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Some Exact Results in the Theory of Fluids*

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Lectures given at the NATO Summer School in Cargese, Corsica, June 1964. (Notes taken by Drs. S. Nielsen and E. Praestgaard.)

* Supported by the Air Force Office of Scientific Research under Grant 508-64.

I. THE GRAND PARTITION FUNCTION AND DISTRIBUTION FUNCTIONS OF A NON-UNIFORM SYSTEM

Our starting point is the grand canonical ensemble formulation of the description of a classical system of particles in equilibrium with a particle and heat reservoir. The ensemble is characterized by a temperature T and a chemical potential μ or fugacity z, where $z = (2\pi m / \beta h^2)^{3/2} e^{\beta\mu}$ and $\beta = 1/kT$. The Hamiltonian of the system with N particles is given by

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{1\le i<j\le N}\sum \varphi(r_{ij}) + \sum_{i=1}^{N} U(r_i) \qquad (1)$$

All the properties of this ensemble are determined by the probability of finding a system of the ensemble containing exactly N particles whose positions and momenta are in a specified 6N-dimensional volume element $d\underline{r}^N\, d\underline{p}^N$ about $\underline{r}^N$, $\underline{p}^N$. This is given by

$$W_N(\underline{r}^N, \underline{p}^N, T, z)\, d\underline{r}^N\, d\underline{p}^N = W(N,T,z)\ \frac{e^{-\beta H_N}\, d\underline{r}^N\, d\underline{p}^N}{\int e^{-\beta H_N}\, d\underline{r}^N\, d\underline{p}^N} \qquad (2)$$

It will be recognized that the second term is just the canonical distribution function for N particles and W(N,T,z) is the probability of having N particles in the system.

$$W(N,T,z) = \frac{e^{\beta\mu N}\, \frac{1}{\lambda^{3N} N!} \int e^{-\beta H_N}\, d\underline{r}^N\, d\underline{p}^N}{\Xi} \qquad (3)$$

$$= \frac{\frac{1}{N!} \int e_N(\underline{r}^N)\, [\prod_{i=1}^{N} e^{\gamma(\underline{r}_i)}]\, d\underline{r}^N}{\Xi\,[\gamma]}$$

where $e_N(\underline{r}^N) = e^{-\beta \sum_{i<j\le N} \varphi(r_{ij})}$

$$\gamma(\underline{r}_i) = \beta\mu + \tfrac{3}{2} \ln [2\pi m / \beta h^2] - \beta U(\underline{r}_i) = \ln z - \beta \mathcal{U}(\underline{r}_i)$$

The grand partition function Ξ is seen to be the normalization constant determined through $\sum_{N=o}^{\infty} W(N,T,z) = 1$. Considered as a functional of γ, $\Xi[\gamma]$ is given by

$$\Xi[\gamma] = \sum_{N=o}^{\infty} \frac{1}{N!} \int e_N(\underline{r}^N) \left[\prod_{i=1}^{N} e^{\gamma(\underline{r}_i)}\right] d\underline{r}^N \tag{4}$$

where $e^{\gamma(\underline{r})} = z\, e^{-\beta U(\underline{r})}$

In a uniform system, $U(\underline{r}) = o$, $\lim_{\Omega\to\infty} \ln \Xi/\Omega = \beta p$, p being the thermodynamic pressure. We shall always imagine in the following that our system is confined to a volume Ω on a periodic torus so that when the external potential is turned off, i.e. $U(\underline{r}) = o$, the system becomes translationally invariant. Actually since we shall be interested exclusively in macroscopically large systems and more particularly in the thermodynamic limit of $\Omega \to \infty$ the exact nature of the boundary conditions is unimportant and we shall generally ignore them.

We shall now consider the distribution functions of our system confining our attention to their configurational part since the momentum part will be simply a product of Maxwellians. Considering functions of the form

$$F_s^N(\underline{y}^N) = \sum_{i_1<i_2\ldots i_s\leq N} F_s(\underline{y}_{i1}, \underline{y}_{i2}, \ldots, \underline{y}_{is}) \tag{5}$$

we define their grand canonical ensembles average

$$\langle F_s^N(\underline{y}^N)\rangle_{G.C.} \equiv \sum_{N=o}^{\infty} W(N,T,z) \frac{\int F_s^N e^{-\beta H_N} d\underline{r}^N d\underline{p}^N}{\int e^{-\beta H_N} d\underline{r}^N d\underline{p}^N} \tag{6}$$

We now define the canonical distribution functions $N_s(\underline{y}^s, N)$ and the grand canonical distribution functions $N_s(\underline{y}^s, [\gamma])$ through the relations

$$\langle F_s^N(y^N) \rangle_{G.C.} \equiv \sum_{N=o}^{\infty} \frac{W(N,T,z)}{s!} \int N_s(y^s,N)\; F_s(y_1 \ldots y_s)\, dy^s \qquad (7)$$

$$\equiv \frac{1}{s!} \int N_s(y^s, [\gamma])\, F_s(y^s)\, dy^s \qquad (8)$$

$$= \frac{1}{\Xi[\gamma]} \sum_{n=s}^{\infty} \frac{1}{N!} \int F_s^N(y^N)\, e_N(y^N) \left[\prod_{i=1}^{N} e^{\gamma(y_i)}\right] dy^N$$

The first two equalities define the canonical and grand canonical distribution functions through the requirement that they hold identically for all functions of the form (5). The last equality follows from the definition of the probability distribution. As an example let us consider the function $\sum_{i=1}^{N} \Psi(\underline{r}_i)$, of the type $F_1^N(r)$. Forming the mean value in the grand canonical ensemble we get:

$$\langle \sum_{i=1}^{N} \Psi(\underline{r}_i) \rangle_{G.C.} = \sum_{N=o}^{\infty} W(N,T,z) \frac{\int [\sum_{i=1}^{N} \Psi(\underline{r}_i)]\, e^{-\beta H_N}\, d\underline{r}^N\, d\underline{p}^N}{\int e^{-\beta H_N}\, d\underline{r}^N\, d\underline{p}^N}$$

$$= \sum_{N=o}^{\infty} W(N,T,z) \frac{\int [\sum_{i=1}^{N} \Psi(\underline{r}_i)]\, e^{-\beta [\Sigma\Sigma \varphi(\underline{r}_{ij}) + \Sigma U(\underline{r}_i)]}\, d\underline{r}^N}{\int e^{-\beta [\Sigma\Sigma \varphi(r_{ij}) + \Sigma U(\underline{r}_i)]}\, d\underline{r}^N}$$

$$= \sum_{N=o}^{\infty} W(N,T,z) \int d\underline{r}_1\, \Psi(\underline{r}_1) \left\{ N \frac{\int e^{-\beta[\Sigma\Sigma \varphi + \Sigma U]}\, d\underline{r}_2 \ldots d\underline{r}_N}{\int e^{-\beta[\Sigma\Sigma \varphi + \Sigma U]}\, d\underline{r}_1 \ldots d\underline{r}_N} \right\}$$

Comparison with (7) gives

$$N_1(\underline{r}_1, N) = N \frac{\int e^{-\beta [\Sigma\Sigma \varphi + \Sigma U]}\, d\underline{r}_2 \ldots d\underline{r}_N}{\int e^{-\beta [\Sigma\Sigma \varphi + \Sigma U]}\, d\underline{r}_1 \ldots d\underline{r}_N} \qquad (9)$$

