Progress of Theoretical Physics, Vol. 44, No. 5, November 1970

Statistical Mechanics of Interacting Systems

P. C. TRIVEDI*)

Department of Physics, Brock University, St. Catharines, Ontario, Canada

(Received February 16, 1970)

A mathematical technique is introduced to sum the iteration series which occurs in the electron gas theory by Montroll and Ward. As a result summation over ring diagrams becomes easier to perform than the case of Montroll and Ward. The binary kernel of Lee and Yang is expressed as a sum of kernels which are solutions of integral equations obtained by iteration. This formalism provides a method to calculate the binary kernel. The grand partition function is calculated by solving the integral equation and is applied to the calculation of the Debye-Hückel equation of state.

§ 1. Introduction

Systematic perturbation theory follows directly from an analysis of the propagator $k^{(N)}(r_2, \beta_2; r_1, \beta_1) \equiv k(2,1)$ which has the property

$$\psi(r_2, \beta_2) = \int_v k^{(N)}(r_2, \beta_2; r_1, \beta_1)\psi(r_1, \beta_1)\, d^{3N}r_1 .$$

Here r_1 and r_2 schematically represent respectively the values of the $3N$ position coordinates of the particles β_1 and β_2. The parameter β is $1/kT$, T being the temperature and k the Boltzmann constant. ψ is the wave function or characteristic function of the Hamiltonian H. It can be shown[1),2)] that $k(2,1)$ satisfies the Green's function equation

$$\left[\frac{\partial}{\partial \beta_2} + H(2)\right] k(2,1) = \delta(r_2 - r_1)\,\delta(\beta_2 - \beta_1), \tag{1·1}$$

the operator in the parenthesis operates on the variables r_2 and β_2.

Let us write

$$H = H_0 + H_1 \tag{1·2}$$

and

$$k(2,1) = k_0(2,1) + k_1(2,1), \tag{1·3}$$

where H_0 is the free particle Hamiltonian and $k_0(2,1)$ the free particle propagator which is the solution of

$$\left[\frac{\partial}{\partial \beta_2} + H_0(2)\right] k_0(2,1) = \delta(\beta_2 - \beta_1)\,\delta(r_2 - r_1). \tag{1·4}$$

Substitution of (1·2), (1·3) and (1·4) into (1·1) gives

*) Present address: Department of Physics and Astrophysics, University of Delhi, Delhi-7, India.

$$k_1(2,1) = -\int_v \int_{\beta_1}^{\beta_2} k_0(2,3) H_1(3) k(3,1) d^{3N}r_3 d\beta_3 .$$

Thus

$$k(2,1) = k_0(2,1) - \int_v \int_{\beta_1}^{\beta_2} k_0(2,3) H_1(3) k(3,1) d^{3N}r_3 d\beta_3 , \tag{1·5}$$

which can be solved by iteration:

$$k(2,1) = k_0(2,1) - \int_v \int_{\beta_1}^{\beta_2} k_0(2,3) H_1(3) k_0(3,1) d^{3N}r_3 d\beta_3$$
$$+ \int_v \int_{\beta_1}^{\beta_2} \int_v \int_{\beta_1}^{\beta_3} k_0(2,3) H_1(3) k_0(3,4) H_1(4) k_0(4,1) d^{3N}r_4 d\beta_4 d^{3N}r_3 d\beta_3 - \cdots . \tag{1·6}$$

If H_1 is proportional to a coupling constant λ, this expansion is a power series in λ and therefore a perturbation series. Each term in this expansion can be identified by Feynman-type diagrams in (r, β) space. Montroll and Ward[1),2)] gave a systematic treatment of the electron gas, based on the summation of this series.

In the following development we introduce a mathematical technique to sum the iteration series (1·6). In this formalism, unlike that of Montroll and Ward, wave functions and energy levels play an important role.

In § 2 a propagator $k(P_2, \beta_2; P_1, \beta_1)$ for two interacting particles is calculated in terms of $g(P_2, \beta_2; P_1, \beta_1)$. The function $g(P_2, \beta_2; P_1, \beta_1)$ is a kernel of a certain integral equation. It is shown in § 3 that the binary kernel of Lee and Yang[4)] can be expressed as a sum of the kernels which are obtained by iterating this integral equation. An expression for the function $g(P_2, \beta_2; P_1, \beta_1)$ for the Coulomb potential is also obtained in this section. In § 4 the integral equation whose kernel is $g(P_2, \beta_2; P_1, \beta_1)$ is solved and in § 5, $k(P_2, \beta_2; P_1, \beta_1)$ is further simplified. Finally, in § 6, the Debye-Hückel equation of state is calculated. Discussion is given in § 7.

§ 2. The propagator $k(P_2, \beta_2; P_1, \beta_1)$ for two interacting particles

It is easier to make calculations in momentum space representation. Let

$$k(r_2, \beta_2; r_1, \beta_1) = \frac{1}{(2\pi\hbar)^{3N}} \int \cdots \int d^{3N}p_1 d^{3N}p_2 \exp\left[i(p_2 \cdot r_2 - p_1 \cdot r_1)\hbar^{-1}\right] k(p_2, \beta_2; p_1, \beta_1), \tag{2·1}$$

then the partition function[1)]

$$Z = \int k(r, \beta; r, 0) d^{3N}r = \int k(p, \beta; p, 0) d^{3N}p . \tag{2·2}$$

The free particle momentum space propagator is

$$k_0(p_2, \beta_2; p_1, \beta_1) = \delta(p_2 - p_1) \exp[-(\beta_2 - \beta_1) p_1^2/2m], \tag{2·3}$$

where $\delta(p_2-p_1)$ is to be interpreted as

$$\delta(p_2-p_1)=\lim_{v\to\infty}\left\{\frac{v\delta p_1 p_2}{(2\pi\hbar)^3}\right\}. \tag{2·4}$$

When v is finite $\delta(p_2-p_1)$ is to be replaced by the quantity in the bracket.

