Zeitschrift: Helvetica Physica Acta
Band: 36 (1963)
Heft: II

Artikel: Classical statistical mechanics of a system af particles
Autor: Ruelle, D.
DOI: https://doi.org/10.5169/seals-113366

Nutzungsbedingungen
Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

Conditions d'utilisation
L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

Terms of use
The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

Download PDF: 30.11.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

Classical Statistical Mechanics of a System of Particles

by **D. Ruelle*)**
Eidgenössische Technische Hochschule, Zürich

(15. VIII. 62)

Abstract. The free energy of a system of particles interacting by a two-body potential is investigated for the canonical ensemble. The existence of a limit for the free energy per particle when the system becomes infinite and the stability conditions are proved rigorously for a large class of potentials. It is also shown that the pressure is a continuous function of the volume for bounded potentials. The grand canonical ensemble is investigated in a similar manner and a generalization of the results of YANG and LEE is given.

Introduction

Let us consider a classical system formed by n particles enclosed in a region Λ and interacting through a spherically symmetric two-body potential. Statistical mechanics yields an expression for the free energy F of the system at temperature T (canonical ensemble). In order to identify F with the thermodynamical free energy one is led to consider the limit of F/n when n and the volume of Λ tend to infinity in such a way that the specific volume has a finite limit. The problem of the existence and of the properties of the limit of F/n was studied by VAN HOVE[4]) and a similar problem was treated by YANG and LEE[6]) for the grand canonical ensemble.

These two investigations have however been restricted to the case of potentials with a hard core. It is indeed clear that a system of particles interacting classically through a two-body potential does not always lead in the limit to the definition of the usual thermodynamical functions**).

In what follows we will give less restrictive sufficient conditions on the potential so that the system behaves in the limit as a thermodynamical system. We will then prove the existence and stability properties of the thermodynamical potentials for the canonical and grand canonical ensembles. We will always assume here Λ to be a cube, but a generalization to other shapes is straightforward.

A detailed knowledge of the analytic properties of the thermodynamical functions could be obtained up to now only for one-dimensional systems (VAN HOVE[5])). We

---

*) Present address: Institute for Advanced Study, Princeton, New Jersey.

**) This difficulty appears when the potential does not decrease fast enough at infinity or when it is not sufficiently repulsive. Suppose for instance that the potential Φ is continuous and that there exist points $\boldsymbol{x}_i$, $i = 1, \ldots, n$, such that $\sum_{i=1}^{n} \sum_{j=1}^{n} \Phi(\boldsymbol{x}_j - \boldsymbol{x}_i) < 0$, it is then easy to see that the minimum energy of a system of N particles becomes negative and diverges quadratically as N goes to infinity. The definition of the usual thermodynamical functions is then no longer possible.

have therefore also given here a proof, valid for bounded potentials, of the continuity of pressure as a function of specific volume at constant temperature.

1. Conditions on the potential

Let us consider a system of n undistinguishable particles having only the translation degrees of freedom and interacting classically through a two-body potential. The total energy is given by

$$E_n(\underline{p}, \underline{x}) = T_n(\underline{p}) + U_n(\underline{x}), \tag{1}$$

$$T_n(\underline{p}) = \sum_{i=1}^{n} \frac{\boldsymbol{p}_i^2}{2m}, \tag{2}$$

$$U_n(\underline{x}) = \sum_{i<j} \Phi(\boldsymbol{x}_j - \boldsymbol{x}_i) \tag{3}$$

where $\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n$ are the particle coordinates and $\boldsymbol{p}_1, \ldots, \boldsymbol{p}_n$ the corresponding momenta.

We will now restrict our attention to the family of potentials defined by the following properties.

Properties A. *One may write*

$$\Phi(\boldsymbol{x}) = \Phi_1(\boldsymbol{x}) + \Phi_2(\boldsymbol{x}) \tag{4}$$

where the functions $\Phi_1(\boldsymbol{x})$ and $\Phi_2(\boldsymbol{x})$ depend only on $|\boldsymbol{x}|$ and satisfy the following conditions.

A_1. *$\Phi_1(\boldsymbol{x})$ is Lebesgue-measurable with values in the closed interval* $[0, +\infty]$ (It would be sufficient to assume that $\Phi_1(\boldsymbol{x})$ is non-negative *almost everywhere*). *The set $\{\boldsymbol{x} : \Phi_1(\boldsymbol{x}) = +\infty\}$ is a sphere of radius $a \geqslant 0$ centered at the origin. There exists a number $R > 0$ such that $\Phi_1(\boldsymbol{x})$ is Lebesgue-integrable for $|\boldsymbol{x}| \geqslant R$.*

A_2. *$\Phi_2(\boldsymbol{x})$ is continuous and Lebesgue-integrable. If one writes*

$$\Phi_2(\boldsymbol{x}) = (2\pi)^{-3/2} \int d\boldsymbol{p}\, e^{i\boldsymbol{p}\boldsymbol{x}} \hat{\Phi}_2(\boldsymbol{p}), \tag{5}$$

$\hat{\Phi}_2(\boldsymbol{p})$ is non-negative and $\hat{\Phi}_2(0) > 0$.

$\Phi_2(\boldsymbol{x})$ is thus a continuous function of positive type and therefore bounded, $\hat{\Phi}_2(\boldsymbol{p})$ is continuous and Lebesgue-integrable.

Let now Λ be a closed cube with the volume $V = \lambda^3$.

Let $\mathcal{M}_+(\Lambda)$ be the family of all positive measures which have their support in Λ. If $n(\boldsymbol{x}) \in \mathcal{M}_+(\Lambda)$ we may write

$$n(\boldsymbol{x}) = (2\pi)^{-3/2} \int d\boldsymbol{p}\, e^{i\boldsymbol{p}\boldsymbol{x}} \hat{n}(\boldsymbol{p}) \tag{6}$$

where $\hat{n}(\boldsymbol{p})^* = \hat{n}(-\boldsymbol{p})$ and $\hat{n}(\boldsymbol{p})$ is entire analytic by the PALEY-WIENER theorem[3]). One has

$$\int d\boldsymbol{y}\, n(\boldsymbol{y})\, n(\boldsymbol{x} + \boldsymbol{y}) = \int d\boldsymbol{p}\, e^{i\boldsymbol{p}\boldsymbol{x}} \hat{n}(\boldsymbol{p})\, \hat{n}(-\boldsymbol{p}), \tag{7}$$

$$\int d\boldsymbol{x}\, d\boldsymbol{y}\, \Phi_2(\boldsymbol{y} - \boldsymbol{x})\, n(\boldsymbol{x})\, n(\boldsymbol{y}) = (2\pi)^{3/2} \int d\boldsymbol{p}\, \hat{\Phi}_2(\boldsymbol{p})\, \hat{n}(\boldsymbol{p})\, \hat{n}(-\boldsymbol{p}). \tag{8}$$

If $\boldsymbol{u}$ is any unit vector, the function $\hat{n}(p\,\boldsymbol{u})\,\hat{n}\,(-\,p\,\boldsymbol{u})$ is entire analytic, non-negative for real p. Term by term minorization of its power series expansion at the origin yields

$$\left.\begin{aligned}\hat{n}(p\,\boldsymbol{u})\,\hat{n}\,(-\,p\,\boldsymbol{u}) &\geqslant (2\,\pi)^{-3}\left(\int d\boldsymbol{x}\,n(\boldsymbol{x})\right)^2\left\{1-\left[\frac{(\sqrt{3}\,\lambda)^2}{2\,!}\,p^2+\frac{(\sqrt{3}\,\lambda)^6}{6\,!}\,p^6+\ldots\right]\right\}\\ &= (2\,\pi)^{-3}\left(\int d\boldsymbol{x}\,n(\boldsymbol{x})\right)^2\left(1-\frac{\operatorname{Ch}\sqrt{3}\,\lambda\,p-\cos\sqrt{3}\,\lambda\,p}{2}\right).\end{aligned}\right\}\tag{9}$$

