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An Approximate Method for Evaluating a Class of Partition Functions

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As a continuation to a previous paper, in §1 a grand partition function is rewritten so as to deal with a system of particles with hard core, in §2 is presented an integral formula expressing the inverse of the volume of the intersection of a sphere and several planes, which formula is employed in §3 to represent the mean value of the weighting factor.

In §3 a partition function with a fixed number of particles is evaluated by applying the method of the previous paper, taking a point representing a probable distribution of particle for the origin of the integration space, and replacing the weighting factor by its average over the intersection of a sphere and two planes, N the number of division of the volume occupied by the system of particles being fixed.

In §4 the limit $N\to\infty$ is taken to reach the final, fairly simple, expression (58). In §5 are described three distributions, a uniform distribution, a crystalline distribution and an interpolation distribution. In §6, the pressure of a system of hard spheres is computed based on three distributions and is shown in Fig. 1.

While the uniform distribution leads to no phase change, the crystalline distribution as well as the interpolation distribution lead to a phase change. The interpolation distribution gives a fairly good result agreeing with the virial expansion and Wainwright-Alder's computations, up to the phase change, diverging from them beyond there. To improve the present method, setting up of a better distribution is proposed in §7.

§1. Reformulation of the partition function

The grand partition function Z of a system consisting of particles interacting through a pair-wise potential $G(\mathbf{r}, \mathbf{r}')$ may be expressed, as in a previous paper[1), by the introduction of variable $x_{\mathbf{r}}$ that describes the number of particles assigned to an infinitesimal cell at the point $\mathbf{r}$,

$$Z=\lim_{N\to\infty}\int \exp\left[-\frac{1}{2}\sum G(\mathbf{r}, \mathbf{r}')x_{\mathbf{r}}x_{\mathbf{r}'}\right]\cdot \prod f(x_{\mathbf{r}})dx_{\mathbf{r}} \tag{1}$$

where the summation $\sum$ extends over all pairs of different $\mathbf{r}$, $\mathbf{r}'$, $f(x)$ being defined by

$$f(x)=\sum_{m=0}^{\infty}\frac{\delta(x-m)}{m\,!}\left(\frac{zV}{N}\right)^m. \tag{2}$$

In the following the interaction potential is assumed to have a repulsive core of infinite strength. The variable $x_{\mathbf{r}}$ will be then limited to take only two values 0 and 1, the possibility of multiple occupation of particles at the point $\mathbf{r}$ being denied, so that the function $f(x)$ is to be

$$f(x)=\delta(x)+\frac{zV}{N}\delta(x-1) \tag{3}$$

instead of (2).

When each of two variables x and x' is limited to take only 0 and 1, one may have an equality

$$\exp(-G(\mathbf{r},\,\mathbf{r}')xx')=1-h_{\mathbf{rr}'}xx' \tag{4}$$

where the $h_{\mathbf{rr}'}$ is a function of only the distance $|\mathbf{r}-\mathbf{r}'|$

$$\begin{aligned} h_{\mathbf{rr}'}&=1-\exp(-G(\mathbf{r},\,\mathbf{r}')) \qquad && \mathbf{r}\neq\mathbf{r}' \\ &=0 && \mathbf{r}=\mathbf{r}'\,. \end{aligned} \tag{5}$$

It is to be noted that the matrix $H=(h_{\mathbf{rr}'})$ has no diagonal elements, so that the eigenvalues of H will be $N\varphi(\mathbf{p})/V-\lim_{r\to 0}h(\mathbf{r})=N\varphi(\mathbf{p})/V-1$, $\varphi(\mathbf{p})$ being defined by

$$\varphi(\mathbf{p})=\frac{V}{N}\sum e^{i\mathbf{p}\cdot\mathbf{r}}h(\mathbf{r})\,. \tag{6}$$

That $\lim h(\mathbf{r})=1$ results from the existence of hard core.

Therefore the partition function Z may be put in the following form

$$Z=\lim_{N\to\infty}\int\prod_{(\mathbf{r},\mathbf{r}')}(1-h_{\mathbf{rr}'}x_{\mathbf{r}}x_{\mathbf{r}'})\cdot\prod_{\mathbf{r}}\left(\delta(x_{\mathbf{r}})+\frac{zV}{N}\delta(x_{\mathbf{r}}-1)\right)dx_{\mathbf{r}} \tag{7}$$

the first product $\prod$ extending over all pairs of different $\mathbf{r}$, $\mathbf{r}'$.

In what follows, the abbreviations

$$W_1=\prod_{(\mathbf{r},\mathbf{r}')}(1-h_{\mathbf{rr}'}x_{\mathbf{r}}x_{\mathbf{r}'}),\quad W_0=\prod_{\mathbf{r}}\left(\delta(x_{\mathbf{r}})+\frac{zV}{N}\delta(x_{\mathbf{r}}-1)\right),\quad dX=\prod_{\mathbf{r}}dx_{\mathbf{r}} \tag{8}$$

will be employed.

The sum of all $x_{\mathbf{r}}$'s represents the total number of particles.

One may decompose the integral into the sum of integrals over parallel planes $\sum x_{\mathbf{r}}=L$, $0\leqq L<\infty$, and rewrite (7)

$$Z=\lim_{N\to\infty}\int_0^{\infty}J(L)dL \tag{9}$$

$$J(L)=\int W_1 W_0 \delta(L-\sum x_{\mathrm{r}})dX\,. \tag{10}$$

In the integral (10), the number of particles is equal to L. It is to be noted that the number density σ is expressed by L/V.

When the total number of particles is given, one may picture a mean distribution of particles. The distribution may be expressed as the mean value of the variable x_{r}. At lower densities a uniform distribution may prevail while a crystalline distribution will be reached at higher densities because of the existence of hard core.

It is an idea to translate the origin of integration space to a point that represents roughly a mean distribution of particles and to carry out the evaluation of (10) around the point.