In the presence of interactions we can find the momentum representation of our fundamental integral equation (1·5) by employing (2·1), (2·3) and using the Fourier transform of the interaction energy $u(q)$. That is, setting

$$u(q)=\frac{1}{(2\pi\hbar)^3}\int u(r)\exp[-i(q\cdot r)/\hbar]d^3r\,, \tag{2·5}$$

with

$$u(r)=\int u(q)\exp[iq\cdot r/\hbar]d^3q\,, \tag{2·6}$$

one finds

$$k(p_2,\beta_2;p_1,\beta_1)=k_0(p_2,\beta_2;p_1,\beta_1)-\int_{\beta_1}^{\beta_2}\int d^{3N}p_3 d\beta_3\sum_{j>k}$$
$$\times\int k_0(p_2,\beta_2;p_3^{(1)},\cdots,p_3^{(k)}-q,\cdots,p_3^{(j)}+q,\cdots,p_3^{(N)},\beta_3)u(q)k(p_3,\beta_3;p_1,\beta_1)d^3q\,. \tag{2·7}$$

The conservation of momentum is apparent from the fact that through an interaction the momentum of the jth particle has been increased by q and that of the kth particle has been decreased by q.

For two interacting particles (2·7) is written as

$$k(P_2,\beta_2;P_1,\beta_1)=k_0(P_2,\beta_2;P_1,\beta_1)-\int_{\beta_1}^{\beta_2}\int d^3P_3 d\beta_3$$
$$\times\int k_0(P_2,\beta_2;p_3^{(1)}-q,p_3^{(2)}+q,\beta_3)u(q)k(P_3,\beta_3;P_1,\beta_1)d^3q\,, \tag{2·8}$$

where

$$P_1=\{p_1^{(1)},p_1^{(2)}\};\ P_2=\{p_2^{(1)},p_2^{(2)}\};\ P_3=\{p_3^{(1)},p_3^{(2)}\}.$$

On iteration (2·8) gives

$$k(P_2,\beta_2;P_1,\beta_1)=k_0(P_2,\beta_2;P_1,\beta_1)-\int_{\beta_1}^{\beta_2}\int d^3P_3 d\beta_3$$
$$\times\int k_0(P_2,\beta_2;p_3^{(1)}-q_3,p_3^{(2)}+q_3,\beta_3)u(q_3)k_0(P_3,\beta_3;P_1,\beta_1)d^3q_3$$
$$+\int_{\beta_1}^{\beta_2}\int\int_{\beta_1}^{\beta_3}\int d^3P_3 d\beta_3 d^3P_4 d\beta_4\int k_0(P_2,\beta_2;p_3^{(1)}-q_3,p_3^{(2)}+q_3,\beta_3)u(q_3)d^3q_3$$
$$\times\int k_0(P_3,\beta_3;p_4^{(1)}-q_4,p_4^{(2)}+q_4,\beta_4)u(q_4)k_0(P_4,\beta_4;P_1,\beta_1)d^3q_4\cdots\cdots. \tag{2·9}$$

Now

$$\int k_0(3,5)\,k_0(5,4)\,d^3P_5 = k_0(3,4),$$

where

$$k_0(3,5) \equiv k_0(P_3, \beta_3; P_5, \beta_5).$$

Similarly

$$\int k_0(P_3, \beta_3; P_5, \beta_5)\,k_0(P_5, \beta_5; p_4^{(1)} - q_4, p_4^{(2)} + q_4, \beta_4)\,d^3P_5$$
$$= k_0(P_3, \beta_3; p_4^{(1)} - q_4, p_4^{(2)} + q_4, \beta_4). \tag{2·10}$$

Let

$$\int_{\beta_1}^{\beta_2}\int d^3P_3 d\beta_3 \int k_0(P_2, \beta_2; p_3^{(1)} - q_3, p_3^{(2)} + q_3, \beta_3)\,u(q_3)\,k_0(P_3, \beta_3; P_1, \beta_1)\,d^3q_3 \equiv g(2,1). \tag{2·11}$$

Similarly

$$\int_{\beta_1}^{\beta_2}\int d^3P_3 d\beta_3 \int k_0(P_2, \beta_2; p_3^{(1)} - q_3, p_3^{(2)} + q_3, \beta_3)\,u(q_3)\,k_0(P_3, \beta_3; P_5, \beta_5)\,d^3q_3$$
$$= \int_{\beta_5}^{\beta_2}\int d^3P_3 d\beta_3 \int k_0(P_2, \beta_2; p_3^{(1)} - q_3, p_3^{(2)} + q_3, \beta_3)\,u(q_3)\,k_0(P_3, \beta_3; P_5, \beta_5)\,d^3q_3$$
$$\equiv g(2,5), \tag{2·12}$$

since

$$k_0(2,3) = \theta(\beta_2 - \beta_3)\,k_0(2,3)$$

and

$$k_0(3,5) = \theta(\beta_3 - \beta_5)\,k_0(3,5),$$

where $\theta(x)$ is the Heaviside function defined as

$$\theta(x) = \begin{cases} 1 & \text{if } x \geq 0, \\ 0 & \text{if } x < 0. \end{cases}$$

Hence for $g(2,5)$ to be non-zero we have $\beta_2 > \beta_3 > \beta_5$. Also

$$\int_{\beta_1}^{\beta_3}\int d^3P_4 d\beta_4 \int k_0(P_5, \beta_5; p_4^{(1)} - q_4, p_4^{(2)} + q_4, \beta_4)\,u(q_4)\,k_0(P_4, \beta_4; P_1, \beta_1)\,d^3q_4$$
$$= \int_{\beta_1}^{\beta_5}\int d^3P_4 d\beta_4 \int k_0(P_5, \beta_5; p_4^{(1)} - q_4, p_4^{(2)} + q_4, \beta_4)\,u(q_4)\,k_0(P_4, \beta_4; P_1, \beta_1)\,d^3q_4$$
$$\equiv g(5,1), \tag{2·13}$$

since

$$k_0(5,4) = \theta(\beta_5 - \beta_4)\,k_0(5,4)$$

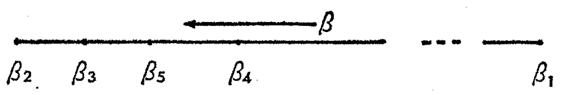

Fig. 1. The β ordering.

and

$$k_0(4, 1) = \theta(\beta_4 - \beta_1) k_0(4, 1).$$

β ordering is shown in Fig. 1.