The continuous non-negative function $f(\boldsymbol{p}) = \max\,(0,\,1-(\operatorname{Ch}\sqrt{3}\,\lambda\,p-\cos\sqrt{3}\,\lambda\,p)/2)$ satisfies $f(0) = 1$ and

$$\left(\int d\boldsymbol{x}\,n(\boldsymbol{x})\right)^2 \geqslant (2\,\pi)^3\,\hat{n}(\boldsymbol{p})\,\hat{n}\,(-\,\boldsymbol{p}) \geqslant \left(\int d\boldsymbol{x}\,n(\boldsymbol{x})\right)^2 f(\lambda\,\boldsymbol{p})\,.\tag{10}$$

From (8) and (10) we obtain

$$\int d\boldsymbol{x}\,d\boldsymbol{y}\,\Phi_2\,(\boldsymbol{y}-\boldsymbol{x})\,n(\boldsymbol{x})\,n(\boldsymbol{y}) \geqslant (2\,\pi)^{-3/2}\left(\int d\boldsymbol{x}\,n(\boldsymbol{x})\right)^2\int d\boldsymbol{p}\,\hat{\Phi}_2(\boldsymbol{p})\,f(\lambda\,p)\tag{11}$$

and there exist positive constants A and λ_0 such that for $\lambda > \lambda_0$ one has

$$(2\,\pi)^{-3/2}\int d\boldsymbol{p}\,\hat{\Phi}_2(\boldsymbol{p})\,f(\lambda\,\boldsymbol{p}) > \frac{A}{V}\,,\tag{12}$$

$$\int d\boldsymbol{x}\,d\boldsymbol{y}\,\Phi_2\,(\boldsymbol{y}-\boldsymbol{x})\,n(\boldsymbol{x})\,n(\boldsymbol{y}) > \left(\int d\boldsymbol{x}\,n(\boldsymbol{x})\right)^2\frac{A}{V}\,.\tag{13}$$

Let now $\underline{x} = (\boldsymbol{x}_1,\ldots,\boldsymbol{x}_n)$, $\boldsymbol{x}_i \in \Lambda$ for $i = 1,\ldots,n$.

We get for the potential energy $U_n(x)$ the inequality

$$\left.\begin{aligned}U_n(\underline{x}) = \sum_{i<j}\Phi\,(\boldsymbol{x}_j-\boldsymbol{x}_i) \geqslant \sum_{i<j}\Phi_2\,(\boldsymbol{x}_j-\boldsymbol{x}_i) &= \left[\sum_{i=1}^{n}\sum_{j=1}^{n}\Phi_2\,(\boldsymbol{x}_j-\boldsymbol{x}_i)-n\,\Phi_2(0)\right]\\ &= \frac{1}{2}\left[\int d\boldsymbol{x}\,d\boldsymbol{y}\,\Phi_2\,(\boldsymbol{y}-\boldsymbol{x})\,n(\boldsymbol{x})\,n(\boldsymbol{y})-n\,B\right],\end{aligned}\right\}\tag{14}$$

where we have written

$$\Phi_2(0) = B > 0\,,\qquad n(\boldsymbol{x}) = \sum_{i=1}^{n}\delta\,(\boldsymbol{x}-\boldsymbol{x}_i)\,.\tag{15}$$

(13) and (14) give

$$U_n(\underline{x}) > \frac{n}{2}\left(A\,\frac{n}{V}-B\right)\quad\text{for}\quad\lambda > \lambda_0\,.\tag{16}$$

We will base our discussion in the next sections mainly on inequality (16) and on a new condition which we will impose on the potential $\Phi(\boldsymbol{x})$.

Property B. *There exists a number* $R > 0$ *such that* $\Phi(\boldsymbol{x}) \leqslant 0$ *for* $|\boldsymbol{x}| \geqslant R$.

This condition emphasizes the integrability condition for Φ_1, given by A_1. It seems likely that B is not essential for the proof of the results below, and that the properties A might be sufficient. In any case there exist many interesting potentials which satisfy both A and B. Some of them are indicated in the appendix.

2. Existence of the free energy per particle

Let us consider a system of n particles enclosed in a cube Λ with edge λ and volume $V = \lambda^3$, let also β be a positive number.

One defines functions f and φ by the following formulae

$$e^{-n\beta f(\beta;\Lambda,n)} = (2\pi)^{-3n}\frac{1}{n!}\int d\boldsymbol{p}_1\ldots d\boldsymbol{p}_n \int\limits_{(\Lambda)^n} d\boldsymbol{x}_1\ldots d\boldsymbol{x}_n\, e^{-\beta E_n(\underline{p},\underline{x})}, \tag{1}$$

$$e^{-n\beta\varphi(\beta;\Lambda,n)} = Q(\beta;\Lambda,n) = \frac{1}{n!}\int\limits_{(\Lambda)^n} d\boldsymbol{x}_1\ldots d\boldsymbol{x}_n\, e^{-\beta U_n(\underline{x})}. \tag{2}$$

We have thus

$$f = \frac{3}{2\beta}\log\frac{2\pi\beta}{m} + \varphi. \tag{3}$$

For $\lambda > \lambda_0$ we have according to (1.16)

$$Q(\beta;\Lambda,n) < \frac{V^n}{n!}e^{-n\beta[1/2(A(n/V)-B)]}, \tag{4}$$

$$\varphi(\beta;\Lambda,n) > \frac{1}{2}\left(A\frac{n}{V} - B\right) - \frac{1}{\beta}\left(\log\frac{V}{n} + 1\right). \tag{5}$$

Let now Λ_m^λ be a cube with the edge $2^m\lambda - R$, m: non-negative integer. We will assume in what follows that $\lambda - R > \lambda_0$ and $\lambda - R > (n/\sqrt{2})^{1/3}a$ in order to obtain a density smaller than that of closest-packing. Let

$$Q_m^\lambda = Q(\beta;\Lambda_m^\lambda, 2^{3m}n), \quad \varphi_m^\lambda = \varphi(\beta;\Lambda_m^\lambda, 2^{3m}n). \tag{6}$$

One can place eight cubes Λ_m^λ inside of a cube Λ_{m+1}^λ in such a manner that the distance between two Λ_m^λ is never smaller than R.

From this one concludes by using property B that

$$Q_{m+1}^\lambda > (Q_m^\lambda)^8, \quad \varphi_{m+1}^\lambda < \varphi_m^\lambda. \tag{7}$$

The sequence $(\varphi_m^\lambda)_{0\leqslant m<\infty}$ being decreasing (7) and bounded (5), has a finite limit φ^λ,

$$\varphi^\lambda \geqslant \frac{1}{2}\left(A\frac{n}{V} - B\right) - \frac{1}{\beta}\left(\log\frac{V}{n} + 1\right). \tag{8}$$

If $\lambda < \lambda'$ one has $Q_m^\lambda < Q_m^{\lambda'}$, thus

$$\varphi^\lambda \geqslant \varphi^{\lambda'} \tag{9}$$

which shows that φ^λ is a decreasing function of λ.

Let $\lambda_1 = (\lambda + \lambda')/2$ one can then place seven cubes Λ_m^λ and one cube $\Lambda_m^{\lambda'}$ inside of $\Lambda_{m+1}^{\lambda_1}$ in such a manner that the distance between two Λ_m is never smaller than R.

