psi_0^{(1)}(x) > 0$, one then can construct a linear combination $\varphi(x)$ of $\psi_0^{(1)}$ and $\psi_0^{(2)}$ which is orthogonal to $\psi_0^{(1)}$, and which fulfills the equation

$$\lambda_0(s) = \frac{\iint dx dy \varphi(x) K_s(x, y) \varphi(y)}{\int dx \varphi^2(x)}. \quad (A.3)$$

Since $\psi_0^{(1)}(x)$ cannot be zero, $\varphi(x)$, being orthogonal to $\psi_0^{(1)}$, must be both positive and negative over some intervals, and this yields a contradiction. The absence of a degeneracy of $\lambda_0(s)$ implies that $\lambda_0(s)$ is an analytic function of s for all real $s > 0$. This is because it is known that the eigenvalues $\lambda_i(s)$ are the zero's in λ of the Fredholm determinant

$D(x, \lambda)$, which is an entire function of λ , and is analytic for all real $s > 0$. Therefore the $\lambda_n(s)$ must be analytic functions of s except at those values of s where two or more eigenvalues cross.

Finally the inequality (21) is proved as follows: With normalized eigenfunctions, one finds from

$$\lambda_0(s) = \iint dx dy \psi_0(x, s) K_s(x, y) \psi_0(y, s),$$

that the quadratic form

$$\begin{aligned} Q(z) &\equiv \lambda_0(s)z^2 + 2\lambda_0'(s)z + \lambda_0''(s) \\ &= \iint_{-\infty}^{+\infty} dx dy \psi_0(x, s)\psi_0(y, s) \\ &\quad \times \left[z^2 K_s(x, y) + 2z \frac{\partial K_s}{\partial s} + \frac{\partial^2 K_s}{\partial s^2} \right] \\ &\quad + \iint_{-\infty}^{+\infty} dx dy \frac{\partial K_s}{\partial s} \left[\psi_0(x, s) \frac{\partial \psi_0(y, s)}{\partial s} \right. \\ &\quad \left. + \psi_0(y, s) \frac{\partial \psi_0(x, s)}{\partial s} \right]. \end{aligned} \tag{A.4}$$

From Eq. (9) for $K_s(x, y)$, it can be seen that the variable s enters only through $p_s(x, y)$, and from Eq. (8) it follows that the first term in Eq. (4) is positive for all z . Also the second term in Eq. (4) is positive, since by using

$$K_s(x, y) = \sum_0^{\infty} \lambda_n(s) \psi_n(x, s) \psi_n(y, s),$$

and the fact that for any s the $\psi_n(x, s)$ form an orthonormal set, it can be transformed into

$$\begin{aligned} 2\lambda_0(s) \int_{-\infty}^{+\infty} dx \left[\frac{\partial \psi_0(x, s)}{\partial s} \right]^2 \\ - 2 \sum_{n=1}^{\infty} \lambda_n(s) \left[\int_{-\infty}^{+\infty} dx \frac{\partial \psi_0(x, s)}{\partial s} \psi_n(x, s) \right]^2, \end{aligned}$$

and since $\lambda_n(s) < \lambda_0(s)$ for $n \geq 1$, this is bigger than

$$2\lambda_0(s) \left[\int_{-\infty}^{+\infty} dx \left(\frac{\partial \psi_0}{\partial s} \right)^2 - \sum_0^{\infty} \left(\int_{-\infty}^{+\infty} dx \psi_n \frac{\partial \psi_0}{\partial s} \right)^2 \right],$$

which is zero because of Parseval's relation applied to the function $\partial \psi_0 / \partial s$. Hence $Q(z) > 0$ for all z , which implies Eq. (21).

Statement (c), Sec. II follows from the relation

$$\begin{aligned} \sum_0^{\infty} \lambda_i &= \int_{-\infty}^{+\infty} dx K_s(x, x) \\ &= \int_s^{\infty} \frac{d\tau}{1 - e^{-\gamma\tau}} \exp \left[-s\tau + \frac{\nu}{2} \frac{1 + e^{-\gamma\tau}}{1 - e^{-\gamma\tau}} \right], \end{aligned}$$

which shows that for $s \rightarrow 0$, the sum of all the eigen-

values goes to infinity as $e^{\frac{1}{2}\nu}/s$, and since this is also the behavior of $\lambda_0(s)$, all other eigenvalues must be finite for $s = 0$.