Substitution of (2·10), (2·11), (2·12) and (2·13) in (2·9) yields

$$k(2, 1) = k_0(2, 1) - g(2, 1) + \int g(2, 5) g(5, 1) d^3P_5$$

$$- \int\int g(2, 5) g(5, 6) g(6, 1) d^3P_5 d^3P_6 + \cdots . \tag{2·14}$$

Now consider the integral equation

$$\lambda_n \Phi_n(2) = \int g(2, 1) \Phi_n(1) d^3P_1 , \tag{2·15}$$

where

$$\Phi_n(2) \equiv \Phi_n(P_2, \beta_2),$$

$$\Phi_n(1) \equiv \Phi_n(P_1, \beta_1)$$

and

$$g(2, 1) \equiv g(P_2, \beta_2; P_1, \beta_1).$$

$\{\Phi_n\}$ and $\{\lambda_n\}$ are the normalized characteristic functions and associated characteristic values respectively. It is known that

$$g(2, 1) = \sum_n \lambda_n \Phi_n(2) \Phi_n^*(1). \tag{2·16}$$

From (2·16) and (2·14) we have

$$k(2, 1) = k_0(2, 1) - \sum_n \lambda_n \Phi_n(2) \Phi_n^*(1) + \sum_n \sum_m \int \lambda_n \lambda_m \Phi_n(2) \Phi_n^*(5) \Phi_m(5) \Phi_m^*(1) d^3P_5$$

$$- \sum_n \sum_m \sum_l \int\int \lambda_n \lambda_m \lambda_l \Phi_n(2) \Phi_n^*(5) \Phi_m(5) \Phi_m^*(6) \Phi_l(6) \Phi_l^*(1) d^3P_5 d^3P_6 + \cdots .$$

Since

$$\int \Phi_n^* \Phi_m d^3P = \delta_{nm} ,$$

$$k(2, 1) = k_0(2, 1) - \sum_n (\lambda_n - \lambda_n^2 + \lambda_n^3 - \cdots) \Phi_n(2) \Phi_n^*(1), \tag{2·17}$$

$$= k_0(2, 1) - \sum_n \frac{\lambda_n}{1 + \lambda_n} \Phi_n(2) \Phi_n^*(1). \tag{2·18}$$

Thus the iteration series $(1\cdot6)$ has been expressed as a geometrical series which can be summed in a closed form.

§ 3. The $g(P_2, \beta_2; P_1, \beta_1)$ function and the binary kernel

In this section we shall obtain an expression for the $g(P_2, \beta_2; P_1, \beta_1)$ function for the Coulomb potential. It is defined by $(2\cdot11)$, viz.

$$g(P_2, \beta_2; P_1, \beta_1) = \int_{\beta_1}^{\beta_2} \int d\beta_3 d^3P_3 \int k_0(P_2, \beta_2; p_3^{(1)}-q, p_3^{(2)}+q, \beta_3) \times u(q) k_0(P_3, \beta_3; P_1, \beta_1) d^3q \,. \tag{2·11}$$

Using $(2\cdot3)$ and integrating over P_3 we obtain

$$g(P_2, \beta_2; P_1, \beta_1) = \int_{\beta_1}^{\beta_2} d\beta_3 \int d^3q \delta(p_2^{(1)}-p_1^{(1)}+q)\delta(p_2^{(2)}-p_1^{(2)}-q) \times \exp\{-(\beta_2-\beta_1)P_1^2/2m\} \exp[-(\beta_2-\beta_3)\boldsymbol{q}\cdot\{\boldsymbol{q}+(\boldsymbol{p}_1^{(2)}-\boldsymbol{p}_1^{(1)})\}/m] u(q), \tag{3·1}$$

where

$$P_1^2 = p_1^{(1)2} + p_1^{(2)2}.$$

The Coulomb interaction is characterized by the potential energy function $u(r) = e^2/r$. Its Fourier transform is obtained by taking the limit of vanishing screening constant $(\xi \to 0)$ in

$$u(q) = \frac{1}{(2\pi\hbar)^3} \int \frac{e^2}{r} \exp(-\xi r) \exp(-iq\cdot r\hbar^{-1}) d^3r = \frac{e^2}{2\pi^2\hbar(q^2+\xi^2\hbar^2)} \longrightarrow \frac{e^2}{2\pi^2\hbar q^2}\,. \tag{3·2}$$

Substitution of $u(q)$ from $(3\cdot2)$ into $(3\cdot1)$ and its integration over q and β_3 yields

$$g(P_2, \beta_2; P_1, \beta_1) = \frac{me^2}{2\pi^2\hbar}\delta(p_2^{(2)}+p_2^{(1)}-p_1^{(2)}-p_1^{(1)}) \exp\{-(\beta_2-\beta_1)P_1^2/2m\} \times \frac{1}{(p_2^{(2)}-p_1^{(2)})^2+\xi^2\hbar^2} \cdot \frac{1}{(\boldsymbol{p}_2^{(2)}-\boldsymbol{p}_1^{(2)})\cdot(\boldsymbol{p}_2^{(2)}-\boldsymbol{p}_1^{(1)})} \times \left[1-\exp\left\{-\frac{(\beta_2-\beta_1)}{m}(\boldsymbol{p}_2^{(2)}-\boldsymbol{p}_1^{(2)})\cdot(\boldsymbol{p}_2^{(2)}-\boldsymbol{p}_1^{(1)})\right\}\right]. \tag{3·3}$$

We introduce the relative momenta and the center of gravity momenta as follows:

$$p_1' = \tfrac{1}{2}(p_1^{(2)}-p_1^{(1)}), \qquad p_2' = \tfrac{1}{2}(p_2^{(2)}-p_2^{(1)}),$$
$$P_1' = p_1^{(2)}+p_1^{(1)}, \qquad P_2' = p_2^{(2)}+p_2^{(1)}. \tag{3·4}$$