From this one concludes that $Q_{m+1}^{\lambda_1} < (Q_m^\lambda)^7 Q_m^{\lambda'}$, thus

$$\varphi^{\lambda_1} \leqslant \frac{7}{8}\varphi^\lambda + \frac{1}{8}\varphi^{\lambda'}. \tag{10}$$

(9) and (10) imply that φ^λ is a continuous function of λ for $\lambda > R + \max(\lambda_0, (n/\sqrt{2})^{1/3}a)$. One proves indeed without difficulty semi-continuity to the left, then to the right. Consider now a sequence $(N_i)_{1\leqslant i<\infty}$ of positive integers such that $N_i \to \infty$ and a sequence $(V_i)_{1\leqslant i<\infty}$ of positive numbers such that $V_i/N_i \to v > a^3/\sqrt{2}$. We will denote by V_i again the cube with volume V_i.

One may then choose numbers n (positive integer) and $V = \lambda^3$ such that $v = V/n$ and $\lambda > R + \max(\lambda_0, (n/\sqrt{2})^{1/3} a)$.

φ^λ being continuous, for any $\varepsilon > 0$ one may choose λ', λ'' such that

$$R + \max\left(\lambda_0, \left(\frac{n}{\sqrt{2}}\right)^{1/3} a\right) < \lambda' < \lambda < \lambda'' \text{ and } \varphi^{\lambda'} - \varphi^\lambda < \varepsilon\,, \quad \varphi^\lambda - \varphi^{\lambda''} < \varepsilon\,.$$

Let $E(x)$ represent the biggest integer not greater than x, one may then find an integer i' such that for $i > i'$ one has

$$\left(E\left[\left(\frac{N_i}{n}\right)^{1/3}\right] + 1\right)\lambda' < (V_i)^{1/3}\,. \tag{11}$$

Let then $2^m \leqslant E[(N_i/n)^{1/3}] < 2^{m+1}$, m integer.

Inside of V_i one can place, starting from one corner and at mutual distances greater than R the following cubes containing in all N_i particles.

1. One cube $\Lambda_m^{\lambda'}$ containing $2^{3m}\, n$ particles.
2. Successive layers of cubes $\Lambda_{m'}^{\lambda'}$ containing $2^{3m'}\, n$ particles, $m' < m$, m' strictly decreasing.
3. A certain number of cubes $\Lambda_0^{\lambda'}$ containing n particles.
4. A cube $\Lambda_0^{\lambda'}$, containing n' particles, $0 < n' \leqslant n$.

We may then write

$$\varphi(\beta;\, V_i, N_i) < \sum_{m'=0}^{m} c_{m'}\, \varphi_{m'}^{\lambda'} + \frac{n'}{N_i}\, \varphi(\beta;\, \Lambda_0^{\lambda'}, n')\,, \tag{12}$$

with $c_{m'} \geqslant 0$, $\sum_{m'=0}^{m} c_{m'} + n'/N_i = 1$. When i tends to infinity the $c_{m'}$, for m' smaller than a given constant, tend to zero.

Therefore, for i big enough

$$\varphi(\beta;\, V_i, N_i) < \varphi^{\lambda'} + \varepsilon\,. \tag{13}$$

On the other hand one may find an integer i'' such that for $i > i''$

$$\left(\frac{n}{N_i}\right)^{1/3} [(V_i)^{1/3} + R] < \lambda''\,. \tag{14}$$

It is then possible to choose m so big that one may place $2^{3m}\, n\, N_i^2$ cubes V_i inside of a cube with edge $2^m N_i \lambda'' - R$ in such a manner that the distance between two V_i is never smaller than R. We get then

$$(Q(\beta;\, V_i, N_i))^{2^{3m} n N_i^2} < Q\,(\beta;\, (2^m N_i \lambda'' - R)^3,\, 2^{3m}\, n\, N_i^3) \tag{15}$$

and if $2^{p-1} < N_i \leqslant 2^p$, p integer, we obtain

$$Q\,(\beta;\, (2^m N_i \lambda'' - R)^3,\, 2^{3m}\, n\, N_i^3)\, (Q_m^{\lambda''})^{2^{3p} - N_i^3} < Q_{m+p}^{\lambda''}\,. \tag{16}$$

(15) and (16) give

$$\varphi(\beta;\, V_i, N_i) > \frac{2^{3p}}{N_i^3}\, \varphi_{m+p}^{\lambda''} - \frac{2^{3p} - N_i^3}{N_i^3}\, \varphi_m^{\lambda''} \tag{17}$$

and if we let m go to infinity

$$\varphi(\beta;\, V_i, N_i) \geqslant \varphi^{\lambda''} \quad \text{for} \quad i > i'' , \tag{18}$$

(13) and (18) show for any given $\varepsilon > 0$ one can find i''' such that

$$\varphi^{\lambda} - \varepsilon < \varphi(\beta;\, V_i, N_i) < \varphi^{\lambda} + 2\,\varepsilon \quad \text{for} \quad i > i''' . \tag{19}$$

Therefore

$$\lim_{i \to \infty} \varphi(\beta;\, V_i, N_i) = \varphi^{\lambda} .$$

Theorem 1. *Let $(N_i)_{1 \leqslant i < \infty}$ be a sequence of positive integers such that $N_i \to \infty$ and $(V_i)_{1 \leqslant i < \infty}$ a sequence of positive numbers such that $V_i/N_i \to v > (a^3/\sqrt{2})$. If one denotes again by V_i the cube with volume V_i the sequence $\varphi(\beta;\, V_i, N_i)_{1 \leqslant i < \infty}$ converges*

$$\lim_{i \to \infty} \varphi(\beta;\, V_i, N_i) = \varphi(\beta, v) \tag{20}$$

and its limit depends only on β and v.

This result has been obtained for cubic domains but it might easily be extended to more general cases. The function $f(\beta, v)$ related to $\varphi(\beta, v)$ by (3) may be interpreted as the thermodynamical free energy per particle at temperature $T = \beta^{-1}$ and for specific volume v.

3. Properties of the free energy per particle

We have found in the last section that $\varphi(\beta, v)$ is a continuous and decreasing function of v. We will prove that it is also convex*).

Let indeed $(a^3/\sqrt{2}) < v < v'$, v/v' rational. We may then write

$$v = \frac{\lambda^3}{n}, \qquad v' = \frac{\lambda^3}{n'}$$

and

$$\varphi\left(\beta;\, \Lambda^{\lambda}_{m+1}, 2^{3m}\, 4\,(n + n')\right) < \frac{n}{n + n'}\, \varphi(\beta;\, \Lambda^{\lambda}_{m}, 2^{3m}\, n) + \frac{n'}{n + n'}\, \varphi(\beta;\, \Lambda^{\lambda}_{m}, 2^{3m}\, n') . \tag{1}$$

Letting m go to infinity we get

$$\varphi\left(\beta, \frac{2}{v^{-1} + v'^{-1}}\right) \leqslant \frac{v^{-1}}{v^{-1} + v'^{-1}}\, \varphi(\beta, v) + \frac{v'^{-1}}{v^{-1} + v'^{-1}}\, \varphi(\beta, v') . \tag{2}$$

(2) and the continuity of φ as a function of v imply its convexity. Let us now come back to the sequences $(N_i)_{1 \leqslant i < \infty}$, $(V_i)_{1 \leqslant i < \infty}$ of theorem 1. If we write

$$\mu_i(\xi) = \frac{1}{N_i\,!} \int\limits_{(V_i)^{N_i}} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_{N_i}\, \delta\left[\xi - U_{N_i}(\underline{x}) + \frac{N_i}{2}\left(A\,\frac{N_i}{V_i} - B\right)\right], \tag{3}$$

*) Convexity and concavity will here be defined with respect to the negative part of the ordinate axis.