In the same way is obtained

$$N_2(\underline{r}_1, \underline{r}_2 \; N) = N(N-1) \quad \frac{\int e^{-\beta [\, \Sigma\Sigma \varphi + \Sigma U \,]} \, d\underline{r}_3 \ldots d\underline{r}_N}{\int e^{-\beta [\, \Sigma\Sigma \varphi + \Sigma U \,]} \, d\underline{r}_1 \ldots d\underline{r}_N} \tag{10}$$

the momentum part always being maxwellian! We notice further that

$$N_1 (\underline{r}_1 \; N) = \langle \sum_{i=1}^{N} \delta (\underline{r}_1 - \underline{y}_i) \rangle = \frac{\int [\sum_{i=1}^{N} \delta(\underline{r}_1 - \underline{y}_i)] e^{-\beta H_N} \, d\underline{y}^N \, d\underline{p}^N}{\int e^{-\beta H_N} \, d\underline{y}^N \, d\underline{p}^N}$$

For the grand canonical distribution function, we find analogously:

$$N_1(\underline{r}_1; [\gamma]) = \langle \sum_{i=1}^{N} \delta(\underline{r}_1 - \underline{y}_i) \rangle_{G.C.}$$

$$N_2(\underline{r}_1, \underline{r}_2; [\gamma] = \langle \sum\sum_{i \neq j \leq N} \delta(\underline{r}_1 - \underline{y}_j) \, \delta(\underline{r}_2 - \underline{y}_i) \rangle_{G.C.} \tag{11}$$

$$N_s(\underline{r}_1 \ldots \underline{r}_s; [\gamma] = \langle \Sigma \ldots \Sigma_{i_1 \neq i_2 \ldots \neq i_s \leq N} \delta(\underline{r}_1 - \underline{y}_{i1}) \ldots \delta(\underline{r}_s - \underline{y}_{is}) \rangle_{G.C.}$$

and using (8) we get the explicit expression

$$N_s(\underline{r}^s; [\gamma]) = 1/\Xi[\gamma] \, [\prod_{i=1}^{s} e^{\gamma(\underline{r}_i)}] \sum_{N=0}^{\infty} (1/N!) \int e_{N+s} (\underline{r}_1^s \underline{y}^N) [\prod_{i=1}^{N} e^{\gamma(\underline{y}_i)}] d\underline{y}^N \tag{12}$$

For an ideal gas $\varphi(r_{ij}) = 0$, $e_{N+s} = 1$, and hence

$$N_1(\underline{r}_1; [\gamma]) = e^{\gamma(r_1)} = z e^{-\beta U(\underline{r}_1)}$$

In general we find

$$\int N_1(\underline{r}_1; [\gamma] d\underline{r}_1 = \langle N \rangle_{G.C.} = \sum_{N=0}^{\infty} W(N,T,z) \; N$$

$$\int N_2(\underline{r}_1, \underline{r}_2; [\gamma] d\underline{r}_1 d\underline{r}_2 = \langle N(N-1) \rangle_{G.C.} = \sum_{N=0}^{\infty} W(N,T,z) N(N-1)$$

In a uniform system, $n_1(\underline{r})$ is independent of $\underline{r}$, $n_1 = \langle N \rangle / \Omega$ and $n_2(\underline{r}_1, \underline{r}_2) = n_2(\underline{r}_1 - \underline{r}_2)$.

II. Definition of Functional Derivatives.

Let Ψ be a functional of $w(\underline{r})$, $\Psi[\omega]$, i.e. Ψ depends on the value of $\omega(\underline{r})$ at each point $\underline{r}$ in space. Ψ could be a constant such as the grand partition function which depends on $\gamma(\underline{r})$ or it could be a space dependent function such as $N_s(\underline{r}^s;[\gamma])$.

Consider now the changes in $\Psi[\omega]$ as $\omega(\underline{r})$ is changed from some initial value $\omega_0(\underline{r})$ to its final value of $\omega(r)$. Physically this may correspond to changes in Ξ or $N_s(\underline{r}^s)$ as the external potential is changed. Let us represent the changes in $\omega(\underline{r})$ by a parameter α

$$\omega(\underline{r},\alpha) = \omega_0(\underline{r}) + \alpha[\omega(\underline{r}) - \omega_0(\underline{r})] = \omega_0(\underline{r}) + \alpha\,\Delta\,\omega(\underline{r}) \tag{13}$$

$\Psi[\omega]$ may now be considered to be simply a function of $\alpha, \Psi(\alpha)$, which may be expanded in a simple Taylor series in α,

$$\Psi(\alpha = 1) = \sum_{j=0}^{\ell} (1/j!)\, d^j\Psi(\alpha)/d\alpha^j\big|_{\alpha=0} + (1/\ell!)\int_0^1 (1-\alpha)^{\ell}\, d^{(\ell+1)}\Psi\,\alpha/d\alpha^{(e+1)}\, d\alpha \tag{14}$$

Now defining functional derivatives for arbitrary changes in ω by the series expansion

$$\begin{aligned}
\Psi[\omega_0 + \Delta\,\omega] &= \Psi[\omega_0] + \int \delta\,\Psi[\omega]/\delta\omega(\underline{r}_1)\big|_0\,\Delta\,\omega(\underline{r}_1)d\underline{r}_1 \\
&+ \tfrac{1}{2}!\iint \delta^2\Psi[\omega]/\delta\omega(\underline{r}_1)\delta\omega(\underline{r}_2)\big|_0\,\Delta\,\omega(\underline{r}_1)\,\Delta\,\omega(\underline{r}_2)d\underline{r}_1\,d\underline{r}_2 \qquad (15) \\
&+ \quad \cdots \\
&\vdots \\
&+ (1/\ell!)\int_0^1 d\alpha(1-\alpha)^{\ell}\int\cdots\int \delta^{\ell+1}\Psi[\omega]/\delta\omega(\underline{r}_1,\alpha)\ldots\delta\omega(\underline{r}_{\ell+1},\alpha)\quad \Delta\,\omega(\underline{r}_1)\ldots\Delta\,\omega(\underline{r}_{\ell+1}) \\
&\qquad d\underline{r}_1\ldots d\underline{r}_{\ell+1}
\end{aligned}$$

and identifying the terms in the two series (14) and (15), we find

$$\int \delta \Psi[\omega]/\delta\omega(\underline{r}_1)\Big|_{\substack{0\\ \downarrow \\ \omega=\omega_0}} \Delta\omega(\underline{r}_1)d\underline{r}_1 = d\Psi(\alpha)/d\alpha\Big|_{\alpha=0} \quad \text{etc.} \tag{16}$$

In particular, setting $\Delta\omega(\underline{r}) = \delta(\underline{r}-\underline{x})$ where $\underline{x}$ is some specified point we have,

$$\omega(\underline{r}) = \omega_0(\underline{r}) + \alpha\delta(\underline{r}-\underline{x})$$

$$\delta\Psi[\omega]/\delta\omega(\underline{x})\Big|_{\omega=\omega_0} = d/d\alpha\ \Psi[\omega_0(\underline{r}) + \alpha\delta(\underline{r}-\underline{x})]\Big|_{\alpha=0}$$

$$\delta^2\Psi[\omega]/\delta\omega(\underline{y})\delta\omega(\underline{x})\Big|_{\omega=\omega_0} = d/d\alpha\ \frac{\delta\psi(\omega_0(r) + \alpha\delta(r-y)]}{\delta\omega(x)}\Big|_{a=0}$$