Using (3·4) in (3·3) we obtain

$$g(P_2, \beta_2; P_1, \beta_1) = \frac{me^2}{2\pi^2\hbar}\delta(P_2' - P_1') \exp\left\{\frac{-(\beta_2-\beta_1)}{4m}P_1'^2\right\}$$
$$\times\left[\exp\left\{-\frac{(\beta_2-\beta_1)p_1'^2}{m}\right\} - \exp\left\{\frac{-(\beta_2-\beta_1)p_2'^2}{m}\right\}\right]\Big/\{(p_2'-p_1')^2+\xi^2\hbar^2\}(p_2'^2-p_1'^2)\,. \tag{3·5}$$

We can also express $k(P_2, \beta_2; P_1, \beta_1)$ in terms of the binary kernel.[3),4)]

$$k(P_2, \beta_2; P_1, \beta_1) = k_0(P_2, \beta_2; P_1, \beta_1) + U_2(P_2, \beta_2; P_1, \beta_1), \tag{3·6}$$

where U_2 is the binary kernel and can be represented as in Fig. 2. Compari-

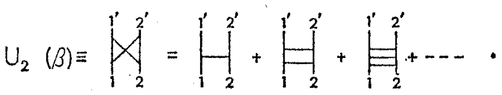

Fig. 2. The binary kernel.

son of (3·6) and (2·17) shows that U_2 can also be expressed in terms of g functions,

$$U_2 = -g_1 + g_2 - g_3 + \cdots,$$

where $g_1 \equiv g(2, 1)$ which is the kernel of the integral equation (2·15), g_2 is the kernel of the integral equation obtained by iterating (2·15) once and has the eigenvalues λ_n^2, g_3 has eigenvalues λ_n^3 and is the kernel of the integral equation obtained by iterating (2·15) twice etc. Thus we have a simple method of calculating the binary kernel.

§ 4. Solution of the integral equation

In this section we consider the integral equation (2·15). Wave functions can be written as follows:

$$\Phi_n(P_1, \beta_1) = \exp\left(\frac{-\beta_1 P_1'^2}{4m}\right)\phi_n(p_1'),$$

$$\Phi_n(P_2, \beta_2) = \exp\left(-\frac{\beta_2 P_2'^2}{4m}\right)\phi_n(p_2'). \tag{4·1}$$

We write (2·15) as

$$\Phi_n(P_2, \beta_2) = \lambda_n^{-1}\int g(P_2, \beta_2; P_1, \beta_1)\Phi_n(P_1, \beta_1)\, d^3P_1. \tag{2·15}$$

Substitution of $g(P_2, \beta_2; P_1, \beta_1)$ from (3·5) and integration over P_1' gives:

$$\Phi_n(P_2, \beta_2) = \lambda_n^{-1}\frac{me^2}{2\pi^2\hbar}\exp\left(\frac{-\beta_2 P_2'^2}{4m}\right)$$

$$\times\int\left\langle\left[\exp\left\{\frac{-(\beta_2-\beta_1)p_1'^2}{m}\right\}-\exp\left\{\frac{-(\beta_2-\beta_1)p_2'^2}{m}\right\}\right]\Big/\{(\boldsymbol{p}_2'-\boldsymbol{p}_1')^2+\xi^2\hbar^2\}(p_2'^2-p_1'^2)\right\rangle$$

$$\times\phi_n(p_1')d^3p_1'.$$

Thus

$$\phi_n(p_2')=\lambda_n'\int\frac{[\exp(-a\boldsymbol{p}_1'^2)-\exp(-a\boldsymbol{p}_2'^2)]}{\{(\boldsymbol{p}_2'-\boldsymbol{p}_1')^2+\xi^2\hbar^2\}(\boldsymbol{p}_2'^2-\boldsymbol{p}_1'^2)}\phi_n(p_1')d^3p_1', \tag{4·2}$$

where

$$a=(\beta_2-\beta_1)/m\,, \qquad \lambda_n'=\lambda_n^{-1}\frac{me^2}{2\pi^2\hbar}. \tag{4·3}$$

For the convenience of notation let

$$\boldsymbol{x}\equiv\boldsymbol{p}_2', \qquad \boldsymbol{t}\equiv\boldsymbol{p}_1'.$$

Then (4·2) becomes

$$\phi_n(\boldsymbol{x})=\lambda_n'\int k(\boldsymbol{x},\boldsymbol{t})\phi_n(\boldsymbol{t})d\boldsymbol{t}\,, \tag{4·4}$$

where

$$k(\boldsymbol{x},\boldsymbol{t})=\frac{\exp(-a\boldsymbol{t}^2)-\exp(-a\boldsymbol{x}^2)}{\{(\boldsymbol{x}-\boldsymbol{t})^2+\xi^2\hbar^2\}(\boldsymbol{x}^2-\boldsymbol{t}^2)}. \tag{4·5}$$

$k(\boldsymbol{x},\boldsymbol{t})$ is a symmetric kernel of the homogeneous equation (4·4). We can use Hilbert-Schmidt theory to solve it. The Fredholm determinant $D(\lambda')$ is defined as[5)]

$$D(\lambda')=1+\sum_{n=1}^{\infty}(-1)^n\frac{\lambda'^n}{n!}A_n\,,$$

where

$$A_n=\int\cdots\int\begin{vmatrix}k(t_1,t_1)\cdots k(t_1,t_n)\\ \cdots\cdots\cdots\cdots\cdots\cdots\\ \cdots\cdots\cdots\cdots\cdots\cdots\\ k(t_n,t_1)\cdots k(t_n,t_n)\end{vmatrix}dt_1\cdots dt_n. \qquad (n>0)$$

Thus

$$D(\lambda')=1-\lambda'\int k(t,t)dt+\frac{\lambda'^2}{2!}\int\int\begin{vmatrix}k(t_1,t_1) & k(t_1,t_2)\\ k(t_2,t_1) & k(t_2,t_2)\end{vmatrix}dt_1dt_2\cdots. \tag{4·6}$$

Let λ_0' be a value of λ' for which $D(\lambda_0')=0$. It is known in the Fredholm's theory of homogeneous integral equations that if $D(\lambda_0')=0$ and $D(x,y_0;\lambda_0')\not\equiv0$, then for a proper choice of y_0, $u(x)=D(x,y_0;\lambda_0')$ is a continuous solution of

$$u(x) = \lambda_0' \int_a^b k(x,t)\,u(t)\,dt,$$

and $u(x) \not\equiv 0$, where $D(x, y_0; \lambda_0')$ is Fredholm's first minor and is defined in (4·8).