The translation of the origin from $x_{\mathrm{r}}=0$ to $x_{\mathrm{r}}=c_{\mathrm{r}}$, $\sum c_{\mathrm{r}}$ being equal to L, leads to the change of variables from x_{r} to y_{r} defined by $x_{\mathrm{r}}=c_{\mathrm{r}}+y_{\mathrm{r}}$. One sees then that

$$\begin{aligned} W_1 &= \exp\left[\frac{1}{2}\sum \log\,(1-h_{\mathrm{rr'}}x_{\mathrm{r}}x_{\mathrm{r'}})\right] \\ &= \exp\left[\frac{1}{2}\sum \log\,(1-h_{\mathrm{rr'}}c_{\mathrm{r}}c_{\mathrm{r'}})-\frac{1}{2}\sum h_{\mathrm{rr'}}y_{\mathrm{r}}y_{\mathrm{r'}}-\sum b_{\mathrm{r}}y_{\mathrm{r}}+M\right] \end{aligned} \tag{11}$$

where the b_{r}'s are defined by

$$b_{\mathrm{r}}=\sum_{\mathrm{r'}} h_{\mathrm{rr'}}c_{\mathrm{r'}} \tag{12}$$

M standing for the remainder term.

Therefore the Bolzmann factor W_1 may be regarded roughly as a function of $\sum y_{\mathrm{r}}^2$ and $\sum b_{\mathrm{r}}y_{\mathrm{r}}$ under the restriction $\sum y_{\mathrm{r}}=\sum (x_{\mathrm{r}}-c_{\mathrm{r}})=0$. In turn the mean value of the weighting factor W_0 may be expressed approximately as a function of $\sum y_{\mathrm{r}}^2$ and $\sum b_{\mathrm{r}}y_{\mathrm{r}}$ under the restriction $\sum y_{\mathrm{r}}=0$, along the reasoning in § 1 of the previous paper.

§ 2. An Integral Formula

In the following it is required to evaluate the mean value of a function over the intersection of a sphere and several planes. In this connection it needs to express the inverse of the volume Ω of the intersection.

In a space of dimension N, let the equation to the sphere be

$$R=\sum x_r^2 \tag{13}$$

and the equations to n planes be

$$S_\alpha=\sum_r a_{\alpha r}x_r \qquad \alpha=1,\,2,\,\cdots,\,n\,, \tag{14}$$

the suffix r ranging from 1 to N.

The volume Ω may be easily evaluated as follows

$$\Omega=\int \delta(R-\sum x_r^2)\cdot \Pi\ \delta(S_\alpha-\sum a_{\alpha r}x_r)\cdot \Pi\ dx_r$$

$$=\frac{1}{2(2\pi i)^{n+1}}\int \Pi\ dx_r\left(\int_{\epsilon-i\infty}^{\epsilon+i\infty}\right)^{n+1}\exp\Big[\frac{u}{2}(R-\sum x_r^2)$$

$$+\sum v_\alpha(S_\alpha-\sum a_{\alpha r}x_r)\Big]du\ \Pi\ dv_\alpha\,,\qquad \epsilon>0$$

$$=\frac{1}{2(2\pi i)^{n+1}}\left(\int_{\epsilon-i\infty}^{\epsilon+i\infty}\right)^{n+1}\exp\Big[\frac{1}{2}uR+\sum v_\alpha S_\alpha+\frac{1}{2u}\sum(\sum v_\alpha a_{\alpha r})^2\Big]$$

$$\cdot\left(\frac{2\pi}{u}\right)^{\frac{N}{2}}\Pi\ dv_\alpha\cdot du$$

$$=\frac{(2\pi)^{\frac{N}{2}}}{2(2\pi i)^{n+1}}\int \exp\Big[\frac{u}{2}R+\sum v_\alpha S_\alpha+\frac{1}{2u}\sum b_{\alpha\beta}v_\alpha v_\beta\Big]$$

$$\cdot u^{-\frac{N}{2}}du\ \Pi\ dv_\alpha \tag{15}$$

where

$$b_{\alpha\beta}=\sum_r a_{\alpha r}a_{\beta r}\,. \tag{16}$$

The integration with respect to v gives

$$\Omega=\frac{(2\pi)^{\frac{(N-n)}{2}}}{4\pi i}\frac{1}{\sqrt{\det B}}\int \exp\Big[\frac{u}{2}(R-\sum (B^{-1})_{\alpha\beta}S_\alpha S_\beta)\Big]\cdot u^{-\frac{(N-n)}{2}}du$$

$$=\frac{(2\pi)^{\frac{(N-n)}{2}}}{\sqrt{\det B}}\cdot\frac{1}{2\Gamma((N-n)/2)}\left(\frac{R-\sum (B^{-1})_{\alpha\beta}S_\alpha S_\beta}{2}\right)^{\frac{(N-n-2)}{2}} \tag{17}$$

$$B=(b_{\alpha\beta})\,.$$

Hence one may prove the equality, with the use of real integration variables $u, v_1, \cdots, v_n$,

$$1/\Omega=(2\pi)^{-\frac{N}{2}}(N-n-2)\cdot\det B\cdot\int_0^\infty du\ \prod_\alpha\int_{-\infty}^\infty dv_\alpha$$

$$\cdot\exp\Big[-\frac{u}{2}R-\sum v_\alpha S_\alpha-\frac{1}{2u}\sum b_{\alpha\beta}v_\alpha v_\beta\Big]\cdot u^{\frac{N}{2}-n-2}\,. \tag{18}$$

§ 3. A representation of the mean value of the weighting factor

A representation of the mean weighting factor $\langle W_0\rangle$ as a function of $R=\sum y_r^2$ and $S=\sum b_r y_r$ under the restriction $\sum y_r=0$ may be given by

$$\langle W_0\rangle=\int W_0\delta(R-\sum y_r^2)\delta(S-\sum b_r y_r)\delta(\sum y_r)dY/\Omega \tag{19}$$

$$\Omega=\int \delta(R-\sum y_r^2)\delta(S-\sum b_r y_r)\delta(\sum y_r)dY\,. \tag{20}$$