To find the expansion (22) for $\lambda_0(s)$, one must make a perturbation calculation around $s = 0$ for the eigenvalue problem

$$\int_{-\infty}^{+\infty} dy K_s(x, y) \psi_0(y, s) = \lambda_0(s) \psi_0(x, s). \tag{A.5}$$

First we expand $K_s(x, y)$ in powers of s . To do this we write $K_s(x, y)$ in the form

$$\begin{aligned} K_s(x, y) &= \exp \left[\frac{1}{2}\nu^{\frac{1}{2}}(x + y) \right] \left\{ \frac{e^{-s}}{s} [W(x)W(y)]^{\frac{1}{2}} \right. \\ &\quad + \sum_{n=0}^{\infty} \frac{(-s)^n}{n!} \int_s^{\infty} d\tau \tau^n \left(\left[\frac{W(x)}{W(y)} \right]^{\frac{1}{2}} P(x | y, \tau) \right. \\ &\quad \left. \left. - [W(x)W(y)]^{\frac{1}{2}} \right) \right\}. \end{aligned} \tag{A.6}$$

Now put

$$\begin{aligned} \lambda_0(s) &= (e^{\frac{1}{2}\nu}/s)(a_{-1} + a_0s + a_1s^2 + \dots), \\ \psi_0(x, s) &= \psi^{(0)}(x) + s\psi^{(1)}(x) + \dots, \end{aligned} \tag{A.7}$$

and let $\psi^{(0)}(x)$ be normalized to one. Introducing (6) and (7) into (5) and equating the terms proportional to $1/s$, one obtains

$$\begin{aligned} \int_{-\infty}^{+\infty} dy [W(x)W(y)]^{\frac{1}{2}} \\ \times \exp \left[\frac{1}{2}\nu^{\frac{1}{2}}(x + y) \right] \psi^{(0)}(y) = a_{-1} \psi^{(0)}(x) e^{\frac{1}{2}\nu}. \end{aligned} \tag{A.8}$$

One easily verifies that this has the solution

$$a_{-1} = 1; \quad \psi^{(0)}(x) = (W(x))^{\frac{1}{2}} \exp \left[-\frac{1}{2}\nu + \frac{1}{2}\nu^{\frac{1}{2}}x \right]. \tag{A.9}$$

Notice that if we try to determine in the same way the values of the other eigenvalues $\lambda_n(s)$ at $s = 0$, we would find in this approximation that $a_{-1}^{(n)} = 0$, so that all $\lambda_n(0)$ for $n > 0$ are degenerate, and to find the actual values, we would have to solve an infinite secular determinant. Only $\lambda_0(s)$ becomes infinite for $s \rightarrow 0$, and only for $\lambda_0(s)$ can we carry the perturbation calculation further.

Equating in Eq. (5) the terms independent of s , one finds

$$\begin{aligned} \int_{-\infty}^{+\infty} dy \exp \left[\frac{1}{2}\nu^{\frac{1}{2}}(x + y) \right] \left\{ \left(-\delta [W(x)W(y)]^{\frac{1}{2}} \right. \right. \\ \left. \left. + \int_s^{\infty} d\tau \left[\frac{W(x)}{W(y)} \right]^{\frac{1}{2}} \right. \right. \\ \left. \left. \times [P(x | y, \tau) - W(y)] \right) \psi^{(0)}(y) \right. \\ \left. + [W(x)W(y)]^{\frac{1}{2}} \psi^{(1)}(y) \right\} \\ = e^{\frac{1}{2}\nu} [\psi^{(1)}(x) + a_0 \psi^{(0)}(x)]. \end{aligned} \tag{A.10}$$

Multiply with $\psi^{(0)}(x)$ and integrate over x . Using Eq. (9), the fact that $\psi^{(1)}(x)$ is orthogonal to $\psi^{(0)}(x)$, and the formula

$$\iint_{-\infty}^{+\infty} dx dy \exp [\nu^{\frac{1}{2}}(x + y)]W(x)P(x | y, \tau) = \exp [\nu(1 + e^{-\gamma\tau})],$$

which is a special case of Eq. (4), one obtains

$$a_0 = -\delta + \int_0^{\infty} d\tau \{ \exp (\nu e^{-\gamma\tau} - 1) \}. \quad (\text{A.11})$$

The right-hand side can be written as

$$\lim_{L \rightarrow \infty} \frac{1}{2L} \iint_L dt_1 dt_2 \left\{ \exp \left[\frac{1}{kT} \varphi(|t_1 - t_2|) \right] - 1 \right\},$$

which is the definition of Mayer's b_2 . One also easily verifies from Eq. (10), that

$$\begin{aligned} \psi^{(1)}(x) = & -(a_0 + \delta)\psi^{(0)}(x) \\ & + e^{-\frac{1}{2}\nu} \int_{-\infty}^{+\infty} dy \psi^{(0)}(y) \exp \left[\frac{\nu^{\frac{1}{2}}}{2}(x + y) \right] \\ & \times \int_0^{\infty} d\tau \left[\frac{W(x)}{W(y)} \right]^{\frac{1}{2}} [P(x | y, \tau) - W(y)]. \end{aligned}$$