From (4·5) we have

$$\int k(\boldsymbol{t}, \boldsymbol{t})\,d^3t = \pi a \int_0^{p_F} dt \exp(-at^2) \log\left(1 + \frac{4t^2}{\xi^2\hbar^2}\right)$$

$$\simeq \frac{4\pi}{3} \frac{a}{\xi^2\hbar^2} p_F^3,$$

where p_F is the cutoff momentum. Using the above theorem and Eq. (4·3) we have

$$\lambda_0 = \frac{2e^2}{3\pi\hbar} (\beta_2 - \beta_1) \frac{p_F^3}{\xi^2\hbar^2}. \tag{4·7}$$

Fredholm's first minor is defined as

$$D(x, y; \lambda') = \lambda' k(x, y) + \sum_{n=1}^{\infty} (-1)^n \frac{\lambda'^{n+1}}{n!} B_n(x, y),$$

where

$$B_n(x, y) = \int \cdots \int \begin{vmatrix} k(x, y) & k(x, t_1) \cdots k(x, t_n) \\ k(t_1, y) & k(t_1, t_1) \cdots k(t_1, t_n) \\ \cdots\cdots\cdots & \cdots\cdots\cdots \quad \cdots\cdots\cdots \\ k(t_n, y) & k(t_n, t_1) \quad k(t_n, t_n) \end{vmatrix} dt_1 \cdots dt_n. \tag{4·8}$$

Thus the above theorem gives

$$\begin{aligned} \phi_n(x) &= D(x, y_0; \lambda_0'), \\ &= \lambda_0' k(x, y_0) - \lambda_0'^2 \int \begin{vmatrix} k(x, y_0) & k(x, t) \\ k(t, y_0) & k(t, t) \end{vmatrix} dt + \cdots, \\ &\simeq \lambda_0' k(x, y_0). \end{aligned} \tag{4·9}$$

The electrons in the plasma are capable of displaying both collective and independent particle behavior, with the Debye length functioning as an indicator of the kind of behavior which might be anticipated.[6] For phenomena involving distances greater than the Debye length, the system behaves collectively and is best characterized by a set of harmonic oscillators representing the plasma oscillations. For phenomena involving distances less than the Debye length, the electron gas is best described as a collection of independent electrons interacting rather weakly via a screened Coulomb force. High electron density and strong interaction favor the collective behavior whereas high temperature opposes it. Let p_D denote the momentum for which we begin to get an effective transition from collective to individual particle behavior then at high temperature

$$p_D < p < p_F ,$$

or if we use a screened potential

$$0 < p < p_F .$$

The cutoff momentum p_F is determined by

$$\frac{v}{(2\pi\hbar)^3}\int_0^{p_F} d^3p = N ,$$

or

$$p_F = \hbar(6\pi^2\rho)^{1/3}, \tag{4·10}$$

where $N/v = \rho$, the electron density.

§ 5. Calculation of $k(P_2, \beta_2; P_1, \beta_1)$

In this section we wish to simplify further Eq. (2·18), viz.

$$k(P_2, \beta_2; P_1, \beta_1) = k_0(P_2, \beta_2; P_1, \beta_1) - \sum_n \frac{\lambda_n}{1+\lambda_n}\Phi_n(P_2, \beta_2)\Phi_n^*(P_1, \beta_1). \tag{2·18}$$

From (4·1) and (4·9) we get an orthonormal set of wave functions

$$\Phi_n(P_2, \beta_2) = \exp\left(\frac{-\beta_2 P_2'^2}{4m}\right)\lambda_0' k(p_2', y_0),$$

$$\Phi_n(P_1, \beta_1) = \exp\left(\frac{-\beta_1 P_1'^2}{4m}\right)\lambda_0' k(p_1', y_0). \tag{5·1}$$

Substituting (5·1) in (2·18) and using (2·4) we obtain

$$\begin{aligned} k(P_2, \beta_2; P_1, \beta_1) &= k_0(P_2, \beta_2; P_1, \beta_1) - \sum_n \frac{\lambda_n}{1+\lambda_n}\exp\left(\frac{-\beta_2 P_2'^2}{4m}\right) \\ &\quad \times \lambda_0' k(p_2', y_0)\exp\left(\frac{\beta_1 P_1'^2}{4m}\right)\lambda_0' k^*(p_1', y_0)\,\delta_{P_1'P_2'} \\ &= k_0(P_2, \beta_2; P_1, \beta_1) - \exp\left\{\frac{-(\beta_2-\beta_1)P_1'^2}{4m}\right\}\delta(P_2'-P_1') \\ &\quad \times \sum_n \frac{(2\pi\hbar)^3}{v}\frac{\lambda_n}{1+\lambda_n}\lambda_0'^2 k(p_2', y_0)k(y_0, p_1'). \end{aligned} \tag{5·2}$$

Dropping the primes, and separation of the center of gravity and relative momenta contributions yield respectively

$$k_0(P_2, \beta_2; P_1, \beta_1) = \delta(P_2 - P_1)\exp\left\{\frac{-(\beta_2-\beta_1)}{4m}P_1^2\right\} \tag{5·3}$$

and

$$k(p_2, \beta_2; p_1, \beta_1) = \frac{(2\pi\hbar)^3}{v} \sum_n \frac{\lambda_n}{1+\lambda_n} \lambda_0'^2 k(p_2, y_0) k(y_0, p_1). \tag{5·4}$$

Fourier transforms of (5·4) and $u(q)$ are

$$k(r_2, \beta_2; r_1, \beta_1) = \frac{1}{(2\pi\hbar)^3} \int\int d^3p_1 d^3p_2 \exp\{-i(p_2 \cdot r_2 - p_1 \cdot r_1)\hbar^{-1}\} k(p_2\beta_2; p_1, \beta_1) \tag{5·5}$$

and

$$u(r_2 - r_1) = \int u(q) \exp\{-iq \cdot (r_2 - r_1)\hbar^{-1}\} d^3q. \tag{5·6}$$

We shall use (5·5) and (5·6) to obtain a propagator for the ring diagrams.