Reference to the formula (18) in § 2 yields

$$1/\Omega=(2\pi)^{-\frac{N}{2}}C\int_0^\infty du\int_{-\infty}^\infty dv\int_{-\infty}^\infty dw\ u^{-4}$$

$$\cdot\exp\Big[-\frac{1}{2}uR-vS-\frac{1}{2u}(v^2\sum b_r^2+2vw\sum b_r+w^2N)+\frac{N}{2}\log u\Big]$$

$$C=(N-4)(N\sum b_r^2-(\sum b_r)^2)\,. \tag{21}$$

As in § 2, one has

$$\Omega\langle W_0\rangle=\int W_0\delta(R-\sum y_r^2)\delta(S-\sum b_r y_r)\delta(\sum y_r)dY$$

$$=\frac{1}{2(2\pi i)^3}\iiint\exp\Big[\frac{1}{2}rR+sS\Big]\cdot drdsdt\ J_0 \tag{22}$$

where the paths of integration for r, s and t are upward straight lines parallel to the imaginary axis with positive real parts, J_0 standing for

$$J_0=\prod_r\int\exp\Big[-\frac{r}{2}y_r^2-sb_ry_r-ty_r\Big]\cdot\Big(\delta(y_r+c_r)+\frac{zV}{N}\delta(y_r+c_r-1)\Big)dy_r$$

$$=\exp\Big[-\frac{r}{2}\sum c_r^2+s\sum b_rc_r+tL$$

$$+\sum\log\Big\{1+\frac{zV}{N}e^{-t-r/2}\exp(rc_r-sb_r)\Big\}\Big]\,. \tag{23}$$

Replacement of W_0 in (10) by $\langle W_0\rangle$ leads to

$$J^*(L)=\int W_1\langle W_0\rangle\delta(\sum y_r)dY$$

$$=\frac{C}{2(2\pi i)^4}\int\cdots\int\exp\Big[\frac{1}{2}\sum\log(1-h_{rr'}c_rc_{r'})-\frac{1}{2u}(v^2\sum b_r^2 \tag{24}$$

$$+2vw\sum b_r+w^2N)+\frac{N}{2}\log u\Big]\cdot J_0I(M)u^{-4}\,dr\,ds\,dt\,du\,dv\,dw\,dq$$

where the representation of the delta function

$$\delta(\sum y_r)=\frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty}\exp q\sum y_r\cdot dq\,,\qquad \epsilon>0$$

is used and $I(M)$ stands for

$$I(M)=\frac{1}{(2\pi)^{\frac{N}{2}}}\int\exp\Big[-\frac{u-r}{2}\sum y_r^2-\frac{1}{2}\sum h_{rr'}y_ry_{r'}$$

$$-(v-s+1)\sum b_ry_r-q\sum y_r\Big]\cdot e^M dY\,. \tag{25}$$

When M is cancelled in the integral $I(M)$, evaluation of $I(0)$ is immediate to give

$$I(0)=\exp\Big[-\frac{1}{2}\log\det(u-r+H)$$

$$+\frac{1}{2}\sum Q_{\mathbf{rr}'}((v-s+1)b_{\mathbf{r}}+q)((v-s+1)b_{\mathbf{r}'}+q)\Big] \tag{26}$$

where the matrix Q denotes the inverse of the matrix $u-r+H$ or $Q=1/(u-r+H)$.

If an integral obtained by substituting A for e^M in $I(M)$ is divided by $I(0)$ to define $\langle A\rangle$, a weighted mean of A, one sees then that

$$I(M)=I(0)\langle e^M\rangle$$

$$=I(0)\sum_{n=0}^{\infty}\frac{1}{n!}\langle M^n\rangle$$

$$=I(0)\exp\Big[\langle M\rangle+\frac{1}{2!}(\langle M^2\rangle-\langle M\rangle^2)$$

$$+\frac{1}{3!}(\langle M^3\rangle-3\langle M^2\rangle\langle M\rangle+2\langle M\rangle^3)+\cdots\Big] \tag{27}$$

(Cumulant expansion)

Finally one gets

$$J^*(L)=\frac{C}{2(2\pi i)^4}\int\exp U\cdot dr\,ds\,dt\,u^{-4}du\,dv\,dw\,dq \tag{28}$$

$$U=\frac{1}{2}\sum\log(1-h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'})-\frac{1}{2u}(v^2\sum b_{\mathbf{r}}^2+2vw\sum b_{\mathbf{r}}+Nw^2)$$

$$+\frac{N}{2}\log u+\log J_0+\log I(0)+\log\langle e^M\rangle\,. \tag{29}$$

§ 4. The limit $N\to\infty$

It is to be noted that the eigenvalues of the matrix $u-r+H$ must be positive for the integration with respect to $y_{\mathbf{r}}$ to be feasible. Since the eigenvalues of the matrix H, that is, $N\varphi(\mathbf{p})/V-1$, grow proportionally to N, the variable u is expected to grow proportionally to N.

Reverse of the order of the limit $N\to\infty$ and the integration in (9) presents no serious difficulty if the variable u is replaced by $N/V\tau$, τ being a new variable.

Prior to passing to the limit $N\to\infty$, one may regroup terms of U as follows

$$U=U_1+U_2+U_3+U_4 \tag{30}$$

$$U_1=\frac{N}{2}\log u-\frac{1}{2}\log\det(u-r+H) \tag{31}$$

$$U_2=\frac{1}{2}\sum Q_{\mathbf{rr}'}((v-s+1)b_{\mathbf{r}}+q)((v-s+1)b_{\mathbf{r}'}+q)$$

$$-\frac{1}{2u}(v^2\sum b_{\mathbf{r}}^2+2vw\sum b_{\mathbf{r}}+w^2N) \tag{32}$$

$$U_3=\log J_0 \tag{33}$$

$$U_4=\frac{1}{2}\sum\log(1-h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'})+\log\langle\exp M\rangle \tag{34}$$

and perform integrations with respect to w and q. These integrations amount to elimination of variables w and q, and reduce U_2 to

$$U_2'=\frac{1}{2}(v-s+1)^2\sum Q_{\mathbf{rr}'}(b_{\mathbf{r}}-b)(b_{\mathbf{r}'}-b)-\frac{v^2}{2u}\sum(b_{\mathbf{r}}-b)^2 \tag{35}$$

where b denotes the mean value of $b_{\mathbf{r}}$, or

$$b=\sum b_{\mathbf{r}}/N\,. \tag{36}$$

Remembering that the matrix H has eigenvalues $N\varphi(\mathbf{p})/V-h(0)$, one may rewrite U_1

$$U_1=\frac{N}{2}\log\frac{u}{u-r-h(0)}-\frac{1}{2}\sum\log(1+N\varphi(\mathbf{p})/V(u-r-h(0)))\,. \tag{37}$$