We can go on in this way, but the calculation soon becomes very lengthy. We have verified that in next approximation, one obtains $a_1 = b_3 - b_2^2$, where Mayer's b_3 is defined by

$$b_3 = \lim_{L \rightarrow \infty} \frac{1}{6L} \iiint_L dt_1 dt_2 dt_3 \times [f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23}]$$

with

$$f_{i,j} = \exp \left[\frac{1}{kT} \varphi(|t_i - t_j|) \right] - 1.$$

The general expression for the a_i in terms of the Mayer b_i is lacking. To obtain the correct equation of state up to the fourth virial coefficient, a_2 should be equal to $b_4 - 3b_2b_3 + 2b_2^3$, but we have not verified this.

APPENDIX II

To indicate the proof of Eq. (24), it will be sufficient to consider the case $n = 3$. One has

$$\begin{aligned} \sum_i \lambda_i^3 = & \iiint_0^{\infty} d\tau_1 d\tau_2 d\tau_3 e^{-\nu(\tau_1 + \tau_2 + \tau_3)} \\ & \times \iiint_{-\infty}^{+\infty} dx_1 dx_2 dx_3 \exp [-(\nu_0\gamma)^{\frac{1}{2}}(x_1 + x_2 + x_3)] \\ & \times P(x_1 | x_2, \tau_1)P(x_2 | x_3, \tau_2)P(x_3 | x_1, \tau_3), \end{aligned}$$

where $P(x | y, \tau)$ is given by Eq. (5). Introduce the new variables

$$\begin{aligned} \xi_1 = & (x_2 - x_1 e^{-\gamma\tau_1})(1 - e^{-2\gamma\tau_1})^{-\frac{1}{2}} \\ \xi_2 = & (x_3 - x_2 e^{-\gamma\tau_2})(1 - e^{-2\gamma\tau_2})^{-\frac{1}{2}} \\ \xi_3 = & (x_1 - x_3 e^{-\gamma\tau_3})(1 - e^{-2\gamma\tau_3})^{-\frac{1}{2}}, \end{aligned}$$

with the Jacobian

$$\frac{\partial(\xi_1, \xi_2, \xi_3)}{\partial(x_1, x_2, x_3)} = \{1 - e^{-\gamma(\tau_1 + \tau_2 + \tau_3)}\} \times \prod_{i=1}^3 (1 - \exp [-2\gamma\tau_i])^{-\frac{1}{2}}.$$

The integral over the x_i then becomes

$$\begin{aligned} & \{(2\pi)^{\frac{3}{2}}[1 - e^{-\gamma(\tau_1 + \tau_2 + \tau_3)}]\}^{-1} \\ & \times \iiint_{-\infty}^{+\infty} d\xi_1 d\xi_2 d\xi_3 \exp [-\frac{1}{2}(\xi_1^2 + \xi_2^2 + \xi_3^2)] \\ & \times \exp \left[\frac{(\nu_0\gamma)^{\frac{1}{2}}}{e^{-\gamma(\tau_1 + \tau_2 + \tau_3)} - 1} \sum_{i=1}^3 A_i \xi_i \right], \end{aligned}$$

with

$$A_i = (1 - e^{-2\gamma\tau_i})^{\frac{1}{2}} [e^{-\gamma(\tau_i + \tau_{i+1} + \tau_{i+2})} + e^{-\gamma\tau_{i+1}} + 1],$$

and $\tau_4 \equiv \tau_1, \tau_5 \equiv \tau_2$.

In this form it is convenient to go to the limit $\gamma \rightarrow 0$. Since the A_i approach $3(2\gamma\tau_i)^{\frac{1}{2}}$, the integrand of the ξ_i integral becomes independent of γ , and one obtains

$$\begin{aligned} \lim_{\gamma \rightarrow 0} \gamma \sum_i \lambda_i^3 = & \iiint_0^{\infty} d\tau_1 d\tau_2 d\tau_3 e^{-\nu(\tau_1 + \tau_2 + \tau_3)} \\ & \times [(2\pi)^{\frac{3}{2}}(\tau_1 + \tau_2 + \tau_3)]^{-1} \iiint_{-\infty}^{+\infty} d\xi_1 d\xi_2 d\xi_3 \\ & \times \prod_{i=1}^3 \exp \left[-\frac{1}{2}\xi_i^2 - \frac{3(2\nu_0\tau_i)^{\frac{1}{2}}\xi_i}{\tau_1 + \tau_2 + \tau_3} \right]. \quad (\text{a}) \end{aligned}$$