μ_i is a positive measure, with support in the positive part of the real line and such that $\| \mu_i \| \leqslant (V_i^{N_i}/N_i!)$. We have

$$\int d\xi \, e^{-\beta\xi} \, \mu_i(\xi) = e^{-N_i \psi_i(\beta)} , \tag{4}$$

$$\psi_i(\beta) = \beta \left[\varphi(\beta; V_i, N_i) - \frac{1}{2} \left(A \frac{N_i}{V_i} - B \right) \right] . \tag{5}$$

According to (4), $\psi_i(\beta)$ is an increasing and concave function of β.

When i goes to infinity it converges pointwise towards $\psi(\beta, v) = \beta \, [\varphi(\beta, v) - (\{A/v\} - B)/2]$. $\psi(\beta, v)$ is thus an increasing and concave function of β, and the same applies to $\psi'(\beta, v) = \beta \, [\varphi(\beta, v) - (\{A/v_2'\} - B)/2]$ when $(a^3/\sqrt{2}) < v \leqslant v_2'$. $\psi'(\beta, v)$ is also an increasing and convex function of v.

Let

$$\left.\begin{aligned} & 0 < \beta_1' < \beta_1 < \beta_2 < \beta_2' , \quad \frac{a^3}{\sqrt{2}} < v_1' < v_1 < v_2 < v_2' , \\ & K' = \{(\beta, v) : \beta_1' \leqslant \beta \leqslant \beta_2', v_1' \leqslant v \leqslant v_2'\} , \\ & \qquad\qquad K = \{(\beta, v) : \beta_1 \leqslant \beta \leqslant \beta_2, v_1 \leqslant v \leqslant v_2\} , \end{aligned}\right\} \tag{6}$$

$\psi'(\beta, v)$ is bounded on K' since $\psi'(\beta_1', v_2') \leqslant \psi'(\beta, v) \leqslant \psi'(\beta_2', v_1')$. From this and the convexity properties of ψ' follows that $\partial\psi'/\partial\beta$ and $\partial\psi'/\partial v$ are bounded on K and therefore that ψ' is continuous with respect to (β, v).

Theorem 2: *The function $\beta \, \varphi(\beta, v)$, defined for $\beta > 0$, $v > (a^3/\sqrt{2})$, is continuous with respect to (β, v) concave in β decreasing and convex in v.*

It satisfies the inequalities

$$\beta \, \varphi(\beta, v) \geqslant \frac{\beta}{2} \left(\frac{A}{v} - B \right) - (\log v + 1) , \tag{7}$$

$$\beta \, \varphi(\beta, v) < - 3 \log (v^{1/3} - R) \quad \text{for} \quad v > R^3 . \tag{8}$$

The first part of the theorem may also be stated as follows: the function $\varphi(\beta, v)$, defined for $\beta^{-1} > 0$, $v > (a^3/\sqrt{2})$, is continuous with respect to (β^{-1}, v) concave in β^{-1}, decreasing and convex in v. The analogous properties for $f(\beta, v) = (3/2\,\beta) \log (2\,\pi\,\beta/m) + \varphi(\beta, v)$ are immediate.

There only remains to prove (8). To do this we use the notations of section 2 and take $n = 1$, $\lambda > R$. Then

$$(Q_0^\lambda)^{2^{3m}} < Q_m^\lambda , \quad Q_0^\lambda = (\lambda - R)^3 . \tag{9}$$

If we let m go to infinity we obtain the inequality

$$\beta \, \varphi_m^\lambda < - \log (\lambda - R)^3 , \tag{10}$$

which is identical to (8).

We will conclude this section by a remark on the way in which φ depends upon the potential.

Let $\mathcal{V}$ be the set of all potentials with the properties A and B. $\mathcal{V}$ is then a convex cone in the vector space it generates.

Let α', α'' be non-negative real numbers such that $\alpha' + \alpha'' = 1$.
If we write $\Phi = \alpha' \Phi' + \alpha'' \Phi''$; $\Phi', \Phi'' \in \mathcal{V}$ and

$$U'_n(\underline{x}) = \sum_{i<j} \Phi'(\boldsymbol{x}_j - \boldsymbol{x}_i), \quad U''_n(\underline{x}) = \sum_{i<j} \Phi''(\boldsymbol{x}_j - \boldsymbol{x}_i), \tag{11}$$

we obtain by HÖLDER's inequality

$$\left.\begin{aligned} Q_\Phi(\beta; \Lambda, n) = \frac{1}{n!} \int_{(\Lambda)^n} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_n \, (e^{-\beta U'_n(\underline{x})})^{\alpha'} \, (e^{-\beta U''_n(\underline{x})})^{\alpha''} \\ \leqslant [Q_{\Phi'}(\beta; \Lambda, n)]^{\alpha'} \, [Q_{\Phi''}(\beta; \Lambda, n)]^{\alpha''}. \end{aligned}\right\} \tag{12}$$

φ_Φ is thus a concave functional of Φ on $\mathcal{V}$:

$$\varphi_\Phi(\beta, v) \geqslant \alpha' \varphi_{\Phi'}(\beta, v) + \alpha'' \varphi_{\Phi''}(\beta, v). \tag{13}$$

4. Continuity of the function $p(v)$

We have seen in section 3 (theorem 2) that the pressure

$$p(\beta, v) = -\frac{\partial \varphi(\beta, v)}{\partial v} \tag{1}$$

is, for fixed β, a decreasing function of v.

We will now prove that for a potential Φ satisfying conditions A and B which is furthermore bounded, i.e. such that

$$\max |\Phi(\boldsymbol{x})| = M < +\infty \tag{2}$$

the function $p(v)$ is absolutely continuous. It would in fact be sufficient to assume that Φ is bounded almost everywhere. For a bounded potential we of course have $a = 0$.

Theorem 3. *For a bounded potential satisfying conditions A and B, p is a continuous decreasing function of v for $v > 0$ and fixed β. Its derivative with respect to v is a negative function, locally integrable and bounded.*

In fact, the hypothese made about Φ are probably too restrictive and one should be able to prove the continuity of $p(v)$ for $v > (a^3/\sqrt{2})$ in much more general cases (see for example[5]).

The proof of the theorem is based on the following result.

Lemma. *If the potential $\Phi(\boldsymbol{x})$ satisfies condition A [conditions A and B] one may write*

$$\Phi(\boldsymbol{x}) = \Phi'(\boldsymbol{x}) + \psi_2(\boldsymbol{x}), \tag{3}$$

where $\Phi'(\boldsymbol{x})$ satisfies condition A [conditions A and B] and $\psi_2(\boldsymbol{x})$ is a continuous strictly positive function of positive type.

Let indeed $\hat{\psi}(\boldsymbol{p})$ be a continuous non-negative function with compact support which depends only on $|\boldsymbol{p}|$ and does not vanish identically.