In the limit $N\to\infty$, U_1 tends to

$$\frac{1}{2}V\tau(r+h(0))-\frac{V}{2(2\pi)^3}\int\log(1+\tau\varphi(\mathbf{p}))d\mathbf{p}$$

$$=\frac{1}{2}V\tau r+\frac{V}{2(2\pi)^3}\int[\tau\varphi(\mathbf{p})-\log(1+\tau\varphi(\mathbf{p}))]d\mathbf{p} \tag{38}$$

because of the relation

$$\frac{1}{(2\pi)^3}\int\varphi(\mathbf{p})d\mathbf{p}=\lim_{\mathbf{r}\to 0}h(\mathbf{r})=h(0)\,. \tag{39}$$

To proceed further, an assumption is made that the $c_{\mathbf{r}}$'s are finite at a finite number of sites and of order $1/N$ elsewhere. One may then establish the following quantities α, β, γ, μ, ν and $B(s)$

$$\alpha=\lim\sum(b_{\mathbf{r}}-b)^2/uL \tag{40}$$

$$\beta=\lim\sum Q_{\mathbf{rr}'}(b_{\mathbf{r}}-b)(b_{\mathbf{r}'}-b)/L \tag{41}$$

$$\gamma=\lim\sum b_{\mathbf{r}}c_{\mathbf{r}}/L=\lim\sum h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'}/L \tag{42}$$

$$\mu=\lim\sum\log(1-h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'})/L \tag{43}$$

$$\nu=\lim\sum c_{\mathbf{r}}^2/L \tag{44}$$

$$B(s)=\lim\sum\exp(rc_{\mathbf{r}}-sb_{\mathbf{r}})/N=\lim\sum\exp(-sb_{\mathbf{r}})/N$$

$$=\frac{1}{V}\int\exp(-sb_{\mathbf{r}})d\mathbf{r}=\text{mean value of }\exp(-sb_{\mathbf{r}})\,. \tag{45}$$

The U_2' may be reduced then, by elimination of v, to

$$\frac{L}{2}\frac{\alpha\beta}{\alpha-\beta}(s-1)^2=\frac{L}{2}\theta(s-1)^2\,,\qquad \theta=\alpha\beta/(\alpha-\beta)\,. \tag{46}$$

The U_3, which tends, in the limit $N\to\infty$, to

$$L\left(-\frac{1}{2}\nu r+\gamma s+t\right)+Vz\exp(-t-r/2)\cdot B(s) \tag{47}$$

reduces, by elimination of t, to

$$L\left(-\frac{1}{2}\nu r+\gamma s-\frac{1}{2}r\right)+L(\log z+\log B(s)-\log\sigma+1)\,. \tag{48}$$

Hence in the limit $N\to\infty$ there remains only one term $(V\tau-L\nu-L)r/2$ that depends on r. Integration of $\exp[(V\tau-L\nu-L)r/2]$ with respect to r along a line parallel to the imaginary axis leads to a delta function $\delta(V\tau-L\nu-L)$ except for a trivial constant factor.

Therefore one gets the relation

$$\tau=L(1+\nu)/V=\sigma(1+\nu)\,. \tag{49}$$

Treatment of $\langle e^M\rangle$ is troublesome. From (11) one sees that

$$M=\frac{1}{2}\sum\{\log(1-h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'}-h_{\mathbf{rr}'}(c_{\mathbf{r}}y_{\mathbf{r}'}+c_{\mathbf{r}'}y_{\mathbf{r}}+y_{\mathbf{r}}y_{\mathbf{r}'}))$$

$$-\log(1-h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'})+h_{\mathbf{rr}'}(c_{\mathbf{r}}y_{\mathbf{r}'}+c_{\mathbf{r}'}y_{\mathbf{r}}+y_{\mathbf{r}}y_{\mathbf{r}'}\}$$

$$=-\frac{1}{2}\sum\left\{\frac{h_{\mathbf{rr}'}{}^2c_{\mathbf{r}}c_{\mathbf{r}'}}{1-h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'}}(c_{\mathbf{r}}y_{\mathbf{r}'}+c_{\mathbf{r}'}y_{\mathbf{r}}+y_{\mathbf{r}}y_{\mathbf{r}'})\right.$$

$$+\frac{1}{2}\left(\frac{h_{\mathbf{rr}'}}{1-h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'}}\right)^2(c_{\mathbf{r}}y_{\mathbf{r}'}+c_{\mathbf{r}'}y_{\mathbf{r}}+y_{\mathbf{r}}y_{\mathbf{r}'})^2$$

$$\left.+\frac{1}{3}\left(\frac{h_{\mathbf{rr}'}}{1-h_{\mathbf{rr}'}c_{\mathbf{r}}c_{\mathbf{r}'}}\right)^3(c_{\mathbf{r}}y_{\mathbf{r}'}+c_{\mathbf{r}'}y_{\mathbf{r}}+y_{\mathbf{r}}y_{\mathbf{r}'})^3+\cdots\right\}\,. \tag{50}$$

The weighted mean values of $y_{\mathbf{r}}$, $y_{\mathbf{r}}y_{\mathbf{r}'}$ and $y_{\mathbf{r}}y_{\mathbf{r}'}y_{\mathbf{r}''}$ are found to be

$$\left.\begin{aligned}&\langle y_{\mathbf{r}}\rangle=-Q_{\mathbf{r}}\\&\langle y_{\mathbf{r}}y_{\mathbf{r}'}\rangle=Q_{\mathbf{rr}'}\\&\langle y_{\mathbf{r}}y_{\mathbf{r}'}y_{\mathbf{r}''}\rangle=Q_{\mathbf{r}}Q_{\mathbf{r}'}Q_{\mathbf{r}''}+Q_{\mathbf{rr}'}Q_{\mathbf{r}''}+Q_{\mathbf{r}'\mathbf{r}''}Q_{\mathbf{r}}+Q_{\mathbf{r}''\mathbf{r}}Q_{\mathbf{r}'}\end{aligned}\right\} \tag{51}$$

respectively, where

$$Q_{\mathbf{r}}=\sum_{\mathbf{r}'}Q_{\mathbf{rr}'}((v-s+1)b_{\mathbf{r}'}+q)\,. \tag{52}$$