§ 6. The Debye-Hückel equation of state

In this section we shall apply our formalism to the study of equation of state of an assembly of charged particles in the regions of high temperatures and low densities. This subject is of interest in physical chemistry regarding the properties of solutions of strong electrolytes, astrophysics and plasma physics. The first correct theoretical calculation of the correction due to interactions between charged particles to the classical perfect gas law, which must hold in the limit of very low densities, was made by Debye who derived the well-known formula

$$\frac{P}{kT} = \rho\left[1 - \frac{1}{3}\pi^{1/2}(e^2\beta\rho^{1/3})^{3/2}\right]. \tag{6·1}$$

The thermodynamic properties of an electron gas are functions of the five independent parameters; the electron mass m, the charge e, the density ρ, $\hbar$ and $\beta = 1/kT$. The only dimensionless parameter which can be constructed from these for a classical gas ($\hbar \to 0$) is $e^2\beta\rho^{1/3}$. Then since as $e \to 0$ the perfect gas law $P/kT = \rho$ must remain true, the correction must be contained in the form

$$\frac{P}{kT} = \rho[1 - f(e^2\beta\rho^{1/3})], \tag{6·2}$$

where f is some function such that $\lim_{e \to 0} f = 0$. Now

$$\sum_n \to \lim_{v \to \infty} \frac{v}{(2\pi\hbar)^3} \int d^3y_0. \tag{6·3}$$

Substitution of (6·3) in (5·4) gives

$$k(p_2, \beta_2; p_1, \beta_1) = \frac{\lambda_0}{1+\lambda_0} \lambda_0'^2 \int k(p_2, y_0) k(y_0, p_1) d^3y_0$$

$$= \frac{\lambda_0}{1+\lambda_0} \lambda_0'^2 k_2(p_2, p_1). \tag{6·4}$$

Combining (5·5) and (6·4) we obtain

$$k(r_2, \beta_2; r_1, \beta_1) = \frac{1}{(2\pi\hbar)^3} \int\int d^3p_1 d^3p_2 \exp\{-i(p_2\cdot r_2 - p_1\cdot r_1)\hbar^{-1}\} \frac{\lambda_0}{1+\lambda_0} \lambda_0'^2 k_2(p_2, p_1). \tag{6·5}$$

Equation (6·5) along with (5·6) gives

$$\begin{aligned} k(r_2, r_1; \beta_2-\beta_1)\, u(r_2-r_1) &= \frac{1}{(2\pi\hbar)^3} \int\int d^3p_1 d^3p_2 \exp\{-i(p_2\cdot r_2 - p_1\cdot r_1)\hbar^{-1}\} \\ &\quad \times \frac{\lambda_0}{1+\lambda_0} \lambda_0'^2 k_2(p_2, p_1)\, u(q_1) \exp\{-iq_1\cdot(r_2-r_1)\hbar^{-1}\} d^3q_1, \\ &= \frac{1}{(2\pi\hbar)^3} \frac{\lambda_0}{1+\lambda_0} \lambda_0'^2 \int d^3p_1 d^3p_2 d^3q_1 k_2(p_2, p_1)\, u(q_1) \\ &\quad \times \exp[-i\{(p_2+q_1)\cdot r_2 - (p_1+q_1)\cdot r_1\}\hbar^{-1}]. \end{aligned} \tag{6·6}$$

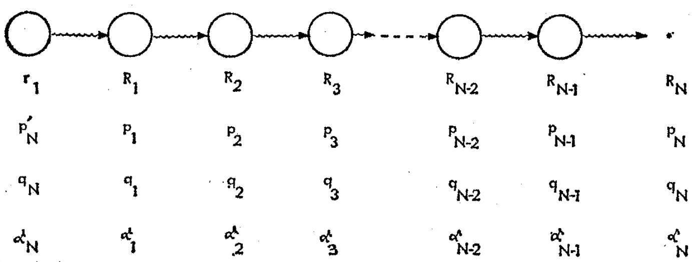

Fig. 3. The open-ended ring cluster which is formed by combining many 1-torons.

Chain integral for Fig. 3 is obtained by iterating (6·6)

$$\begin{aligned} k_N(r_1, R_N; \beta) &= \int_0^\beta \int \prod_{m=1}^{N-1} \{k(R_{m+1}, R_m; \alpha_m)\, u(R_{m+1}-R_m)\} \\ &\quad \times k(R_1, r_1; \alpha_N)\, u(R_1-r_1)\, dR_1 \cdots dR_{N-1} d\alpha_1 \cdots d\alpha_N \\ &= \int_0^\beta \left\{\frac{1}{(2\pi\hbar)^3} \frac{\lambda_0}{1+\lambda_0} \lambda_0'^2\right\}^N \int \cdots \int \end{aligned}$$

$$\times d^3p_1 d^3p_2 d^3q_1 k_2(p_1, p_2)\, u(q_1) \exp[-i\{(p_2+q_1)\cdot R_2 - (p_1+q_1)\cdot R_1\}\hbar^{-1}] d^3R_1 d\alpha_1$$

$$\times d^3p_2 d^3p_3 d^3q_2 k_2(p_2, p_3)\, u(q_2) \exp[-i\{(p_3+q_2)\cdot R_3 - (p_2+q_2)\cdot R_2\}\hbar^{-1}] d^3R_2 d\alpha_2$$

$$\times d^3p_3 d^3p_4 d^3q_3 k_2(p_3, p_4)\, u(q_3) \exp[-i\{(p_4+q_3)\cdot R_4 - (p_3+q_3)\cdot R_3\}\hbar^{-1}] d^3R_3 d\alpha_3$$

....