Then $\psi(\boldsymbol{x}) = \psi(-\boldsymbol{x}) = \psi(x)^*$, and the function

$$\psi_1(\boldsymbol{x}) = \psi(\boldsymbol{x})^2 = (2\pi)^{-3/2} \int d\boldsymbol{p}\, e^{i\boldsymbol{p}\boldsymbol{x}} (2\pi)^{-3/2} \int d\boldsymbol{q}\, \hat{\psi}(\boldsymbol{q})\, \hat{\psi}(\boldsymbol{p}-\boldsymbol{q}) \tag{4}$$

is non-negative and of positive type. It depends on $|\boldsymbol{x}|$ only and cannot vanish on an open set as a consequence of the PALEY-WIENER theorem[3]). Let us now write

$$\hat{\psi}_2(\boldsymbol{p}) = \hat{\psi}_1(\boldsymbol{p})^2 = \left[(2\pi)^{-3/2} \int d\boldsymbol{q}\, \hat{\psi}(\boldsymbol{q})\, \hat{\psi}(\boldsymbol{p}-\boldsymbol{q})\right]^2. \tag{5}$$

Then

$$\psi_2(\boldsymbol{x}) = (2\pi)^{-3/2} \int d\boldsymbol{y}\, \psi_1(\boldsymbol{y})\, \psi_1(\boldsymbol{x}-\boldsymbol{y})$$

is a strictly positive function depending only on $|\boldsymbol{x}|$ and satisfying condition A_2. If we write the decomposition

$$\Phi(\boldsymbol{x}) = \Phi_1(\boldsymbol{x}) + \Phi_2(\boldsymbol{x}),$$

where Φ_1 and Φ_2 satisfy respectively the conditions A and B one may always choose $\hat{\psi}(\boldsymbol{p})$ such that $\Phi_2(\boldsymbol{x}) - \psi_2(\boldsymbol{x})$ satisfies again condition A_2. The functions $\psi_2(\boldsymbol{x})$ and $\Phi'(\boldsymbol{x}) = \Phi_1(\boldsymbol{x}) + [\Phi_2(\boldsymbol{x}) + \psi_2(\boldsymbol{x})]$ satisfy then the conditions of the lemma.

Let now Φ be a bounded potential satisfying conditions A and B.

By using the inequality of SCHWARZ for a cube Λ of volume V one finds

$$\left.\begin{aligned}
&(n+1)!\, Q(\beta; \Lambda, n+1) = \int\limits_{(\Lambda)^n} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_n\, e^{-\beta U_n(\underline{x})} \int\limits_{\Lambda} d\boldsymbol{x}_{n+1} \\
&\times \exp\left[-\beta \sum_{i=1}^{n} \Phi(\boldsymbol{x}_{n+1} - \boldsymbol{x}_i)\right] \leqslant \left[\int\limits_{(\Lambda)^n} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_n\, e^{-\beta U_n(\boldsymbol{x})}\right]^{1/2} \\
&\times \left[\int\limits_{(\Lambda)^{n+2}} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_n\, d\boldsymbol{x}_{n+1}\, d\boldsymbol{x}_{n+2}\, e^{-\beta U_n(\underline{x})} \prod_{\alpha=1}^{2} \exp\left[-\beta \sum_{i=1}^{n} \Phi(\boldsymbol{x}_{n+\alpha} - \boldsymbol{x}_i)\right]\right]^{1/2} \\
&\qquad = [n!\, Q(\beta; \Lambda, n)]^{1/2} \left[\int\limits_{(\Lambda)^{n+2}} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_{n+2}\, e^{-\beta U_{n+2}(\underline{x})}\, e^{\beta \Phi(\boldsymbol{x}_{n+2} - \boldsymbol{x}_{n+1})}\right]^{1/2}.
\end{aligned}\right\} \tag{6}$$

Therefore

$$\left.\begin{aligned}
&\frac{n+1}{n+2} \frac{[Q(\beta; \Lambda, n+1)]^2}{Q(\beta; \Lambda, n)} \\
&\qquad \leqslant \frac{1}{(n+2)!} \int\limits_{(\Lambda)^{n+2}} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_{n+2}\, e^{-\beta U_{n+2}(\underline{x})}\, e^{\beta \Phi(\boldsymbol{x}_{n+2} - \boldsymbol{x}_{n+1})}.
\end{aligned}\right\} \tag{7}$$

For any bounded measurable function $\Psi(\boldsymbol{x})$ depending only on $|\boldsymbol{x}|$ we write

$$\left.\begin{aligned}
&\varphi_{\Phi}^{(1)}(\beta; \Lambda, n)(\Psi) = \left[\frac{d}{dh} \varphi_{\Phi + h\Psi}(\beta; \Lambda, n)\right]_{h=0} \\
&\qquad = \frac{n-1}{2} \frac{\int\limits_{(\Lambda)^n} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_n\, e^{-\beta U_n(\underline{x})}\, \Psi(\boldsymbol{x}_n - \boldsymbol{x}_{n-1})}{\int\limits_{(\Lambda)^n} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_n\, e^{-\beta U_n(\underline{x})}}.
\end{aligned}\right\} \tag{8}$$

This definition allows us to rewrite (7) in the form

$$\frac{n+1}{n+2}\,\frac{[Q(\beta;\Lambda,n+1)]^2}{Q(\beta;\Lambda,n)\,Q(\beta;\Lambda,n+2)} \leqslant 1+\frac{2}{n+1}\,\varphi_{\Phi}^{(1)}(\beta;\Lambda,n+2)\,(e^{\beta\Phi}-1)\,. \tag{9}$$

Let now

$$m=\min_{x^2\leqslant R^2}\psi_2(x)\,, \tag{10}$$

where the function ψ_2 is given by the above lemma.

According to (2) and (10), the potential

$$\Phi(h)=\Phi+h\,(e^{\beta\Phi}-1) \tag{11}$$

satisfies the conditions A and B as soon as

$$-\frac{m}{e^{\beta M}-1}\leqslant h\,, \tag{12}$$

(For $h\geqslant 0$, this is a consequence of the inequality $\beta\,\Phi(x)\leqslant e^{\beta\,\Phi(x)}-1$). When (12) is satisfied $\varphi_{\Phi(h)}(\beta;\Lambda,n)$ and $\varphi_{\Phi(h)}(\beta,v)$ are both well defined concave functions of h.

Let $0<v_1<v_2$ and $0<h_1<h_2=m/(e^{\beta M}-1)$. We have

$$\varphi_{\Phi}^{(1)}(\beta;\Lambda,n)\,(e^{\beta\Phi}-1)\leqslant\frac{\varphi_{\Phi(-h_1)}(\beta;\Lambda,n)-\varphi_{\Phi(-h_2)}(\beta;\Lambda,n)}{h_2-h_1}\,, \tag{13}$$

$\varphi_{\Phi(h)}(\beta;\Lambda,n)$ is a continuous decreasing function of $v=V/n$ for fixed β, h and n. It converges towards $\varphi_{\Phi(h)}(\beta,v)$ when n tends to infinity. This last function being also continuous and decreasing in v, it follows that the convergence is uniform for $v_1\leqslant v\leqslant v_2$.

For $v_1\leqslant v\leqslant v_2$ and fixed β, h the functions $\varphi_{\Phi(h)}(\beta;\Lambda,n)$ are thus bounded uniformly in n. It follows then from (13) that the functions $\varphi_{\Phi}^{(1)}(\beta;\Lambda,n)\,(e^{\beta\Phi}-1)$ are also bounded uniformly in n:

$$\varphi_{\Phi}^{(1)}(\beta;\Lambda,n)\,(e^{\beta\Phi}-1)\leqslant L<+\infty\quad\text{for}\quad v_1\leqslant\frac{V}{n}\leqslant v_2\,. \tag{14}$$

For $v_1\leqslant V/(n+2)\leqslant v_2$ we have thus, according to (9)

$$\frac{n+1}{n+2}\,\frac{[Q(\beta;\Lambda,n+1)]^2}{Q(\beta;\Lambda,n)\,Q(\beta;\Lambda,n+2)}\leqslant 1+\frac{2}{n+1}\,L\,. \tag{15}$$