Since the matrix Q is the inverse of $u-r+H$ and u is assumed to be of order of N, one sees that

$$Q_{\mathbf{r}\mathbf{r}'}=\begin{cases}0(1/N) & \mathbf{r}=\mathbf{r}'\\ 0(1/N^2) & \mathbf{r}\neq\mathbf{r}'\end{cases} \tag{53}$$

$$Q_{\mathbf{r}}=0(1/N) \tag{54}$$

consequently

$$\left.\begin{aligned}
&\langle y_{\mathbf{r}}\rangle=0(1/N)\\
&\langle y_{\mathbf{r}}y_{\mathbf{r}'}\rangle=\begin{cases}0(1/N) & \mathbf{r}=\mathbf{r}'\\ 0(1/N^2) & \mathbf{r}\neq\mathbf{r}'\end{cases}\\
&\langle y_{\mathbf{r}}y_{\mathbf{r}'}y_{\mathbf{r}''}\rangle=0(1/N^2)\\
&\text{and further}\\
&\langle y_{\mathbf{r}}^2y_{\mathbf{r}'}\rangle=0(1/N^2) \qquad \mathbf{r}\neq\mathbf{r}'\\
&\langle y_{\mathbf{r}}^2y_{\mathbf{r}'}^2\rangle=0(1/N^2) \qquad \mathbf{r}\neq\mathbf{r}'\,.
\end{aligned}\right\} \tag{55}$$

In general the weighted mean of the product of $2m-1$ or $2m$ factors $y_{\mathbf{r}}$'s is of order of N^{-m} at the highest. Therefore one gets in the limit $N\to\infty$

$$\begin{aligned}
\langle M\rangle&=-\frac{1}{4}\lim\sum\left(\frac{h_{\mathbf{r}\mathbf{r}'}}{1-h_{\mathbf{r}\mathbf{r}'}c_{\mathbf{r}}c_{\mathbf{r}'}}\right)^2(2c_{\mathbf{r}'}{}^2\langle y_{\mathbf{r}}{}^2\rangle+\langle y_{\mathbf{r}}{}^2\rangle\langle y_{\mathbf{r}'}{}^2\rangle)\\
&=-\frac{1}{4}\lim\sum h_{\mathbf{r}\mathbf{r}'}{}^2\left(\frac{2c_{\mathbf{r}'}^2}{u-r}+\frac{1}{(u-r)^2}\right)\\
&=-\frac{L\tau\nu}{4}\int h^2(\mathbf{r})\,d\mathbf{r}-\frac{V\tau^2}{4}\int h^2(\mathbf{r})d\mathbf{r}\,.
\end{aligned} \tag{56}$$

Other terms in the expansion of $\log\langle\exp M\rangle$ vanish in the limit $N\to\infty$.

The last term of (56) may be changed into

$$-\frac{V\tau^2}{4}\frac{1}{(2\pi)^3}\int\varphi^2(\mathbf{p})d\mathbf{p}$$

and incorporated in U_1.

One reaches then a fairly simple expression of U

$$\begin{aligned}
U=&\frac{V}{2(2\pi)^3}\int\left[\tau\varphi-\frac{1}{2}\tau^2\varphi^2-\log(1+\tau\varphi)\right]d\mathbf{p}\\
&+L\Bigg(\log z-\log\sigma+1+\mu-\frac{\nu\tau}{4}\int h^2(\mathbf{r})d\mathbf{r}\\
&+\frac{1}{2}\theta(s-1)^2+\gamma s+\log B(s)\Bigg)\,.
\end{aligned} \tag{57}$$

It is to be added that the factor $u^{-4}du$ in the expression of $J^*(L)$ is changed into $-(V/N)^3\tau^2 d\tau$ while the coefficient C turns out to be of order of N^3. Therefore the integral $J^*(L)$ has a definite expression in the limit $N\to\infty$.

In the limit $V\to\infty$, the limit of $V^{-1}\log Z$ is to give P/kT, where P means the pressure of the system at the temperature T, k denoting the Boltzmann constant. Hence one reaches the final expression

$$P/kT=\lim_{V\to\infty} V^{-1}\log Z=\operatorname*{Maximum}_{\sigma}\,[\sigma\log z+F] \tag{58}$$

$$F=\Phi+\sigma\left(-\log\sigma+1+\mu-\frac{1}{4}\nu\tau\int h^2(\mathbf{r})d\mathbf{r}+\operatorname*{Extremum}_{s} E\right) \tag{59}$$

$$E=\frac{1}{2}\theta(s-1)^2+\gamma s+\log B(s) \tag{60}$$

$$\Phi=\frac{1}{2(2\pi)^3}\int\left[\tau\varphi-\frac{1}{2}\tau^2\varphi^2-\log(1+\tau\varphi)\right]d\mathbf{p}\,. \tag{61}$$

Obviously one sees that the density σ defined as L/V in § 1 agrees with the density defined according to statistical mechanics

$$\lim\frac{\partial}{\partial\log z}V^{-1}\log Z\,. \tag{62}$$

§ 5. Three distributions

Selection of a distribution $c_{\mathbf{r}}$ would give no effect on the final result if subsequent integrations could be performed exactly.

In the present approximation, the selected distributions present fairly wide discrepancies in final results. To select a good distribution is an important problem. This paper examines three distributions.

1) A uniform distribution $c_{\mathbf{r}}=L/N$. (63)
This distribution seems to prevail at lower densities.