$$\begin{aligned} &\times d^3p_{N-2} d^3p_{N-1} d^3q_{N-2} k_2(p_{N-2}, p_{N-1})\, u(q_{N-2}) \exp[-i\{(p_{N-1}+q_{N-2})\cdot R_{N-1} \\ &\qquad - (p_{N-2}+q_{N-2})\cdot R_{N-2}\}\hbar^{-1}] d^3R_{N-2} d\alpha_{N-2} \\ &\times d^3p_{N-1} d^3p_N d^3q_{N-1} k_2(p_{N-1}, p_N)\, u(q_{N-1}) \exp[-i\{(p_N+q_{N-1})\cdot R_N \\ &\qquad - (p_{N-1}+q_{N-1})\cdot R_{N-1}\}\hbar^{-1}] d^3R_{N-1} d\alpha_{N-1} \\ &\times d^3p_N' d^3p_1 d^3q_N k_2(p_N', p_1)\, u(q_N) \exp[-i\{(p_1+q_N)\cdot R_1 - (p_N'+q_N)\cdot r_1\}\hbar^{-1}] d\alpha_N. \end{aligned} \tag{6·7}$$

Introducing $\delta_{p_N' p_N} = \{(2\pi\hbar)^3/v\}\delta(p_N' - p_N)$ in (6·7) one obtains

$$k_N(r_1, R_N; \beta) = \int_0^\beta \left\{\frac{1}{(2\pi\hbar)^3}\left(\frac{\lambda_0}{1+\lambda_0}\right)\lambda_0'^2\right\}^N \int \cdots \int d^3R_1 \cdots d^3R_{N-1} d\alpha_1 \cdots d\alpha_N$$
$$\times d^3q_1 \cdots d^3q_N d^6p_1 \cdots d^6p_N u(q_1) \cdots u(q_N) k_2(p_1, p_2) k_2(p_2, p_3)$$
$$\times k_2(p_3, p_4) \cdots k_2(p_{N-1}, p_N) k_2(p_N', p_1) \exp[-i\{((p_N + q_{N-1}) \cdot R_N$$
$$-(p_N' + q_N) \cdot r_1) + (q_N - q_1) \cdot R_1 + (q_1 - q_2) \cdot R_2 + \cdots$$
$$+ (q_{N-2} - q_{N-1}) \cdot R_{N-1}\}\hbar^{-1}] \frac{(2\pi\hbar)^3}{v} \delta(p_N' - p_N). \tag{6·8}$$

R integration yields

$$\delta(q_N - q_1)\delta(q_1 - q_2) \cdots \delta(q_{N-2} - q_{N-1}) \exp[-i\{(p_N + q_{N-1}) \cdot R_N - (p_N + q_N) \cdot r_1\}\hbar^{-1}]$$

so that

$$q_1 = q_2 = \cdots = q_N \equiv q .$$

Also

$$\alpha_1 = \alpha_2 = \cdots \alpha_N \equiv \alpha .$$

We close the chain by putting $r_1 = R_N$ and integrating over R_N, obtaining

$$\int k_N(R_N, \beta) dR_N = \int_0^\beta \left\{\frac{\lambda_0}{1+\lambda_0}\lambda_0'^2\right\}^N d^N\alpha \int d^3q \{u(q)\}^N d^6p_1 \cdots d^6p_N \delta(p_N' - p_N)$$
$$\times k_2(p_1, p_2) k_2(p_2, p_3) \cdots k_2(p_{N-1}, p_N) k_2(p_N, p_1). \tag{6·9}$$

Now

$$\int k_2(p_1, p_2) k_2(p_2, p_3) \cdots k_2(p_N, p_1) d^3p_2 \cdots d^3p_N = k_{2N}(p_1, p_1).$$

Also

$$\lambda_0'^{2N} \int k_{2N}(p_1, p_1) d^3p_1 = 1 .$$

Equation (6·9) reduces to

$$\int k_N(R_N, \beta) dR_N = \left(\frac{3}{4\pi p_F^3}\right) \int \left[\frac{4\pi}{3} p_F^3 \int_0^\beta \left(\frac{\lambda_0}{1+\lambda_0}\right) d\alpha u(q)\right]^N d^3q. \tag{6·10}$$

In computing the contribution of a particular ring integral to the $\log Z_G$ where Z_G is the grand partition function, we must assign the appropriate statistical weight to that ring.[1] In this case the weight factor is $(1/N!)\{(N-1)!/2\cdot 2\} \times (-1)^N z^N$ where z is the fugacity. The contribution of ring integrals to $\log Z_G$ is then (using Eq. (6·10) with the appropriate weight)

$$\left(\frac{3}{4\pi p_F^3}\right) \int \sum_{N=2}^\infty \frac{(-1)^N}{4N} \left\{\frac{4\pi}{3} p_F^3 \int_0^\beta \left(\frac{\lambda_0}{1+\lambda_0}\right) d\alpha z u(q)\right\}^N d^3q. \tag{6·11}$$

The summation starts at $N=2$ because the integral which corresponds to the emission and absorption of a single quantum by a single toron vanishes.

Contribution of (5·3) to $\log Z_G$ is

$$\int \delta(P_2-P_1)\exp\left\{-N(\beta_2-\beta_1)\frac{P_1^2}{4m}\right\}d^3P_1$$

$$=\frac{V}{(2\pi\hbar)^3}\int \exp\left\{-N\frac{(\beta_2-\beta_1)P_1^2}{4m}\right\}\delta_{P_2P_1}d^3P_1$$

$$=\frac{v}{(2\pi\hbar)^3}\left(\frac{4\pi m}{\beta}\right)^{3/2}. \tag{6·12}$$

Using (6·11), (6·12) and adding the result to the perfect gas contribution ($\log Z_G^{(0)}$) we find the ring integral approximation to the equation of state:

$$\frac{Pv}{kT}=\log Z_G=\log Z_G^{(0)}+\frac{v}{(2\pi\hbar)^3}\left(\frac{4\pi m}{\beta}\right)^{3/2}\left(\frac{3}{4\pi p_F^3}\right)$$