Therefore

$$\left.\begin{aligned}&(n+2)\,\varphi(\beta;\Lambda,n+2)-2\,(n+1)\,\varphi(\beta;\Lambda,n+1)+n\,\varphi(\beta;\Lambda,n)\\&\qquad\leqslant\frac{1}{\beta}\left[\log\left(1+\frac{2}{n+1}\,L\right)+\log\frac{n+2}{n+1}\right]<\frac{2\,L+1}{\beta\,(n+1)}\,.\end{aligned}\right\} \tag{16}$$

Λ being fixed, the function $\varphi(\beta,\varrho^{-1};\Lambda)$ defined by

$$\varphi\left(\beta,\left(\frac{n}{V}\right)^{-1};\Lambda\right)=\varphi(\beta;\Lambda,n)\,,$$

when $\varrho\,V$ is an integer satisfies thus, for $\varrho=n/V$, the inequality

$$\left.\begin{aligned}&\left[\frac{n+2}{n}\,\varrho\,\varphi\left(\beta,\left(\frac{n+2}{n}\,\varrho\right)^{-1};\Lambda\right)-2\,\frac{n+1}{n}\,\varrho\,\varphi\left(\beta,\left(\frac{n+1}{n}\,\varrho\right)^{-1};\Lambda\right)\right.\\&\qquad\left.+\,\varrho\,\varphi(\beta,\varrho^{-1};\Lambda)\right]\left(\frac{\varrho}{n}\right)^{-2}<\frac{2\,L+1}{\beta}\,\frac{V}{n+1}\,.\end{aligned}\right\} \tag{17}$$

Let now k, l be positive integers such that $v_2^{-1} \leqslant n/V < (n+k+l)/V \leqslant v_1^{-1}$ one may then deduce from (17) that

$$\left.\begin{aligned}&\left[\frac{n+k+l}{n}\varrho\,\varphi\left(\beta, \left(\frac{n+k+l}{n}\varrho\right)^{-1}; \Lambda\right) - \frac{n+k}{n}\varrho\,\varphi\left(\beta, \left(\frac{n+k}{n}\varrho\right)^{-1}; \Lambda\right)\right.\\ &\left.-\frac{n+l}{n}\varrho\,\varphi\left(\beta, \left(\frac{n+l}{n}\varrho\right)^{-1}; \Lambda\right) + \varrho\,\varphi(\beta, \varrho; \Lambda)\right]\left(\frac{k\varrho}{n}\right)^{-1}\left(\frac{l\varrho}{n}\right)^{-1} < \frac{2L+1}{\beta v_1}.\end{aligned}\right\} \tag{18}$$

Thus, if ϱ, ϱ_1, ϱ_2 are positive numbers such that $v_2^{-1} \leqslant \varrho < \varrho + \varrho_1 + \varrho_2 \leqslant v_1^{-1}$, we have

$$\left.\begin{aligned}&[(\varrho+\varrho_1+\varrho_2)\,\varphi(\beta_1(\varrho+\varrho_1+\varrho_2)^{-1}) - (\varrho+\varrho_1)\,\varphi(\beta_1(\varrho+\varrho_1)^{-1})\\ &\qquad - (\varrho+\varrho_2)\,\varphi(\beta, (\varrho+\varrho_2)^{-1}) + \varrho\,\varphi(\beta, \varrho^{-1})]\,\varrho_1^{-1}\varrho_2^{-1} \leqslant \frac{2L+1}{\beta v_1}.\end{aligned}\right\} \tag{19}$$

The function $\varphi(\beta, v)$ being convex in v, it follows that the function $\varrho\,\varphi(\beta, \varrho^{-1})$ is convex in $\varrho = v^{-1}$.

The derivative $\partial/\partial\varrho\,(\varrho\,\varphi(\beta, \varrho^{-1})) = \psi(\varrho)$ exists a priori almost everywhere. If it exists at ϱ and $\varrho + \varrho_1$, $v_2^{-1} < \varrho < \varrho + \varrho_1 < v_1^{-1}$ we have according to (19)

$$\frac{\psi(\varrho+\varrho_1) - \psi(\varrho)}{\varrho_1} \leqslant \frac{2L+1}{\beta v_1}, \tag{20}$$

which shows that $\psi(\varrho)$ may be extended to a continuous function for $v_2^{-1} < \varrho < v_1^{-1}$ (20) furthermore insures that $\psi(\varrho)$ is the indefinite integral of a bounded integrable function[2]).

Theorem 3 follows then immediately.

5. Grand canonical ensemble

In what follows we will limit ourselves*) to the study of potentials for which $a = 0$.

Let again Λ be a cube of volume V and let β, z be positive numbers. We write $Q(\beta; \Lambda, 0) = 1$ and define a function p by the following formula

$$e^{\beta V p(\beta, z; \Lambda)} = \Xi(\beta, z; \Lambda) = \sum_{n=0}^{\infty} z^n\, Q(\beta; \Lambda, n)\,. \tag{1}$$

According to (2.4) the series (1) has an infinite radius of convergence, in fact

$$z^n\, Q(\beta; \Lambda, n) \leqslant \frac{1}{n!}\,[z\,V\,e^{(1/2)\beta B}]^n \leqslant \left[z\,\frac{V}{n}\,e^{(1/2)\beta B+1}\right]^n, \tag{2}$$

β and z being fixed, let $v_0 = (1/2)\,z^{-1}\,e^{-(1/2)\beta B-1} > 0$. We obtain then

$$\sum_{n > \frac{V}{v_0}} z^n\, Q(\beta; \Lambda, n) \leqslant \sum_{n > \frac{V}{v_0}} \left(\frac{1}{2}\right)^n. \tag{3}$$

Let also $v_1 > z^{-1}\,e^{-(1/2)\beta B}$, then

$$\sum_{n < \frac{V}{v_1}} z^n\, Q(\beta; \Lambda, n) \leqslant \sum_{n < \frac{V}{v_1}} \left[z\,\frac{V}{n}\,e^{(1/2)\beta B+1}\right]^n < \frac{V}{v_1}\,[z\,v_1\,e^{(1/2)\beta B+1}]^{V/v_1}. \tag{4}$$

*) For the case $a > 0$, see [6]).

The last inequality follows from the fact that for $\alpha > 0$, $(\alpha/n)^n$ is an increasing function of n when $0 \leqslant n < \alpha\, e^{-1}$.

We have furthermore

$$\lim_{v_1 \to \infty} [z\, v_1\, e^{(1/2)\,\beta B + 1}]^{1/v_1} = 1\,. \tag{5}$$

Let $z = e^{\beta\gamma}$. It follows from (3, 8) that for any γ one may choose v so big that $\gamma - \varphi(\beta, v) > 0$. Let thus v be such that $\beta\,(\gamma - \varphi(\beta, v)) > \delta + \varepsilon$, $\delta > 0$, $\varepsilon > 0$. For big enough Λ, there always exists a positive integer n such that $n > (V/v)$ and $\beta\,(\gamma - \varphi(\beta; \Lambda, n)) > \delta$, then

$$\Xi(\beta, z; \Lambda) > z^n\, Q(\beta; \Lambda, n) > e^{\delta V/v}\,. \tag{6}$$

According to (5) one can fix v_1 such that

$$[z\, v_1\, e^{(1/2)\,\beta B + 1}]^{1/v_1} < e^{\delta/v} \tag{7}$$

and therefore, if Λ is big enough

$$\Xi(\beta, z; \Lambda) > \sum_{\frac{V}{v_1} \leqslant n \leqslant \frac{V}{v_0}} z^n\, Q(\beta; \Lambda, n) > \frac{1}{2}\,\Xi(\beta, z; \Lambda)\,. \tag{8}$$

We know that $\varphi\,(\beta; n\, v, n)$, which is a continuous decreasing function of v for $v > 0$ converges uniformly on the compacts towards $\varphi(\beta, v)$ when n goes to infinity.