2) A crystalline distribution $c_{\mathbf{s}}=1$, $\mathbf{s}$ denoting lattice points of a face-centered lattice, $c_{\mathbf{r}}=0$ elsewhere. (64)

More definitely speaking, the face-centered lattice is generated by three unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$

$$\mathbf{e}_1=l(0,\ 1/2,\ 1/2),\quad \mathbf{e}_2=l(1/2,\ 0,\ 1/2),\quad \mathbf{e}_3=l(1/2,\ 1/2,\ 0) \tag{65}$$

or

$$\mathbf{s}=n_1\mathbf{e}_1+n_2\mathbf{e}_2+n_3\mathbf{e}_3$$

where n_1, n_2, n_3 stand for integers and the lattice constant l is so chosen that the volume of a unit cell $l^3/4$ may be equal to the volume assigned to one particle $V/L=1/\sigma$.

This distribution seems to prevail at the highest density.

3) An interpolation distribution

$$
\begin{aligned}
c_s &= c+(1-c)L/N \qquad \text{at lattice points} \\
c_s &= \quad (1-c)L/N \qquad \text{elsewhere}
\end{aligned}
\tag{66}
$$

The parameter c should vanish at $\sigma=0$ and reach 1 at $\sigma=\sigma_{\max}$ the highest density. It is assumed here that c is proportional to σ, or

$$c=\sigma/\sigma_{\max}\,. \tag{67}$$

1) For the uniform distribution $c_{\mathbf{r}}=L/N$, all $b_{\mathbf{r}}$'s have the same value $\sigma\int h(\mathbf{r})d\mathbf{r}=\sigma\varphi(0)$. Hence one sees that

$$
\left.
\begin{aligned}
&\alpha=0\,, \quad \beta=0\,, \quad \gamma=b=\sigma\varphi(0) \\
&\mu=-\frac{b}{2}\,, \quad \nu=0\,, \quad B(s)=\exp(-sb)
\end{aligned}
\right\}
\tag{68}
$$

$$U=V\Phi(\sigma)+L\left(\log z-\log\sigma+1-\frac{1}{2}\sigma\varphi(0)\right). \tag{69}$$

2) For the face-centered lattice

$$\mathbf{s}=n_1\mathbf{e}_1+n_2\mathbf{e}_2+n_3\mathbf{e}_3 \tag{70}$$

generated by $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, there exists an inverse lattice, that is, a body-centered lattice generated by three vectors $\mathbf{f}_1$, $\mathbf{f}_2$, $\mathbf{f}_3$,

$$\mathbf{f}_1=(-1,\,1,\,1)/l\,, \quad \mathbf{f}_2=(1,\,-1,\,1)/l\,, \quad \mathbf{f}_3=(1,\,1,\,-1)/l \tag{71}$$

that satisfy the orthogonality condition

$$\mathbf{e}_i\cdot\mathbf{f}_j=\delta_{ij}\,.$$

In general a distribution $c_{\mathbf{r}}$ periodic with respect to the face-centered lattice may be expressed as a Fourier series

$$c_{\mathbf{r}}=\frac{L}{N}\sum f(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}\,, \qquad f(0)=1 \tag{72}$$

where $\mathbf{q}$ ranges over all lattice points of a body-centered lattice, or

$$\mathbf{q}=2\pi(m_1\mathbf{f}_1+m_2\mathbf{f}_2+m_3\mathbf{f}_3) \tag{73}$$

m_1, m_2, m_3 ranging over integers.

The condition $f(0)=1$ ensures that the sum $\sum c_{\mathbf{r}}$ is equal to L the number of particles.

One gets then

$$
\begin{aligned}
b_{\mathbf{r}} &= \sum h_{\mathbf{r}\mathbf{r}'}c_{\mathbf{r}'} \\
&= \frac{L}{N}\sum\sum f(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}'}h_{\mathbf{r}\mathbf{r}'}=\frac{L}{N}\sum f(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}\sum e^{i\mathbf{q}(\mathbf{r}'-\mathbf{r})}h_{\mathbf{r}\mathbf{r}'} \\
&= \frac{L}{V}\sum\varphi(\mathbf{q})f(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}
\end{aligned}
\tag{74}
$$

and further

$$\alpha=\tau\sigma\sum{}'f^2(\mathbf{q})\cdot\varphi^2(\mathbf{q}) \tag{75}$$

$$\beta=\tau\sigma\sum{}'\frac{\varphi^2(\mathbf{q})f^2(\mathbf{q})}{1+\tau\cdot\varphi(\mathbf{q})} \tag{76}$$

$$\gamma=\sigma\varphi(0)+\sigma\sum{}'\varphi(\mathbf{q})f^2(\mathbf{q}) \tag{77}$$

where the summation $\sum{}'$ excludes the term at $\mathbf{q}=0$.

In particular the crystalline distribution (64) gives all $f(\mathbf{q})=1$ and

$$\mu=\sum_{\mathbf{s}}{}'\log(1-h(s))\,,\quad \nu=1\quad\text{and}\quad \tau=2\sigma \tag{78}$$

while the interpolation distribution (66) leads to $f(0)=1$ and $f(\mathbf{q})=c$ for $\mathbf{q}\neq0$, and further

$$\left.\begin{aligned}&\nu=c^2\,,\quad \tau=\sigma(1+c^2)\\ &\alpha=c^2\tau\sigma\sum{}'\varphi^2(\mathbf{q})\,,\quad \beta=c^2\tau\sigma\sum{}'\frac{\varphi^2(\mathbf{q})}{1+\tau\varphi(\mathbf{q})}\\ &\gamma=\sigma\varphi(0)+c^2\sigma\sum{}'\varphi(\mathbf{q})\end{aligned}\right\}. \tag{79}$$

§ 6. A system of hard spheres

The interaction potential $G(\mathbf{r},\mathbf{r}')$ between two hard spheres of diameter 1 at $\mathbf{r}$ and $\mathbf{r}'$ is infinite at the distance $|\mathbf{r}-\mathbf{r}'|$ less than 1 and vanishes at $|\mathbf{r}-\mathbf{r}'|>1$. So one gets

$$h(\mathbf{r})=\begin{cases}1 & |\mathbf{r}|<1\\ 0 & |\mathbf{r}|>1\end{cases} \tag{80}$$

$$\begin{aligned}\varphi(\mathbf{p})&=\int\exp(i\mathbf{p}\cdot\mathbf{r})d\mathbf{r}\qquad |\mathbf{r}|<1\\ &=\varphi(0)\Lambda(p)\end{aligned} \tag{81}$$

where

$$\varphi(0)=\frac{4\pi}{3}\,,\quad \Lambda(p)=3\cdot\frac{\sin p-p\cos p}{p^3}\,. \tag{82}$$