Example:

$$\Psi = \int\omega^2(\underline{r})d\underline{r} = \int[\omega_0(\underline{r}) + \alpha\,\Delta\omega(\underline{r})]^2 d\underline{r}$$

$$d\Psi/d\alpha\Big|_{\alpha=0} = \int 2\omega_0(\underline{r})\ \Delta\omega(\underline{r})d\underline{r}$$

so that

$$\delta\Psi[\omega]/\delta\omega(\underline{x}) = 2\omega\ (\underline{x})$$

Getting back to the grand partition function:

$$\Xi[\gamma] = \sum_{N=0}^{\infty} 1/N!\int e_N(\underline{r}^N)\prod_{i=1}^{N} e^{\gamma(\underline{r}_i)}d\underline{r}^N$$

we see that

$$1/\Xi[\gamma]\ \delta\Xi[\gamma]/\delta\gamma(\underline{r}_1) = 1/\Xi[\gamma]d/d\alpha\ \{\sum_{N=0}^{\infty}(1/N!)\int e_N(\underline{y}^N)[\prod_{i=1}^{N} e^{\gamma(\underline{y}_i)+\alpha\delta(\underline{r}_1-\underline{y}_i)}]d\underline{y}^N\}_{\alpha=0}$$

$$= \langle\sum_{i=1}^{N}\delta(\underline{r}_1-\underline{y}_i)\rangle_{G.C.} = \sum_{N=0}^{\infty} W(N,T,Z)\langle\sum_{i=1}^{N}\delta(\underline{r}_1-\underline{y}_i)\rangle_C \tag{17}$$

Hence,

$$\delta\ln\Xi[\gamma]/\delta\gamma(\underline{r}_1) = N_1(\underline{r}_1;[\gamma]$$

The last equality follows from the fact that according to our definition functional derivatives obey the same chain rules of differentiation as ordinary derivatives

$$\delta/\delta\omega(x)\ f(\Psi[\omega]) = df/d\Psi\ \ \delta\Psi[\omega]/\delta\omega(x)$$

We could go on in this way to get the higher variational derivatives of $\ln \Xi\,[\gamma]$ or $\Xi\,[\gamma]$ but we shall circumvent this by using the method of generating functions.

III. Functional Derivative Expressions for the Correlation Functions

In equations (11) we defined grand canonical distribution functions of s distinct particles. It is often of value to introduce as well the distributions $\hat{N}_s$ in which the arguments are allowed to refer to identical particles

$$\hat{N}_s(\underline{r}^s;[\gamma]) = \langle \sum_{i_1=1}^{N} \sum_{i_2=1}^{N} \cdots \sum_{i_3=1}^{N} \delta(\underline{r}_i - \underline{y}_{i_1}) \cdots \delta(\underline{r}_s - \underline{y}_{i_s}) \rangle_{G.C.} \qquad (18)$$

and the following relationships are easily derived

$$\hat{N}_1(\underline{r}_1;[\gamma]) = N_1(\underline{r}_1;[\gamma])$$

$$\hat{N}_2(\underline{r}_1,\underline{r}_2;[\gamma]) = N_2(\underline{r}_1,\underline{r}_2;[\gamma]) + N_1(\underline{r}_1;[\gamma])\,\delta(\underline{r}_1-\underline{r}_2) \qquad (19)$$

$$\begin{aligned}\hat{N}_3(\underline{r}_1,\underline{r}_2,\underline{r}_3;[\gamma]) = N_3(\underline{r}_1,\underline{r}_2,\underline{r}_3;[\gamma]) &+ N_2(\underline{r}_1,\underline{r}_2;[\gamma])\delta(\underline{r}_2-\underline{r}_3)\\ &+ N_2(\underline{r}_1,\underline{r}_3;[\gamma])\delta(\underline{r}_1-\underline{r}_2)\\ &+ N_2(\underline{r}_2,\underline{r}_3;[\gamma])\delta(\underline{r}_3-\underline{r}_1)\\ &+ N_1(\underline{r}_1,[\gamma])\delta(\underline{r}_1-\underline{r}_2)\delta(\underline{r}_1-\underline{r}_3)\end{aligned}$$

etc.

Both sequences of distributions possess generating functions. If $\lambda(\underline{y})$ is a suitably well-behaved test function, then according to (18) and (4)

$$\int \hat{N}_s(\underline{y}^s;[\gamma]) \prod_{i=1}^{s} \lambda(\underline{y}_i) d\underline{y}^s$$

$$= (1/\Xi[\gamma]) \sum_{N=0}^{\infty} (1/N!) \int e_N(\underline{r}^N) \, [\prod_{i=1}^{N} e^{\gamma(\underline{r}_i)}] \; (\sum_{i=1}^{N} \lambda(\underline{r}_i))^s d\underline{r}^N \tag{20}$$

or

$$\sum_{s=0}^{\infty} (1/s!) \int \hat{N}_s(\underline{y}^s,[\gamma]) \prod_{i=1}^{s} \lambda(\underline{y}_i) d\underline{y}^s$$

$$= (1/\Xi[\gamma]) \sum_{N=0}^{\infty} (1/N!) \int e_N(\underline{r}^N) [\prod_{i=1}^{N} e^{\gamma(\underline{r}_i)}] \, e^{\sum_{i=1}^{N} \lambda(\underline{r}_i)} d\underline{r}^N$$

$$= (1/\Xi[\gamma]) \sum_{N=0}^{\infty} (1/N!) \int e_N(\underline{r}^N) \; [\prod_{i=1}^{N} e^{\gamma(\underline{r}_i) + \lambda(\underline{r}_i)}] d\underline{r}^N \tag{21}$$

$$= \Xi[\gamma + \lambda]/\Xi[\gamma]$$

Comparison with (15) shows that (21) is itself a functional power series in λ, λ corresponding to $\Delta\omega$ and γ to ω_0. By direct comparison we obtain

$$\hat{N}_s(\underline{y}^s;[\gamma]) = (1/\Xi[\gamma]) \;\; \delta^s\Xi[\gamma]/\delta\gamma(\underline{y}_1)\ldots\delta\gamma(\underline{y}_s) \tag{22}$$

On the other hand, using a test function defined by $\Delta e^{\gamma(\underline{y})} \equiv e^{\Delta\gamma(\underline{y})} - 1$ and applying equation (8) we can write

$$1/s! \int N_s(\underline{y}^s;[\gamma]) \prod_{i=1}^{s} \Delta e^{\gamma(\underline{y}_i)} d\underline{y}^s$$

$$= \Xi[\gamma]^{-1} \sum_{N=s}^{\infty} (1/N!) \int \sum_{i_1 \neq i_2 \ldots \neq i_s \leq N} \!\!\ldots\!\! \sum (\Delta e^{\gamma(\underline{r}_{i_1})} \ldots \Delta e^{\gamma(\underline{r}_{i_s})}) \times e_N(\underline{r}^N) \prod_{i=1}^{N} e^{\gamma(\underline{r}_i)} d\underline{r}^N \tag{23}$$