$$\times\int\sum_{N=2}^{\infty}\frac{(-1)^N}{4N}\left\{\frac{4\pi}{3}p_F^3\int_0^\beta\left(\frac{\lambda_0}{1+\lambda_0}\right)d\alpha z u(q)\right\}^N d^3q,$$

$$=\log Z_G^{(0)}+\frac{v}{(2\pi\hbar)^3}\left(\frac{4\pi m}{\beta}\right)^{3/2}\left(\frac{3}{4\pi p_F^3}\right)\frac{1}{4}\int[Q-\log(1+Q)]d^3q, \tag{6·13}$$

where

$$Q=\frac{4\pi}{3}p_F^3u(q)z\frac{\beta}{2}. \tag{6·14}$$

Now we substitute

$$\log Z_G^{(0)}=\frac{zv}{(2\pi\hbar)^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}, \tag{6·15}$$

$$u(q)=\frac{e^2}{2\pi^2\hbar q^2}, \tag{6·16}$$

$$p_F=\left(\frac{2m\log z}{\beta}\right)^{1/2}, \tag{6·17}$$

and notice that q integral is of the form

$$\int_0^\infty\{sz-q^2\log(1+szq^{-2})\}dq=\frac{\pi}{3}(sz)^{3/2}. \tag{6·18}$$

Substitution of (6·14) ~ (6·18) into (6·13) and expansion of $\log z$ in terms of z yield

$$\frac{Pv}{kT}=\frac{zv}{(2\pi\hbar)^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}+\frac{2\pi v}{(2\pi\hbar)^3}\frac{\pi}{3}z^{3/2}\left\{\frac{e^2}{\hbar}(2/\pi)^{1/2}\left(\frac{m}{\beta}\right)^{3/2}\beta\right\}^{3/2}. \tag{6·19}$$

The fugacity z is related to the density ρ through

$$\rho=\frac{z}{v}\frac{\partial}{\partial z}\log Z_G$$

$$=\frac{z}{(2\pi\hbar)^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}+\frac{2\pi}{(2\pi\hbar)^3}\frac{3}{2}\frac{\pi}{3}z^{3/2}\left\{\left(\frac{2}{\pi}\right)^{1/2}\frac{e^2}{\hbar}\left(\frac{m}{\beta}\right)^{3/2}\beta\right\}^{3/2}. \tag{6·20}$$

The appropriate value of z in the limit $e\rightarrow 0$ is

$$z_0=(2\pi\hbar)^3\left(\frac{\beta}{2\pi m}\right)^{3/2}\rho\,. \tag{6·21}$$

When ρ is small but finite we substitute $z=z_0+\delta z$ in (6·20) and obtain

$$\delta z=-\frac{\pi^2}{(2\pi\hbar)^3}\frac{z_0^{5/2}}{\rho}\left\{(2/\pi)^{1/2}\frac{e^2}{\hbar}\left(\frac{m}{\beta}\right)^{3/2}\beta\right\}^{3/2}. \tag{6·22}$$

Thus

$$z=(2\pi\hbar)^3\left(\frac{\beta}{2\pi m}\right)^{3/2}\rho\{1-e^3\beta^{3/2}\rho^{1/2}\pi^{1/2}+O(\rho)\}. \tag{6·23}$$

Substituting (6·23) in (6·19) we obtain the Debye-Hückel equation of state

$$\frac{P}{kT}=\rho\left\{1-\frac{1}{3}\pi^{1/2}e^3\beta^{3/2}\rho^{1/2}\right\}. \tag{6·24}$$

Higher order correction to the Debye-Hückel formula (6·24) has been calculated by Abe by using the giant cluster expansion theory,[7] and quantum and relativistic corrections have been investigated by Ninham[8] by using the electron gas theory by Montroll and Ward.[1]

§ 7. Concluding remarks

A mathematical technique is introduced to sum the iteration series which occurs in the electron gas theory by Montroll and Ward. As a result summation over ring diagrams becomes easier to perform than the case of Montroll and Ward. The binary kernel of Lee and Yang is expressed as a sum of kernels which are solutions of integral equations obtained by iteration. This formalism provides a method to calculate the binary kernel. The grand partition function is calculated by solving the integral equation, and its application is made to calculate the Debye-Hückel equation of state.

The formulation presented here can be generalized to fermions and bosons. Higher order diagrams can be taken into consideration. Its application to calculate the correlation energy and the specific heat of an electron gas is in progress.

The operator $\exp(-\beta H)$ plays a decisive role in equilibrium statistical mechanics while $\exp(itH/\hbar)$ is the operator from which dynamics can be developed.

That is, the real part of the complex variable $\beta + it\hbar^{-1}$ is associated with thermodynamics and the imaginary part with dynamics while both the real and imaginary parts find their place in the statistical mechanics of nonequilibrium processes. Most of the theories dealing with nonequilibrium processes start with Liouville equation which contains too much dynamical part through the Hamiltonian.[9] Perhaps by adjusting statistical and dynamical parts, as is possible in the above formulation, one might get better results. Work in this direction is under consideration.

Acknowledgment

The author wishes to thank Professor A. Isihara for advice and discussions. The financial support of the National Research Council is gratefully acknowledged.

References

1) E. W. Montroll and J. C. Ward, Phys. Fluids **1** (1958), 55.
2) E. W. Montroll, *La Théorie des Gaz Neutres et Ionisés* (Les Houches, 1959), P. 17.
3) L. Colin, J. Math. Phys. **1** (1960), 87.
4) T. D. Lee and C. N. Yang, Phys. Rev. **13** (1959), 1165.
5) W. V. Lovitt, *Linear Integral Equations* (Dover Publications Inc., New York, 1950), p. 23.
6) D. Pines, *Solid State Physics,* F. Seitz and D. Turnbull Eds. (Academic Press, New York), Vol. 1 (1955), p. 376.
7) R. Abe, Prog. Theor. Phys. **22** (1959), 213.
8) B. Ninham, Thesis (1962), University of Maryland.
9) T. Y. Wu, *Kinetic Theory of Gases and Plasmas* (Addition-Wesley Publishing Company, Reading, Massachusetts, 1966), p. 8.