From this follows that for $V/v_1 \leqslant n \leqslant V/v_0$ one may write

$$\left.\begin{aligned} Q(\beta; \Lambda, n) &= e^{-n\,\beta\,(\varphi(\beta, V/n) + \chi(\beta; \Lambda, n))}\,, \\ z^n\, Q(\beta; \Lambda, n) &= \exp \beta\, V \left[\frac{\gamma - \varphi(\beta, V/n)}{V/n} - \frac{n\,\chi}{V}\right], \end{aligned}\right\} \tag{9}$$

$$|\,\chi(\beta; \Lambda, n)\,| < \varepsilon(\beta, \Lambda)\,, \qquad \lim_{V \to \infty} \varepsilon(\beta, \Lambda) = 0\,. \tag{10}$$

We will now study the behaviour of $[\gamma - \varphi(\beta, v)]/v$ as a function of v. One has

$$\frac{\partial}{\partial v}\left(\frac{\gamma - \varphi(\beta, v)}{v}\right) = -\,\frac{1}{v^2}\left(\gamma - \varphi(\beta, v) + v\,\frac{\partial\varphi}{\partial v}\right), \tag{11}$$

$$\frac{\partial}{\partial v}\left(\gamma - \varphi(\beta, v) + v\,\frac{\partial\varphi}{\partial v}\right) = v\,\frac{\partial^2\varphi}{\partial v^2}\,. \tag{12}$$

From (12) it follows that the function $\gamma - \varphi(\beta, v) + v\,(\partial\varphi/\partial v)$ is increasing, because of (3, 7), it is negative when v is small enough. It must become positive when v is big enough. The inequality

$$\gamma - \varphi(\beta, v) \leqslant -\,v\,\frac{\partial\varphi}{\partial v} \quad \text{for} \quad v > 0\,, \tag{13}$$

would indeed imply, when $\gamma - \varphi > 0$

$$\frac{\partial}{\partial v}\,(\log\,(\gamma - \varphi)) \geqslant \frac{1}{v}\,, \qquad \log\,(\gamma - \varphi) \geqslant \log C\, v\,, \qquad \gamma - \varphi \geqslant C\, v\,, \tag{14}$$

with $C > 0$ in contradiction with (3, 7).

The function $[\gamma - \varphi(\beta, v)]/v$ has thus a maximum which occurs between v_0 and v_1. It follows then from (1), (8), (9), (10) that this maximum is the limit of $p(\beta, z; \Lambda)$ when V tends to infinity.

Theorem 4. *When V tends to infinity, $p(\beta, z; \Lambda)$ has a limit*

$$\lim_{V\to\infty} p(\beta, z; \Lambda) = p(\beta, z) = \max_{0<v<+\infty} \frac{\gamma - \varphi(\beta, v)}{v} \tag{15}$$

and if $\varphi - v\,(\partial\varphi/\partial v) = \gamma$, $z = e^{\beta\gamma}$, we have $p(\beta, z) = [\gamma - \varphi(\beta, v)]/v = -\,\partial\varphi/\partial v$.

We may thus identify $p(\beta, z)$ with the pressure and write $\gamma = g - (3/2\beta)\log(2\pi\beta/m)$ where g is the chemical potential.

We will conclude this section by a remark about the entire analytic function $\Xi(\beta, z; \Lambda)$ defined by (1) when z is made complex.

For $r \geqslant 0$, we have

$$\max_{|z|\leqslant r} \Xi(\beta, z; \Lambda) = \Xi(\beta, r; \Lambda)\,. \tag{16}$$

According to (3) and (2, 5) we have the inequalities

$$\left.\begin{aligned}
\Xi(\beta, r; \Lambda) &< 1 + \sum_{n<\frac{V}{v_0}} r^n\, Q(\beta; \Lambda, n) \leqslant 1 + \frac{V}{v_0} \max_n \left[r\,\frac{V}{n}\, e^{1+(1/2)\beta(B-A(n/V))}\right]^n \\
&\leqslant 1 + \frac{V}{v_0} \max_v \left[r\, v\, e^{1+(1/2)\beta(B-(A/v))}\right]^{V/v} \\
&= 1 + \frac{V}{v_0} \max_v \exp\left[\beta V\, \frac{(1/\beta)\,(\log v + 1) + (1/\beta)\log r + (B/2) - (1/2)\,A/v}{v}\right] \\
&\leqslant 1 + \frac{V}{v_0} \exp\left[\beta V \max_v \left(\frac{1}{\beta} + \left(\frac{1}{\beta}\log r + \frac{B}{2}\right)\frac{1}{v} - \frac{1}{2}\,\frac{A}{v^2}\right)\right] \\
&= 1 + V \exp\left[\beta V \left(\frac{1}{\beta} + \frac{1}{2}\,\frac{((1/\beta)\log r + (B/2))^2}{A}\right) - \log v_0\right] \\
&= 1 + V \exp\left[V + \frac{\beta V}{2A}\left(\frac{1}{\beta}\log r + \frac{B}{2}\right)^2 + \log 2r + \frac{1}{2}\beta B + 1\right].
\end{aligned}\right\} \tag{17}$$

Therefore

$$\lim_{r\to\infty} \frac{\log\log \Xi(\beta, r, \Lambda)}{\log r} = 0\,, \tag{18}$$

(16) and (18) show that the entire analytic function $\Xi(\beta, z; \Lambda)$ is of order zero*). From this follows that its zeros ζ_i are in infinite number, that for every $\varepsilon > 0$ the series $\sum_{i=1}^{\infty} |\zeta_i|^{-\varepsilon}$ converges and that

$$\Xi(\beta, z; \Lambda) = \prod_{i=1}^{\infty} \left(1 - \frac{z}{\zeta_i}\right), \tag{19}$$

where the infinite product in the right-hand side converges absolutely and uniformly on the compacts.

This allows us to generalize to the case of a potential satisfying conditions A and B and for which $a = 0$ the results obtained by YANG and LEE[6]) when $a > 0$. These results follow indeed directly from the theorem of STIELTJES-VITALI*).

*) See for instance [1]).

Conclusion

The aim of this note was to study in a rigorous manner the application of statistical mechanics to a classical system of particles in the limit where the system becomes infinite.

In several respects the results obtained here do not appear to be the best possible. This gives rise to interesting mathematical problems, for instance that of characterizing the continuous potentials such that

$$\sum_i \sum_j \Phi\,(\boldsymbol{x}_j - \boldsymbol{x}_i) \geqslant 0$$

for all systems of vectors x_i

On the other hand, it appears that our methods can be used to attack also the quantum mechanical problem, which has not been investigated up to now.

In conclusion I wish to thank Profs. R. JOST, M. FIERZ and H. ARAKI for interesting discussions and criticisms.

Note added in proof: Dr. M. E. FISHER has informed the author of the fact that he reached results similar to those described here by similar methods (using monotonicity to prove the existence of a limit, convexity to prove continuity). Dr. FISHER also pointed out the relevance of a paper by L. WITTEN [Phys. Rev. *93*, 1131 (1954)]. I am indebted to Dr. FISHER for correspondence on these questions.

It shoud be noted that no proof seems to exist for the fact that the closest-packing density ϱ_c of spheres is $\sqrt{2}/a^3$. Our proofs are however independent of this fact (except for the replacement of $a^3/\sqrt{2}$ by ϱ_c^{-1}).