Summing over s on both sides and interchanging the two summations on the right hand side we get

$$\sum_{s=0}^{\infty} (1/s!) \int N_s(\underline{y}^s;[\gamma] \prod_{i=1}^{s} \Delta e^{\gamma(\underline{y}_i)} \; d\underline{y}^s$$

$$= (1/\Xi[\gamma]) \sum_{N=0}^{\infty} (1/N!) \int e_N(\underline{r}^N)[\prod_{i=1}^{N} e^{\gamma(\underline{r}_i)}] \{\sum_{s=0}^{N} \sum_{i_1 \neq \dots i_s} (\Delta e^{\gamma(\underline{r}_{i_1})} \dots \Delta e^{\gamma(\underline{r}_{i_s})}\} d\underline{r}^N$$

$$= (1/\Xi[\gamma]) \sum_{N=0}^{\infty} (1/N!) \int e_N(\underline{r}^N)[\prod_{i=1}^{N} e^{\gamma(\underline{r}_i)}][\prod_{i=1}^{N} (1+ \Delta e^{\gamma(\underline{r}_i)})] d\underline{r}^N$$

$$= (1/\Xi[\gamma]) \sum_{N=0}^{\infty} (1/N!) \int e_N(\underline{r}^N)[\prod_{i=1}^{N} e^{\gamma(\underline{r}_i) + \Delta \gamma(\underline{r}_i)}] d\underline{r}^N \qquad (24)$$

$$= \Xi[\gamma + \Delta \gamma]/\Xi[\gamma]$$

We may write equation (24) in the form

$$\sum_{s=0}^{\infty} (1/s!) \int N_s(\underline{y}^s;[\gamma]) / [\prod_{i=1}^{s} e^{\gamma(\underline{y}_i)}] \prod_{i=1}^{s} e^{\gamma(\underline{y}_i)} \Delta e^{\gamma(\underline{y}_i)} d\underline{y}^s =$$

$$\Xi[e^{\gamma} + e^{\gamma} \Delta e^{\gamma}]/\Xi[e^{\gamma}] \qquad (25)$$

and according to the definition equation (15) we can now express N_s as a functional derivative

$$N_s(\underline{y}^s;[\gamma]) = (1/\Xi[\gamma]) \prod_{i=1}^{s} e^{\gamma(\underline{y}_i)} \, \delta^s \Xi[\gamma]/\delta e^{\gamma(\underline{y}_1)} \dots \delta e^{\gamma(\underline{y}_s)} \qquad (26)$$

Finally, we may similarly consider the Ursell distributions F_s and $\hat{F}_s$ associated with N_s and $\hat{N}_s$. Indeed, they are most simply defined by relating their generating function. We define using the above notation

$$\sum_{1}^{\infty} (1/s!) \int \hat{F}_s(\underline{y}^s;[\gamma]) \prod_{1}^{s} \lambda(\underline{y}_i) d\underline{y}^s = \ln(\Xi[\gamma+\lambda]/\Xi[\gamma]) \qquad (27)$$

$$\sum_{1}^{\infty} (1/s!) \int F_s(\underline{y}^s;[\gamma]) \prod_{1}^{s} \Delta e^{\gamma(\underline{y}_i)} d\underline{y}^s = \ln(\Xi[\gamma+ \Delta\gamma]/\Xi[\gamma]) \qquad (28)$$

By expansion we find the relations

$$F_1(\underline{y}) = N_1(\underline{y})$$

$$F_2(\underline{y}_1,\underline{y}_2) = N_2(\underline{y}_1,\underline{y}_2) - N_1(\underline{y}_1)N_1(\underline{y}_2) \qquad (29)$$

$$F_3(\underline{y}_1,\underline{y}_2,\underline{y}_3) = N_3(\underline{y}_1,\underline{y}_2,\underline{y}_3) - N_2(\underline{y}_1,\underline{y}_2)N_1(\underline{y}_3) - N_2(\underline{y}_2,\underline{y}_3)N_1(\underline{y}_1) -$$

$$N_2(\underline{y}_3,\underline{y}_1)N_1(\underline{y}_2) + 2N_1(\underline{y}_1)N_1(\underline{y}_2)N_1(\underline{y}_3)$$

and precisely the same relations hold between the $\hat{F}_s$ and $\hat{N}_s$. The definitions through generating functions, equations (27) and (28), now give

$$\hat{F}_s(\underline{y}^s;[\gamma]) = \delta^s \ln \Xi[\gamma]/\delta\gamma(\underline{y}_1)\ldots\delta\gamma(\underline{y}_s) \tag{30}$$

$$F_s(\underline{y}^s;[\gamma]) = \prod_1^s e^{\gamma(\underline{y}_i)}\ \delta^s \ln\ \Xi[\gamma]/\delta e^{\gamma(\underline{y}_i)}\ldots\delta e^{\gamma(\underline{y}_s)} \tag{31}$$

The characteristic property of the Ursell distributions is that they vanish whenever their arguments decompose into two or more independent sets. This is expected to happen in a <u>one-phase system</u> whenever the arguments are not all close together; e.g. $F_2(\underline{r}_1,\underline{r}_2), \sim 0$ whenever $|\underline{r}_1-\underline{r}_2| > \ell$, where ℓ is some correlation length roughly of the same magnitude, (in classical fluids), as the range of the intermolecular potential.

IV. Basic Integral Equations.

If one holds s particles fixed, the k-particle distribution becomes a conditional (k + s)-particle distribution

$$N_{k+s}(\underline{x}^k,\underline{y}^s;[\gamma])/N_s(\underline{y}^s;[\gamma]) \tag{32}$$

In a classical grand ensemble, particles may be fixed by placing their force fields at fixed points. Thus the higher-order distributions are related to lower-order distributions with external potentials. We can write equation (12)

$$N_s(\underline{y}^s;[\gamma]) = \Xi[\gamma]^{-1} \prod_{i=1}^s e^{\gamma(\underline{y}_i)}$$

$$\sum_{N=0}^{\infty} (1/N!) \int e_N(\underline{r}^N) \prod_{i=1}^N e^{\gamma(\underline{r}_i)}\ e_{N+s}(\underline{r}^N,\underline{y}^s)/e_N(\underline{r}^N)\quad d\underline{r}^N$$

and noticing that for two-body forces

$$e_{N+s}(\underline{r}^N,\underline{y}^s)/e_N(\underline{r}^N) = e_s(\underline{y}^s)\ \exp(-\beta\ \Sigma\ \varphi(\underline{r}_i,\underline{y}_j))$$

$$N_s(\underline{y}^s;\ [\gamma]) = e_s(\underline{y}^s) \prod_1^s e^{\gamma(\underline{y}_i)}\quad \Xi[\gamma-\beta \sum_{j=1}^s \varphi_{\underline{y}_j}\quad]/\Xi[\gamma] \tag{33}$$

where $\varphi_{\underline{y}}(\underline{r}) = \varphi(\underline{r}-\underline{y})$.

Comparison with equation (26) now yields the functional differential equation

$$\delta^s \Xi[\gamma]/\delta e^{\gamma(\underline{y}_1)} \ldots \delta e^{\gamma(\underline{y}_s)} = e_s(\underline{y}^s)\ \Xi\ [\gamma - \beta \sum_{j=1}^{s} \varphi_{\underline{y}_j}] \tag{34}$$

When differentiated k times with respect to $e^{\gamma(\underline{x}_1)}$ the equation (34) may be written as

$$N_{k+s}(\underline{x}^k, \underline{y}^s; [\gamma]) / N_s(\underline{y}^s; [\gamma]) = N_k(\underline{x}^k; [\gamma - \beta \sum_{j=1}^{s} \varphi_{\underline{y}_j}]) \tag{35}$$

giving the intuitively understandable expression for the conditional distribution as mentioned above.