To uncouple the τ_i integrals, introduce the auxiliary variable

$$\eta = \frac{1}{\tau_1 + \tau_2 + \tau_3} \sum_{i=1}^3 \xi_i \tau_i^{\frac{1}{2}},$$

and multiply (a) with

$$\begin{aligned} 1 = & \int_{-\infty}^{+\infty} d\eta \delta \left(\eta - \frac{1}{\tau_1 + \tau_2 + \tau_3} \sum_{i=1}^3 \xi_i \tau_i^{\frac{1}{2}} \right) \\ = & \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} dv \\ & \times \exp \left[i v \left(\eta - \frac{1}{\tau_1 + \tau_2 + \tau_3} \sum_{i=1}^3 \xi_i \tau_i^{\frac{1}{2}} \right) \right], \end{aligned}$$

using the Fourier representation of the δ function. Set $v = w(\tau_1 + \tau_2 + \tau_3)$, and integrate first over the ξ_i . We then obtain

$$\lim_{\gamma \rightarrow 0} \gamma \sum_i \lambda_i^3 = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} dw \times \left\{ \int_{\delta}^{\infty} d\tau \exp \left[-\eta(2\nu_0)^{\frac{1}{2}} + i\tau\eta w - \frac{\tau}{2} w^2 \right] \right\}^3.$$

Finally, setting $w = \xi + i\eta$, one obtains Eq. (24) for $n = 3$. The proof for arbitrary n follows the same procedure.

APPENDIX III

The solution of Eq. (42) can be written in the form

$$H_n^{(1)}(z) = N_n [P_n D_{n+3}(z) + Q_n D_{n+1}(z) + R_n D_{n-1}(z) + S_n D_{n-3}(z)],$$

where

$$P_n \equiv P = \frac{\nu_0^{\frac{1}{2}}(l - \delta)^3(l - 3\delta)}{18l^{5/2}B^{5/2}},$$

$$Q_n = 9(n + 1)P + (n + 1)V - W,$$

$$R_n = -9n^2P - n^2V + nW,$$

$$S_n = -n(n - 1)(n - 2)P,$$

with

$$V = \nu_0^{\frac{1}{2}}(l - \delta)^2/l^{\frac{1}{2}}B^{\frac{1}{2}}, \quad W = \nu_0^{\frac{1}{2}}(l - \delta)^2/2l^{\frac{1}{2}}B^{\frac{1}{2}}.$$

To obtain the equation for the next approxima-

tion, the left-hand side of Eq. (35) must be expanded to terms of order γ^2 . Using the expansions (36), and equating terms of order γ^2 , one obtains

$$\begin{aligned} \frac{d^2 H_n^{(2)}}{dz^2} + \left(n + \frac{1}{2} - \frac{z^2}{4} \right) H_n^{(2)} &= \frac{\mu_n^{(2)}}{B} H_n^{(0)} \\ &+ \frac{\nu_0^{\frac{1}{2}}(l - \delta)^2 l^{\frac{1}{2}}}{4B^{5/2}} \left(\frac{4\nu_0}{3l^2} - 1 \right) z^3 H_n^{(1)} \\ &+ \frac{\nu_0^{\frac{1}{2}}(l - \delta)^2}{l^{\frac{1}{2}}B^{\frac{1}{2}}} z \frac{d^2 H_n^{(1)}}{dz^2} + \frac{\nu_0^{\frac{1}{2}}(l - \delta)^2}{l^{\frac{1}{2}}B^{\frac{1}{2}}} \\ &\times \left\{ \frac{1}{2} z H_n^{(1)} + \frac{B}{l} \frac{dH_n^{(1)}}{dz} \right\} \\ &+ H_n^{(0)}(z) \left[\frac{\nu_0^2(l - \delta)^4(l^2 - 2l\delta - \delta^2)}{8l^4B^3} z^4 \right. \\ &+ \frac{\nu_0(l + \delta)(l - \delta)^3}{2l^3B} \left(n + \frac{1}{2} - \frac{l}{2B} \right) z^2 \\ &- \frac{\nu_0}{12l^2B} (15l^3 - 36l^2\delta + 30l\delta^2 - 8\delta^3) \\ &+ \frac{1}{2B} (2l^2 - 2l\delta + \delta^2) \\ &\times \left. \left\{ \frac{1}{4} + (n + \frac{1}{2}) \frac{B}{l} - (n^2 + n + \frac{3}{4}) \frac{B^2}{l^2} \right\} \right] \\ &- \frac{\nu_0(l - \delta)^3(l + \delta)}{l^3B} z \frac{dH_n^{(0)}}{dz}, \end{aligned}$$

from which $\mu_n^{(2)}$ and then $H_n^{(2)}$ can be determined in the usual way.