In evaluating Φ, use is made of the relation

$$\begin{aligned}&\int_0^\infty\left[x\Lambda-\frac{1}{2}x^2\Lambda^2-\log(1+x\Lambda)\right]p^2dp\\ &=\int_0^\infty\left[\sum_{n=1}^{6}\frac{(-1)^{n-1}}{n}x^n\Lambda^n-\log(1+x\Lambda)\right]p^2dp-\sum_{n=3}^{6}\frac{(-1)^{n-1}x^n}{n}\lambda_n\end{aligned} \tag{83}$$

where the abbreviation

$$\lambda_n=\int_0^\infty\Lambda^np^2dp \tag{84}$$

is used. Complex integration gives

$$\left.\begin{aligned}&\lambda_1=\lambda_2=\frac{3\pi}{2}\\&\lambda_3=\frac{3\pi}{2}\cdot\frac{15}{32},\quad \lambda_4=\frac{3\pi}{2}\cdot\frac{34}{105},\quad \lambda_5=\frac{3\pi}{2}\cdot\frac{40949}{172032}\\&\lambda_6=\frac{3\pi}{2}\cdot\frac{92377}{500500}\end{aligned}\right\}\tag{85}$$

The integrand of the right side of (83) tends to zero far more rapidly than that of the left side as p tends to infinity.

In evaluating α, γ, use is made of Poisson's summation formulas[2)]

$$[\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3]\sum_{\mathbf{s}}\delta(\mathbf{r}-\mathbf{s})=\sum_{\mathbf{q}}e^{i\mathbf{r}\cdot\mathbf{q}}\tag{86}$$

$$\sum_{\mathbf{q}}\delta(\mathbf{p}-\mathbf{q})=\frac{[\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3]}{(2\pi)^3}\sum_{\mathbf{s}}e^{-i\mathbf{p}\cdot\mathbf{s}}\tag{87}$$

where $[\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3]$ denotes the volume of a unit cell spanned by three unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, $\mathbf{s}$ and $\mathbf{q}$ being defined by (65), (70) and (73). Multiplying both sides of (87) by any function $g(\mathbf{p})$ and integrating with respect to $\mathbf{p}$, one gets

$$\begin{aligned}\sigma\sum_{\mathbf{q}}g(\mathbf{q})&=\sum_{\mathbf{s}}\frac{1}{(2\pi)^3}\int e^{-i\mathbf{p}\cdot\mathbf{s}}g(\mathbf{p})\cdot d\mathbf{p}\\&=\sum_{\mathbf{s}}\frac{1}{2\pi^2 s}\int_0^\infty g(p)\sin sp\cdot p\cdot dp\,,\qquad s=|\mathbf{s}|\end{aligned}\tag{88}$$

and, in particular, for $g(\mathbf{q})=\varphi(\mathbf{q})$, $\varphi^2(\mathbf{q})$,

$$\sigma\sum_{\mathbf{q}}\varphi(\mathbf{q})=\sum_{\mathbf{s}}h(\mathbf{s})=\sum_{\mathbf{s}}\epsilon(1-s)\tag{89}$$

$$\sigma\sum_{\mathbf{q}}\varphi^2(\mathbf{q})=\frac{\pi}{12}\sum_{\mathbf{s}}(s^3-12s+16)\epsilon(2-s)\,.\tag{90}$$

Evaluation of $B(s)$ is cumbersome. Twelve planes, each of which bisects perpendicularly the segment connecting a lattice point to one of its twelve adjacent points, cut out a dodecahedron[3)], which is divided into twelve similar pyramids having their respective vertices at the lattice point and their respective bases on the above planes. One of the pyramids is bisected by a plane into two similar tetrahedrons. $B(s)$ is evaluated by averaging $\exp(-sb_{\mathbf{r}})$ over one of the tetrahedrons, that has its four vertices at

$$\left.\begin{aligned}&\mathbf{a}_1=l/4\cdot(2,0,0)\,,\quad \mathbf{a}_2=l/4\cdot(1,1,0)\,,\quad \mathbf{a}_3=l/4\cdot(1,1,1)\\ \text{and}\quad&\\&(0,0,0)\end{aligned}\right.\tag{91}$$

The average of a function $g(\mathbf{r})$ is approximated by

$$\sum w(\mathbf{s}) \cdot g(\mathbf{s})/m^3 \tag{92}$$

where $\mathbf{s}$ stands for $(m_1\mathbf{a}_1+m_2\mathbf{a}_2+m_3\mathbf{a}_3)/m$, m_1, m_2, m_3 ranging from 0 to m under the restriction $m_1+m_2+m_3 \leqq m$, and the weight $w(\mathbf{s})$ is defined to be

1/4	when $\mathbf{s}$ is at a vertex
7/6	on an edge
3	on a face
6	inside

of the tetrahedron. A more detailed description will be found in a separate paper[4].

Instead of the density $\sigma=L/V$, a dimensionless quantity $\rho=\sigma\varphi(0)$ is used in the following as a modified density. At the closest packing the lattice constant l falls to its minimum value $\sqrt{2}$ while the modified density ρ attains to its maximum value

$$\rho_{\max}=\sigma_{\max}\varphi(0)=\frac{4\pi}{3}\sqrt{2}=5.92384\ 39151.$$

Fig. 1 shows curves $\varphi(0)P/kT$ versus the modified density ρ, among which the curve (1) is based on the uniform distribution, the curve (2) on the crystalline distribution, the curve (3) on the interpolation distribution, and the curve (4) on the virial expansion[5]

$$\varphi(0) \cdot P/kT=\rho+\frac{1}{2}\rho^2+\frac{5}{32}\rho^3+0.03580\,\rho^4+0.00718\,\rho^5. \tag{93}$$