We wish to relate distributions of different orders for the same system. This may be accomplished by using equation (35) and eliminating the external potential. To this end the external potential is turned on by means of a parameter α and the resulting expressions are expanded in a series of the form of equation (15). We set

$$\begin{aligned} e^{\gamma(\underline{r}|0)} &= z \\ e^{\gamma(\underline{r}|\alpha)} &\equiv z\ \{1 + \alpha(e^{-\beta \sum_{i=1}^{s} \varphi(\underline{y}_i, \underline{r})} - 1)\} \\ &\equiv z\ \{1 + \alpha\ f(\underline{y}^s, \underline{r})\} \\ e^{\gamma(r|1)} &\equiv z\ e^{-\beta \sum_{1}^{s} \varphi(\underline{y}_i, \underline{r})} \end{aligned} \tag{36}$$

$f(\underline{y}^s, \underline{r})$ being a generalized Mayer f function. The turning on parameter is α. For $\alpha = 0$ the system is uniform, while for $\alpha = 1$ the full interaction case, there is an external potential acting on the system corresponding to keeping s particles fixed. We want to follow the corresponding transition of a function $G_{k,s}(\alpha)$,

$$G_{k,s}(\underline{x}^k, \underline{y}^s|\alpha) \equiv \delta^k \Xi[\alpha] / \delta e^{\gamma(x_1|\alpha)} \ldots \delta e^{\gamma(x_k|\alpha)} \tag{37}$$

$$= \Xi(\alpha)\ [\prod_{i=1}^{k} e^{-\gamma(x_i|\alpha)}]\ N_k(\underline{x}^k|\alpha) \tag{38}$$

$\Xi\,(\alpha)$ means $\Xi[\gamma(|\alpha)]$, etc.

We notice that

$$G_{k,s}(\underline{x}^k,\underline{y}^s|0) = \Xi(0)\; z^{-k}\; N_k(\underline{x}_k|0) \tag{39}$$

where $N_k(\underline{x}^k|0)$ is the uniform k-body distribution $N_k(\underline{x}^k)$ and using equations (35) and (33)

$$G_{k,s}(\underline{x}^k,\underline{y}^s|1) = \Xi(0)\; N_{k+s}(\underline{x}^k,\underline{y}^s)e_k(\underline{x}^k)/z^{k+s}e_{k+s}(\underline{x}^k,\underline{y}^s) \tag{40}$$

A functional Taylor expansion about G(0) now yields,

$$\begin{aligned} G_{k,s}(1) = \sum_{j=0}^{\ell}(1/j!)\int \delta^j G_{k,s}(\alpha)/\delta e^{\gamma(\underline{r}_1)}\ldots\delta e^{\gamma(\underline{r}_j)}\Big|_{\alpha=0} \\ \prod_{i=1}^{j}[z\; f(\underline{y}^s;\underline{r}_i)] \quad e_{k+j}(\underline{x}^k,\underline{y}^s,\underline{r}^j)\; d\underline{r}^j \\ + \int_0^1\int (1-\alpha)^{\ell}/\ell!\quad \delta^{\ell+1}G_{k,s}(\alpha)/\delta\ell^{\gamma(\underline{r}_1|\alpha)}\ldots\delta\ell^{\gamma(\underline{r}_{\ell+1}|\alpha)}\ldots\delta\ell^{\gamma(\underline{r}_{\ell+1}|\alpha)} \end{aligned} \tag{41}$$

Employing the definition of $G_{k,s}(\alpha)$ for $\alpha = 1$, equation (40), and the relation

$$\delta^j G_{k,s}(\underline{x}^k,\underline{y}^s|\alpha)/\delta e^{\gamma(\underline{r}_1|\alpha)}\ldots\delta e^{\gamma(\underline{r}_j|\alpha)} = G_{k+j,s}(\underline{x}^k\underline{r}^j,\underline{y}^s|\alpha) \tag{42}$$

we finally can write

$$N_{k+s}(\underline{x}^k\underline{y}^s)\; e_k(\underline{x}^k)/z^s\; e_{k+s}(\underline{x}^k\underline{y}^s) = N_{k,s}^{(\ell)} + R_{k,s}^{(\ell)} \tag{43}$$

$$N_{k,s}^{(\ell)} = \sum_{j=0}^{\ell}(1/j!)\int N_{k+j}(\underline{x}^k\underline{r}^j)\prod_{i=1}^{j} f(\underline{y}^s;\underline{r}_i)\; d\underline{r}^j$$

$$R_{k,s}^{(\ell)} = z^{\ell+1}\int_0^1 (1-\alpha)^{\ell}/\ell!\quad \Xi(\alpha)/\Xi(0)\prod_{i=1}^{k} e^{-\gamma(\underline{x}_i|\alpha)}$$

$$\Big\{\int\prod_{i=1}^{\ell+1}[f(\underline{y}^s;\underline{r}_i)e^{-\gamma(\underline{r}_i|\alpha)}]\,N_{k+\ell+1}(\underline{x}^k\underline{r}_{\ell+1}|\alpha)\; d\underline{r}^{\ell+1}\Big\}\; d\alpha$$

If this series would converge, so that the remainder term vanishes for $\ell\to\infty$, then for any choise of $k \geq 0$ we shall get a set of recursive equations for the distributions in the system without external potential as s is varied. Similarly for any choise of $s \geq 1$ we obtain a set of equations for different k's. In particular the choice $k = 0$ recovers the Mayer-Montroll equations, while $s = 1$ gives the Kirkwood-Salsburg equations.

5. Upper and Lower Bounds on the Distributions.

Using the series expansion (43) we are now able to obtain rigorous inequalities satisfied by the distribution functions for all values of the fugacity z. Considering positive potentials, first studied by Lieb, we find using the definitions of f given in equation (36)

$$\varphi\,(r_{ij}) \geq 0 \Rightarrow \; -1 \leq f(\underline{y}^s;\underline{r}) \leq 0 \tag{44}$$

so that the remainder term $F^{(\ell)}_{k,s}$ of equation (43) will be alternately positive and negative according to the sign of $(-1)^{\ell+1}$.

$$F^{(\ell)}_{k,s} \Rightarrow \begin{cases} \leq 0, & \text{for even } \ell \\ \geq 0, & \text{for odd } \ell \,, \end{cases} \tag{45}$$

and we have at once the result

$$\frac{N_{k+s}\,(\underline{x}^k\underline{y}^s)\; e_k(\underline{x}^k)}{z^s\;\epsilon_{k+s}(x^k y^s)} \begin{matrix} \geq \\ \\ \leq \end{matrix} \Big\}\; N^{(\ell)}_{k,s}\;(\underline{x}^k\underline{y}^s) \text{ for } \begin{cases} \ell \text{ odd} \\ \ell \text{ even} \end{cases} \tag{46}$$

Eventually we may have a steady decrease in the interval hemmed in by successive bounds, if the series converges as $\ell \to \infty$, but rigorous bounds under all circumstances.

We generate explicitely the Kirkwood-Salsburg set of integral equations, that is we put $s = 1$, in (43), (47)

$$\frac{N_{k+1}\;(x^k,\underline{y})\; e_k\,(\underline{x}^k)}{z\; e_{k+1}\;(\underline{x}^k\underline{y})} = \sum_{j=0}^{\ell} \frac{1}{j!} \int N_{k+j}(\underline{x}^k\underline{r}^j) \prod_{i=1}^{j} f(\underline{y},\underline{r}_i)d\underline{r}^j + R^{(\ell)}_{k,1}$$

where $f(\underline{y},\underline{r})$ is the ordinary Yvon-Mayer f-function. Writing out the equation for $k = 0$ we find, keeping series terms up to $\ell = 2$,

$$\frac{N_1(y)}{z} = 1 + \int N_1(\underline{r})\, f(\underline{y}-\underline{r})\, d\underline{r} + 1/2 \int N_2\, (\underline{r}_1 \underline{r}_2) f(\underline{y}-\underline{r}_1)\, f(\underline{y}-\underline{r}_2) d\underline{r}_1 d\underline{r}_2 + R^{(2)}_{0,1} \qquad (48)$$

From the inequalities (46) valid for non-negative potentials we obtain using a uniform system notation $N_1(\underline{y}) = \rho$, $k = 0$, $\ell = 0,1,2\ldots$,

$$\frac{\rho}{z} \leq 1$$

$$\frac{\rho}{z} \geq 1 + \rho \int f(r)\, d\underline{r} \qquad (49)$$

$$\frac{\rho}{z} \leq 1 + \rho \int f(\underline{r})\, d\underline{r} + 1/2 \int N_2\, (\underline{r}_1 \underline{r}_2) f(\underline{y}-\underline{r}_1) f(y-r_2) d\underline{r}_1 d\underline{r}_2$$

etc.