Appendix. Potentials satisfying conditions *A* and *B*

The conditions A and B are satisfied in the following cases:

a. $\Phi(\boldsymbol{x}) \geqslant 0, \Phi(\boldsymbol{x}) = 0$ for $|\boldsymbol{x}| > R > 0$; $\Phi(\boldsymbol{x}) \geqslant A > 0$ in a neighbourhood of the origin.

b. $a > 0$; $\Phi(\boldsymbol{x}) = 0$ for $|\boldsymbol{x}| > R \geqslant \alpha$; $\Phi(\boldsymbol{x}) \geqslant A > -\infty$.

c. $\Phi(\boldsymbol{x}) = 4\,\varepsilon\,[(R/|\boldsymbol{x}|)^{12} - (R/|\boldsymbol{x}|)^6]$ (LENNARD-JONES potential).

d. $\Phi(\boldsymbol{x}) = \varepsilon\,(e^{-2\alpha(|\boldsymbol{x}|-R')} - 2\,e^{-\alpha(|\boldsymbol{x}|-R')})$ (MORSE potential) for $e^{\alpha R'} > 16$.

Let $\alpha(\boldsymbol{x})$ be a continuous non-negative function with compact support which depends only on $|\boldsymbol{x}|$ and does not vanish identically.

$$\beta(\boldsymbol{x}) = \int d\boldsymbol{y}\,\alpha(\boldsymbol{y})\,\alpha\,(\boldsymbol{x}-\boldsymbol{y}) = \int d\boldsymbol{p}\,e^{i\boldsymbol{p}\boldsymbol{x}}\,\hat{\alpha}(\boldsymbol{p})^2 \tag{1}$$

is of positive type and one may choose $\alpha(\boldsymbol{x})$ such that $\beta(\boldsymbol{x}) < \Phi(\boldsymbol{x})$ in the case a.

One may then take $\Phi_1 = \Phi - \beta$, $\Phi_2 = \beta$.

As far as b is concerned, from the relation

$$(2\,\pi)^{-3/2} \int d\boldsymbol{x}\,e^{-i\boldsymbol{p}\boldsymbol{x}}\,e^{-\alpha(\boldsymbol{x}^2-a^2)} = (2\,\alpha)^{-3/2}\,e^{\alpha a^2}\,e^{-\boldsymbol{p}^2/4\alpha}\,, \tag{2}$$

we see that the function

$$\gamma(\boldsymbol{x}) = e^{-\alpha(\boldsymbol{x}^2-a^2)} - e^{-\beta(\boldsymbol{x}^2-b^2)} \tag{3}$$

is of positive type as soon as

$$\alpha > \beta\,, \quad \frac{e^{\alpha a^2}}{(2\,\alpha)^{3/2}} > \frac{e^{\beta b^2}}{(2\,\beta)^{3/2}}\,, \tag{4}$$

a is fixed and $e^{-\alpha(x^2-a^2)} = 1$ for $|x| = a$. For α given, $\alpha > 0$, we may thus choose b and β such that $\gamma(x) < \Phi(x)$. Finally we may increase α and take it so big that the inequalities (4) are satisfied. We write then $\Phi_1 = \Phi - \gamma$, $\Phi_2 = \gamma$. For the LENNARD-JONES potential (c) we put

$$\Phi_2(x) = 4\,\varepsilon\left[\left(\frac{R^2}{x^2+\alpha^2 R^2}\right)^6 - 2\left(\frac{R^2}{x^2+\alpha^2 R^2}\right)^3\right], \quad 0 < \alpha^2 < \sqrt[3]{2} - 1\,. \tag{5}$$

We first prove that Φ_1 is positive. $\alpha^2 < \sqrt[3]{2} - 1$ implies $\sqrt[3]{2} - \alpha^2 > (\alpha^2/(\sqrt[3]{2} - 1))$. We have thus either $x^2 < \sqrt[3]{2} - \alpha^2$, i. e. $2\,(1/(x^2+\alpha^2))^3 > 1$ or $x^2 > (\alpha^2/(\sqrt[3]{2} - 1))$ i. e. $2\,(1/(x^2+\alpha^2))^3 > (1/x^2)^3$, Φ_1 is thus always positive as follows from the identity

$$\left.\begin{aligned}&\left(\frac{1}{x^2}\right)^3\left[\left(\frac{1}{x^2}\right)^3 - 1\right] - \left(\frac{1}{x+\alpha^2}\right)^3\left[\left(\frac{1}{x^2+\alpha^2}\right)^2 - 2\right]\\ &\quad = \left[\left(\frac{1}{x^2}\right)^3 - \left(\frac{1}{x^2+\alpha^2}\right)^3\right]\left[\left(\frac{1}{x^2}\right)^3 + \left(\frac{1}{x^2+\alpha^2}\right)^3 - 1\right] + \left(\frac{1}{x^2+\alpha^2}\right)^3.\end{aligned}\right\} \tag{6}$$

There remains to prove that

$$\left.\begin{aligned}&\left(\frac{1}{x^2+\alpha^2}\right)^3\left[\left(\frac{1}{x^2+\alpha^2}\right)^3 - 2\right]\\ &= \left[\left(\frac{1}{x^2+\alpha^2}\right)^3 - \sqrt[3]{2}\left(\frac{1}{x^2+\alpha^2}\right)^2\right]\left[\left(\frac{1}{x^2+\alpha^2}\right)^3 + \sqrt[3]{2}\left(\frac{1}{x^2+\alpha^2}\right)^2 + \sqrt[3]{4}\left(\frac{1}{x^2+\alpha^2}\right)\right]\end{aligned}\right\} \tag{7}$$

is of positive type. To do this we prove that each factor of the right-hand side is of positive type. We have namely

$$(2\pi)^{-3/2}\int dx\, e^{-ipx}\,(x^2+\alpha^2)^{-1} = \sqrt{\frac{\pi}{2}}\,\frac{e^{-p\alpha}}{p}, \tag{8}$$

$$(2\pi)^{-3/2}\int dx\, e^{-ipx}\,(x^2+\alpha^2)^{-2} = \sqrt{\frac{\pi}{2}}\,\frac{e^{-p\alpha}}{2\alpha}, \tag{9}$$

$$(2\pi)^{-3/2}\int dx\, e^{-ipx}\,(x^2+\alpha^2)^{-3} = \sqrt{\frac{\pi}{2}}\,\frac{e^{-p\alpha}}{4\alpha^2}\left(\frac{p}{2} + \frac{1}{2\alpha}\right). \tag{10}$$

The first factor is thus of positive type when α is sufficiently small, the second is also of positive type, being a sum of positive type functions.

For the MORSE potential (d.) we may take $\Phi_1 = 0$, it is indeed a function of positive type if $e^{\alpha R'} > 16$ since

$$(2\pi)^{-3/2}\int dx\, e^{-ipx}\,\Phi(x) = \varepsilon\,\frac{8\alpha}{\sqrt{2\pi}}\,e^{\alpha R'}\left[\frac{e^{\alpha R'}}{(p^2+4\alpha^2)^2} - \frac{1}{(p^2+\alpha^2)^2}\right]. \tag{11}$$

Bibliography

1) H. MILLOUX et C. PISOT, Traité de théorie des fonctions. T.I. Fasc. 1. Gauthier-Villars. Paris (1953).

2) F. RIESZ et B. SZ-NAGY, Leçons d'analyse fonctionnelle. 3e éd. Acad. Sc. Hongrie. Budapest (1954).

3) L. SCHWARTZ, Théorie des distributions. vol. 2, 2e éd. Hermann. Paris (1959).

4) L. VAN HOVE, Physica, *15*, 951 (1949).

5) L. VAN HOVE, Physica, *16*, 137 (1950).

6) C. N. YANG and T. D. LEE. Phys. Rev. *87*, 404 (1952).