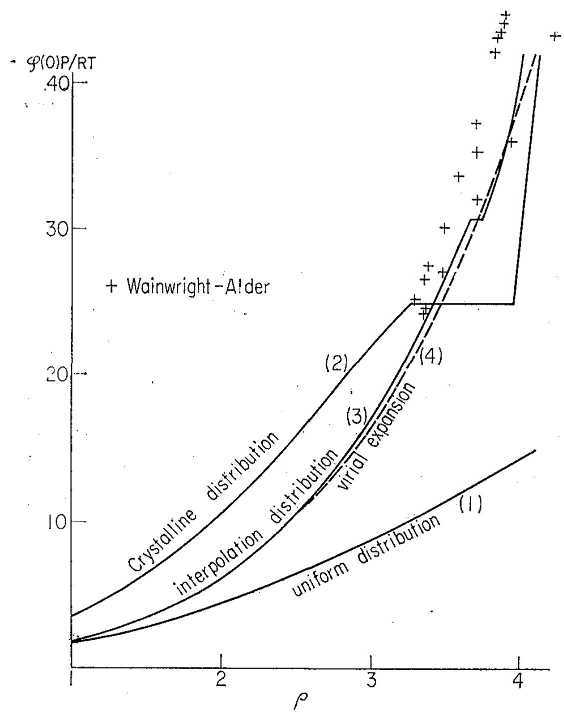

Fig. 1.

Crosses represent the result of Wainwright and Alder[6], expressed in terms of $\varphi(0) \cdot P/kT$ and ρ.

The curve (2) shows the existence of a phase change at $\rho=3.26$, to 3.94, $\varphi(0) \cdot P/kT=24.9$ while the curve (3) does at $\rho=3.69$ to 3.73, $\varphi(0) \cdot P/kT=30.70$. The appearance of the phase change is due to the existence of two maxima in $\sigma \log z+F$ (cf. (58)). In turn this is due to the existence of a common tangent to $F(\sigma)$. Fig. 2 shows the curves $(12.5+\log\varphi(0))\rho+\varphi(0)F$ based on the interpolation distribution (66) for $m=40$ and $m=50$. The curves are seen to have two peaks. The appearance of these peaks is traced back to the behavior of θ with respect to the modified density ρ, as is shown in Fig. 3. At least, while other quantities vary fairly smoothly in the neighborhood of the phase change, θ shows its fairly sharp peak there.

The substitution of u by $N/V\tau$ in (4) leads to

$$\alpha = \frac{\tau}{\sigma}\langle(b_r - b)^2\rangle$$

where b_r means the potential felt by a particle at the site $\mathbf{r}$ (cf. (12)).

Therefore α measures the dispersion of the potential due to a distribution. For the uniform distribution $\alpha = 0$. Likewise β measures the dispersion of the potential in the presence of the interference represented by the matrix Q (cf. (26)). One can say safely that so long as the distribution remains nearly uniform a phase change never occurs, and that if a phase change should occur it is likely to do in the range where θ shows its peak.

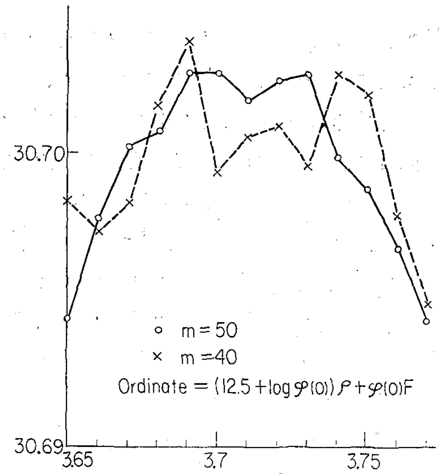

Fig. 2.

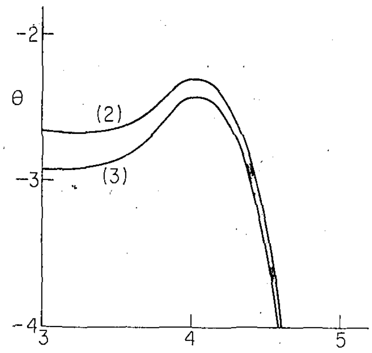

Fig. 3.

Estimation of errors in the computation of $B(s)$ is difficult, so results on $(12.5 + \log\varphi(0))\rho + \varphi(0)F$ are shown in Fig. 2 for $m = 40$ and $m = 50$. They disagree slightly in the range of phase change, but they both show tne existence of a common tangent, hence, of a phase change.

§ 7. Reflections

As to the pressure of the system of hard spheres, reliable data are considered to be supplied by the virial expansion up to the vicinity of the phase change, by Wainwright-Alder's calculations there, by the cell theory beyond there.

As is obviously shown in Fig. 1, the curve (2) based on the crystalline distribution rises too steeply and presents an earlier phase change, while the curve (1) based on the uniform distribution rises too slowly and shows no phase change.

Fig. 1 shows that the curve (3) based on the interpolation distribution coincides fairly good with the curve (4) based on the virial expansion and shows a phase change in a region expected from Wainwright-Alder's computations. But the curve (3) diverges from

Wainwright-Alder's results as well as the curve predicted by the cell theory beyond the region.

The defect seems to stem from the interpolation distribution being inappropriate at higher densities.

Improvement of the present method may be found in
1) setting up a better distribution, and
2) replacing W_0 by a more accurate, and yet integrable, function.

An equation to the distribution might be established in the form of an integral equation. To solve it would be another task.

A forthcoming paper will introduce a device to circumvent it.

To get a more accurate $\langle W_0 \rangle$, one may augment the number of planes S_α. But the introduction of n planes leads to the introduction of $2n$ variables v_α, s_α $\alpha=1, 2, \cdots, n$. After elimination of v_α, one will be faced with a task to seek an extremum with respect to n variables s_α. So n should be small as far as possible.

One may be tempted to use other quadratic surfaces besides the sphere. But it accompanies serious difficulties in integrals (22) and (26).

A few words must be added to explain the introduction of the sign Extremum in (59).

The method of steepest descent should give a saddle point which is maximum with respect to real variables u, v, w and minimum with respect to imaginary variables r, s, t. In some situation, the coefficient of v^2 in U_2 (cf. (32)), which is equal to $L(\beta-\alpha)/2$, is positive, so that the elimination of v gives not the maximum but the minimum. Consequently one must seek the maximum with respect to s. It is mystifying.

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