Using the following set $k = 1$ we can express the higher order distribution function N_2 in an inequality involving N_1 and we get to lowest order

$$\frac{N_2(\underline{x},\underline{y})}{z\, e_2(\underline{X},y)} \leq \rho$$

$$N_2\, (\underline{X},\underline{y}) \leq \rho\, z\, e^{-\beta \varphi (\underline{x}-\underline{y})} \qquad (50)$$

Substituting (50) into the last inequality (49) we get an inequality involving the ρ's only

$$\rho \leq z + \rho \left\{ z \int f(\underline{r}) d\underline{r} + z^2\, 1/2!\ \ e^{-\beta \phi (r)}\, f(\underline{r}) f(\underline{r}-\underline{y})\, d\underline{y} d\underline{r} \right\} \qquad (51)$$

Carrying on this procedure we obtain a general set of inequalities, Lieb's inequalities,

$$\rho \begin{matrix} \leq \\ \geq \end{matrix} \Big\} z + \rho \sum_{j=1}^{\ell} a_j \begin{cases} \ell \text{ even} \\ \ell \text{ odd} \end{cases} \tag{52}$$

or rearranging

$$\rho \begin{matrix} \leq \\ \geq \end{matrix} \Big\} \; z/1 - \sum_{j=1}^{e} a_j z^j \begin{cases} \ell \text{ even} \\ \ell \text{ odd} \end{cases} \tag{53}$$

and it is important to note that a_j is independent of ℓ. Cf. (Penrose) Continuing this expansion we may compare u with the Mayer-expansion

$$\rho = z/1 - \sum_{j=1}^{\infty} a_j z^j = \sum_{\ell=1}^{\infty} \ell \, b_\ell \, z^\ell \tag{54}$$

and using a formular of Gradstein and Riezkic (Collection of Formulas, Four Continent Publishing Co., N.Y. 1962) we can express the a_j's in terms of the cluster integrals b_j. The result is

$$a_j = (-1)^{j+1} \begin{vmatrix} 2b_2 & 1 & 0 & 0 & \cdots & 0 \\ 3b_3 & 2b_2 & 1 & 0 & \cdots & 0 \\ 4b_4 & 3b_3 & 2b_2 & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ (j+1)b_{j+1} & jb_j & (j-1)b_{j-1} & \cdots & \cdots & 2b_2 \end{vmatrix} \tag{55}$$

The method developed above may be applied to obtain directly the fugacity expansion, with or without remainder, of the Ursell function, $F_s(\underline{r}^s,[\gamma])$, equation (31). A "turning-on process" which takes $e^{\gamma}(\underline{y}|\alpha)$ from initial value 0 to final value z, that is $e^{\gamma(\underline{y}|\alpha)} = \alpha e^{\gamma(y)}$ is considered. An expansion of (31) at $\alpha = 1$ about the value at $\alpha = 0$ finally gives

$$F_s(y^s,[\gamma]) = \prod_{i=1}^{s} e^{\gamma(y_i)} \left\{ \sum_{j=0}^{\infty} \frac{1}{j!} \int \prod_{i=1}^{j} e^{\gamma(x_i)}\, U_{s+j}(y^s, x^j)\, dx^j \right\} \tag{56}$$

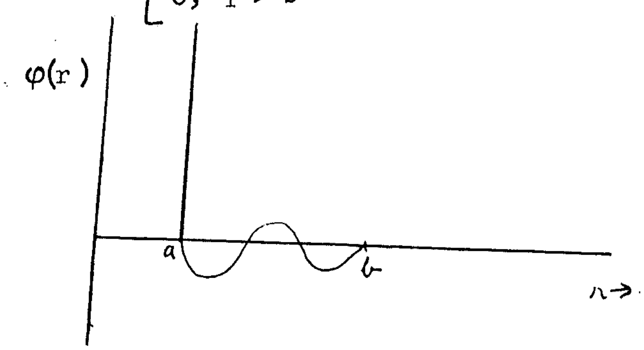
where $U_k(y^k) = \lim_{e^{\gamma(y)} \to 0} \dfrac{F_k(y^k\,[\gamma])}{\prod_{i=1}^{k} e^{\gamma(y_i)}}$; $(-1)^{\ell+1} U_\ell \geq 0$, for $\varphi(r) \geq 0$.

is the sum of all 'connected clusters' with k-vertices. The limit $e^{\gamma(y)} \to 0$ corresponds to the situation in which all the particles are "squeezed" out of the system, i.e. vanishing density. For a uniform system we have of course $e^{\gamma(y)} = z$ and (56) is the usual fugacity expansion.

6. Convergence of the fugacity expansions

Let us first mention the ideas of Yang and Lee on the theory of condensation. They considered a system of particles interacting with a finite range potential having a hard core

$$\varphi(n) = \begin{cases} \infty, & n < a \\ \varphi(r), & b < r < a \\ 0, & r > b \end{cases}$$



Let the system be confined to a volume Ω, and define the pressure $p(z,\Omega)$ as

$$\beta p(z,\Omega) = \frac{\log \Xi(z,\Omega)}{\Omega} \tag{57}$$

The grand partition function $\Xi(\Omega,z)$ defined in (4) will now assume the form,

$$\Xi(z,\Omega) = \sum_{0}^{M(\Omega)} \frac{z^N}{N!} \int_{\Omega} e_N(r^N)\, dr^N . \tag{58}$$

$M(\Omega)$ is the largest number of molecules that can be squeezed into the volume Ω, it is a finite number due to the hard core part of the potential.

The thermodynamic pressure $p(z)$ is given by

$$p(z) = \lim_{\Omega\to\infty} p(z,\Omega) \tag{59}$$

This limit was shown to exist for the above type of potential by Yang and Lee, and a similar proof was first given for the canonical pressure by Van Hove. The proofs have been extended by Ruelle and Fisher to a much more general class of potentials. Instead of the requirements of hard core and finite range it is sufficient to have the condition

$$\sum_{1\le i<j\le s}^{s} \varphi(r_i - r_j) \geq - s\,\Phi, \qquad \Phi \text{ a constant} \tag{60}$$

This condition can be said to imply that the energy is linear in the number of particles. The condition is satisfied for a $\varphi(r)$ that falls off faster than $r^{-(3+\epsilon)}$ for $r \to \infty$ and rises faster than $r^{-(3+\epsilon)}$ as $r \to 0$.

Let us now return to the Yang and Lee theory for potentials with a hard core, where $\Xi\,(Z,\Omega)$ is seen to be a polynomial in z, we can therefore write it in terms of its zeros in the form

$$\Xi\,(\Omega,z) = \sum_{N=1}^{M(\Omega)} (1/N!)\, Q_N(\Omega) z^N = \prod_{\alpha=1}^{M(\Omega)} (1 - z/z_\alpha) \tag{61}$$

The zeros, $z_\alpha(\Omega)$ will be either complex and come in conjugate pairs, or will be negative since the coefficients $_N$ are positive.

If we look on the pressure,

$$\beta\, p(z,\Omega) = \frac{1}{\Omega} \log \Xi\,(z,\Omega) = \frac{1}{\Omega} \sum_{1}^{M} \log\,(1 - z/z_\alpha) \tag{62}$$

we notice that it has singularities at $z = z_\alpha$, so it can have no singularities for real positive values of z, that is for the physically significant values of $z = e^{\beta\mu}$. Thus $p(z,\Omega)$ is an analytical function fo z on the real positive axis and the density $\rho(z,\Omega)$, given by

$$\rho(z,\Omega) = \langle N \rangle/\Omega = z \quad d \log \Xi \ (z,\Omega)/ \ dz \ , \tag{63}$$

is also analytical on the real positive axis, and from the equation

$$z d\rho/dz = \langle (N- \langle N \rangle)^2/\Omega \geq 0 \tag{64}$$

ρ is seen to be a monotonic function of z which is analytic for finite Ω. But a phase transition corresponds to some singularity or discontinuity in the thermodynamic functions, e.g. in a first order phase transition there is a break in the slope of the p-z curve and a discontinuity in the ρ-z curve. We thus conclude that we cannot have a phase transition in a finite system. In the limit $\Omega \to \infty$, the zeros of Ξ, z_α, can approach the real axis as Ξ ceases to be a polynomial in z. If this happens for some z, $z > 0$, there may be a phase transition at that value of the fugacity. We can thus conclude that phase transitions only appear in the thermodynamic limit $\Omega \to \infty$.

Now while the zero's z_α provide all the desired information about the system there is, unfortunately, no general method for obtaining them explicitely. The most useful method for obtaining usable information from the general formulations of statistical mechanics has been the method of series expansion of the pressure and other quantities in powers of the fugacity or the density. We shall now discuss the properties of these series and, in particular, the relation between their radii of convergence and phase transitions. We write,

$$\beta p(z,\Omega) = \frac{\ln \Xi(z,\Omega)}{\Omega} = \sum_{\ell=1}^{\infty} b_{\ell}(\Omega)\, z^{\ell}, \tag{65}$$

The $b_{\ell}(\Omega)$ are the Mayer cluster integrals for a finite volume involving only ℓ particle functions,

$$\begin{aligned} b_1(\Omega) &= 1 \\ b_2(\Omega) &= (1/\Omega)\tfrac{1}{2!} \int_{\Omega}\!\!\int d\underline{r}_1\, d\underline{r}_2\, f(r_{12}), \\ b_{\ell}(\Omega) &= (1/\Omega)(1/\ell!)\int_{\Omega}\!\cdots\!\int U_{\ell}(\underline{r}^{\ell})\, dr^{\ell} \end{aligned} \tag{66}$$

with the $U_{\ell}(\underline{r}^{\ell})$ defined in Eq. (56). Comparison with Eq. (62) also gives, for systems with hard cores,

$$\Omega\, \ell\, b_{\ell}(\Omega) = -\sum_{\alpha=1}^{M} [z_{\alpha}(\Omega)]^{-\ell} \tag{67}$$

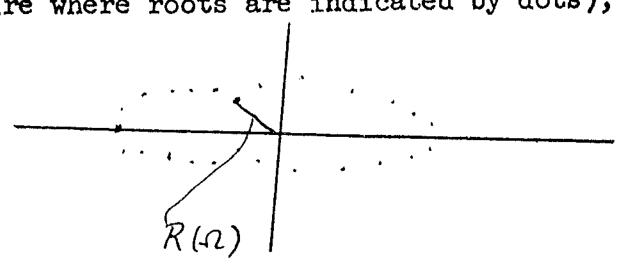
For practical purposes it is more convenient to work with the Mayer series,

$$\beta p^{0}(z) = \sum_{\ell=1}^{\infty} b_{\ell}\, z^{\ell} \tag{68}$$

where

$$b_{\ell} = \lim_{\Omega\to\infty} b_{\ell}(\Omega) = 1/\ell! \int\cdots U_{\ell}(\underline{r}_1,\ldots \underline{r}_{\ell})\, d\underline{r}_2 \ldots d\underline{r}_{\ell} \tag{69}$$

We shall now discuss the radii of convergence $R(\Omega)$ and R of the series (65) and (68) and the relation between the thermodynamic pressure $p(z)$ and $p^{0}(z)$. $R(\Omega)$ is given by the distance from the origin of the nearest zero, z_{α}, (cf. figure where roots are indicated by dots),



and $R(\infty)$ is the limiting value of this distance. For $|z| < R(\infty)$ the function $\beta p(z) = \lim_{\Omega \to \infty} \sum b_\ell (\Omega) z^\ell$ will be analytic and there will be no phase transition.

It follows from the work of Yang and Lee (for the general class of potentials see Penrose) that for $|z| \leq R(\infty)$ the limit $\Omega \to \infty$ and the sum over ℓ may be interchanged and hence

$$p^0(z) = p(z) \text{ for } |z| < R(\infty) \quad \text{and hence } R \leq R\ (\infty) \tag{70}$$

Ruelle and Penrose have derived lower bounds on $R(\Omega)$. Their result is:

$$R(\Omega) \geq [\ e^{(1+2\bar{\Phi})} \int_\Omega |f(r)|\ d\underline{r}\ ]^{-1}, \tag{71}$$

For non-negative potentials $\varphi(r) \geq 0$, $\Phi = 0$, the bound becomes:

$$R\ (\Omega) \geq\ 1/e.2\ |b_2(\Omega)|, \tag{72}$$

a result first derived by Groeneveld who also showed that for non-negative potentials

$$0 \leq (-1)^{\ell+1}\ b_\ell(\Omega) \leq (-1)^{\ell+1}\ b_\ell, \tag{73}$$

so that the nearest singularity of $p(z,\Omega)$ is on the negative real axis and $R(\Omega) \leq R$. Combining this with the above general relation (70) for the radii of convergence, we arrive at the following result for non-negative potentials:

$$R = R\ (\Omega) \tag{74}$$

Let us illustrate by an example:

Consider a one-dimentional gas of hard rods,

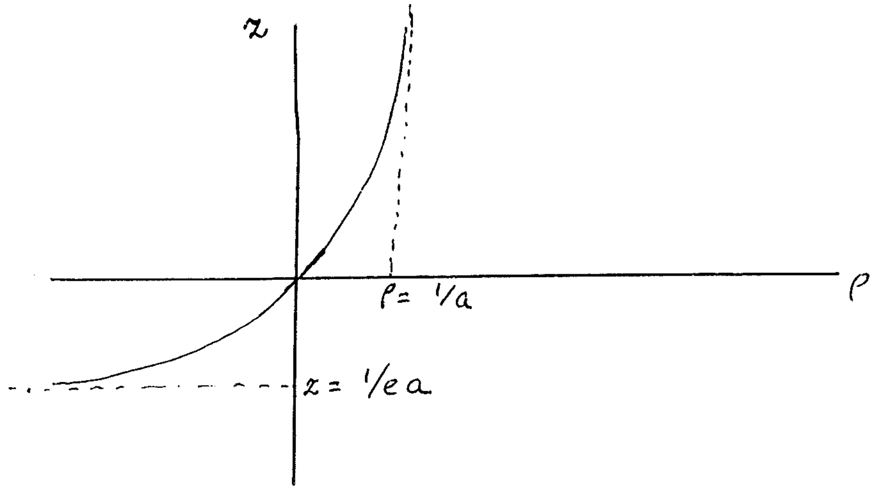
$$\varphi(x) = \begin{cases} \infty, & |x| < a \\ 0, & |x| > a \end{cases}$$

The equation of state in the thermodynamic limit is,

$$\beta p(z) = \rho/1-\rho a \tag{75}$$

and the fugacity is given by:

$$z(\rho) = \rho/1-\rho a \quad \exp(\rho a/1-\rho a) \tag{76}$$



The coefficients in the fugacity expansion can be calculated by means of Lagranges' inversions theorem, the result is:

$$b_\ell = (-a\ell)^{\ell-1}/\ell! \qquad (77)$$

thus the function $\beta p^0(z) = \sum b_\ell z^\ell$ is analytic on the real positive z-axis but has a branch point at $z = -1/ea$ so that $R = R(\infty) = 1/ea$. This example also illustrates the fact that convergence of the fugacity series need not have any relation to phase transitions. The lower bound on R for this potential is from (72) and (74),

$$R \geq 1/2\,ea \qquad (78)$$

Having shown now that $p^0(z)$ converges for $|z| < R(\infty)$ and coincides with $p(z)$ in that domain it is also clear that $p^0(z)$ or its analytic continuation along the positive z-axis (also denoted by $p^0(z)$) will coincide with $p(z)$ for all $z < z'$, where z' is the first singularity of $p(z)$ on the positive real axis. The converse of this is not true however, i.e. if $p^0(z)$ has its first singularity on the positive axis at $z = z''$ it is not possible to conclude that $p(z)$ coincides with $p^0(z)$ for $z < z''$. All we can conclude, from this behaviour of $p^0(z)$ is that z', the first real positive singularity of $p(z)$, is either equal to or less than z'', $z' \leq z''$, i.e. the system must have some kind of a phase transition for the fugacity z in the range,

$$R(\infty) \leq z \leq z''$$

Upper bounds on $R(\Omega)$ were also derived by Penrose using the relation between the coefficients $b_\ell(\Omega)$ and the zeros of $\Xi(z,\Omega)$ given in Eq. (67). This equation yields the inequality,

$$|\Omega \ell\, b_\ell(\Omega)| \leq \sum_{1}^{M} |z_\alpha|^{-1} \leq M(\Omega)/R(\Omega) \tag{79}$$

since $|z_\alpha(\Omega)| \geq R(\Omega)$. Thus,

$$R(\Omega) \leq \left[M(\Omega)/\Omega^{1/\ell} |b_\ell(r)| \right]^{-1/\ell}, \quad \ell = 1,2,\ldots \tag{80}$$

For the hard rod system we get, setting $\ell = 1$,

$$R(\infty) \leq \lim_{\Omega \to \infty} M/\Omega = 1/a, \tag{81}$$

the close packing density.

For non-negative potentials one can derive (Groeneveld) stronger upper bounds. For the hard rod system these yield

$$R(\infty) \leq 1/2|b_2| = 1/2a = e/2\ R(\infty) \tag{82}$$

Let us next outline the method used by Penrose for obtaining the lower bounds on R. He obtains them from bounds on the coefficients in the fugacity expansion for the distribution functions. The s-particle distribution function is: see (12)

$$N_s(r^s|z) = \sum \frac{z^N}{(N-s)!} \int_\Omega e_N(r^N)\, d\underline{r}^{N-s} / \Xi(z,\Omega) \tag{83}$$

By the same reasoning as used before we see that for particles with hard cores and finite Ω, this is the ratio of 2 finite polynomials in z, so that N_s is a rational function; for the more general class of potentials it will be the ratio of two entire functions so that it is a meromorphic function that can be expanded in powers of z.

$$N_s (r^s|z) = \sum_0^\infty N_{s,\ell} (r^s) z^{s+\ell}$$

The radius of convergence will be at least $R(\Omega)$ since Ξ has its smallest zero for $|z| = R(\Omega)$. It can be larger than $R(\Omega)$ due to cancellations of zeros. The coefficients $n_{1;\ell}$ are related to the Mayer coefficients since

$$\int n_1(r|z)\, d\underline{r} = z\, d \log \Xi/dz = \Omega \sum b_\ell (\Omega)\, z^\ell \tag{84}$$

which leads to

$$\Omega\, \ell\, b_\ell (\Omega) = \int_\Omega n_{1,\ \ell-1} (\underline{r})\, d\underline{r} \tag{85}$$

so that bounds on $N_{1,\ell}$ will provide bounds on b_ℓ, that is on $R(\Omega)$. The actual calculations are done by substituting the fugacity expansion into the Kirkwood-Salsburg or the Mayer-Montroll integral equation (cf. comments following Eq. (43)) and equating equal powers of z. This gives recurrence relations for the coefficients $N_{s,\ell}$, and from these relations bounds can be obtained. The result is

$$|N_{1,\ell}(r)| \leq \ell^{2(\ell-1)\beta\Phi} (1+\ell)^{\ell-1} B(\Omega)^\ell/\ell \tag{86}$$

with $B(\Omega)$ given by

$$B(\Omega) = \mathop{Max}_{\underline{r}} \int_\Omega |f(\underline{r}-\underline{r}')|\, dr' \tag{87}$$

This relation leads to

$$|\ell b_\ell (\Omega)| \leq \ell^{2(\ell-2)\beta\Phi} [\ell\ B(\Omega)]^{\ell-1}/\ell\,! \tag{88}$$

The radius of convergence is then obtained as

$$R(\Omega) = \lim_{\ell\to\infty} |b_\ell (\Omega)|^{-1/\ell} \geq 1/B(\Omega)\, [e^{1+2\beta\Phi}]^{-1} \tag{89}$$

7. Convergence of the virial series.

For many purposes it is convenient to work with the virial series, that is expansions of the pressure and distribution function in powers of the density. Lebowitz and Penrose have studied the radius of convergence $\mathcal{R}(\Omega)$ for the virial series,

$$\beta p(p,\Omega) = \rho[1 - \sum (k/k+1) \beta_k(\Omega) \rho^k] \tag{90}$$

where $\rho \equiv \langle N \rangle / \Omega = \rho(z,\Omega)$.

The $\beta_k(\Omega)$ can be expressed in terms of $b_\ell(\Omega)$'s by algebraic relations, such as

$$\beta_1(\Omega) = 2b_2(\Omega), \ \beta_2(\Omega) = 3b_3(\Omega) - 6 \ b_2^2(\Omega),$$

etc., which do not involve Ω explicitely. We may similarly define the $\beta p^0(\rho)$ by the series,

$$\beta p^0(\rho) = \rho[1 - \sum k/k+1 \ \beta_k \ \rho^k], \tag{91}$$

where the β_k,

$$\beta_k = \lim_{\Omega \to \infty} \beta_k(\Omega)$$

are the irreducible cluster integrals. The radius of convergence of (91) will be denoted by $\mathcal{R}$. Using methods of complex variable theory Lebowitz and Penrose showed that,

$$\mathcal{R}(\Omega) \geq c. \ 289/(1+e^{2\beta \Phi}) \ B(\Omega) \tag{92}$$

and

$$\mathcal{R} \geq R(\infty) = \lim_{\Omega \to \infty} R(\Omega)$$

Acknowledgements

I would like to thank Drs. Swenn Eric Nielsen and Eigel Praestgeard who took notes and wrote up a draft of these lectures.

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