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A SOLUBLE MODEL FOR A SYSTEM WITH NEGATIVE SPECIFIC HEATP. Hertel^{*)}

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ABSTRACT

The statistical mechanics of an explicitly soluble model is investigated where classical particles interact by an attractive, quasi-translation invariant but particle number dependent potential. Two phases result: one gaseous, the other consisting of gas and one cluster of condensed matter. In the microcanonical ensemble there is a region of negative specific heat and a transition between the two phases at a certain energy where temperature and density jump. In the canonical ensemble -- which is not equivalent to the former in this region -- the phase transition manifests itself by a jump in energy and density at the transition temperature.

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1. INTRODUCTION

In a recent paper¹⁾ one of the present authors (W.T.) studied the thermodynamic behaviour of a system of particles which attract each other by their gravitational forces. He arrived at the conjecture that such a system-- if the micro-canonical ensemble is studied-- exhibits negative specific heat. The corresponding instability is obviously of crucial importance for astrophysics and had previously been discussed by Lynden-Bell and Wood²⁾.

To substantiate these findings the following model was investigated in Ref. 1. The volume V , inside which the N particles are confined to move, contains a condensation region V_0 . The potential between two particles is

$$U^{(2)}(\underline{x}_j, \underline{x}_k) = \begin{cases} -2U_0 & \text{if } \underline{x}_j \text{ and } \underline{x}_k \text{ are inside } V_0 \\ 0 & \text{otherwise,} \end{cases} \quad (1)$$

the total potential energy is

$$U(\underline{x}_1, \underline{x}_2, \dots, \underline{x}_N) = \frac{1}{2} \sum_{j \neq k} U^{(2)}(\underline{x}_j, \underline{x}_k) . \quad (2)$$

The phase space integration can be done and results in the following relation between temperature T , energy E , volume V , and number N of particles ($k = \text{Boltzmann's constant} = 1$):

$$\frac{T}{NU_0} = f\left(\frac{E}{N^2U_0} + 1, \frac{V}{V_0}\right) \text{ for large } N \quad (3)$$

with

$$f(\epsilon, M) = \frac{2}{3} \lim_{N \rightarrow \infty} \frac{\sum_{k=0}^N \theta(\epsilon - \epsilon_k) (\epsilon - \epsilon_k)^{(3N/2)} \binom{N}{k} (M-1)^{-k}}{\sum_{k=0}^N \theta(\epsilon - \epsilon_k) (\epsilon - \epsilon_k)^{(3N/2)-1} \binom{N}{k} (M-1)^{-k}}$$

$$\epsilon_k = 1 - \frac{k(k-1)}{N(N-1)} . \quad (4)$$

For sufficiently large values of M there is a region of energy where $f(\epsilon, M)$ decreases if ϵ increases, i.e. a region of negative specific heat.

The stimulus for this note is the following possible objection to the relevance of the model.

A certain region of space within the volume V was singled out to provide for attraction between particles. Therefore, just one cluster of condensed matter can form. One may think that if there were many condensation regions, more than one cluster of condensed matter would form and, possibly, more than one phase transition could result. In particular, one might wonder whether a cluster is stable or tends to split up-- which was not possible in the simple model described above.

2. EXTENDED MODEL

Here we shall analyse an extension of the original model in which clusters may form everywhere.

Let the volume V be divided into M cubic (say) boxes with equal volume V_0 . We now assume a potential

$$U^{(2)}(\underline{x}_j, \underline{x}_k) = \begin{cases} -2U_0 & \text{if } \underline{x}_j \text{ and } \underline{x}_k \text{ in the same box} \\ 0 & \text{otherwise} \end{cases} \quad (5)$$

which is quasi-translation invariant. $V_0^{1/3}$ measures the range of the interaction, U_0 its strength. We keep M fixed and study the limit $N \rightarrow \infty$ with $V_0 \sim N$, $U_0 \sim N^{-1}$. This particular limit is similar to that in the well-known investigation of the van der Waals gas³⁾ and assures that entropy and energy are extensive quantities, $S \sim N$, $E \sim N$.

We describe a particular configuration by stating that there are

- a) n_i particles in the cell labelled i ($i = 1, 2, \dots, M$); or
- b) σ_ℓ boxes containing ℓ particles each.

Thus the following restrictions hold:

$$n_i \in \{0, 1, \dots, N\}, \quad \sum_{i=1}^M n_i = N \quad (6)$$

or

$$\sigma_\ell \in \{0, 1, \dots, M\}, \quad \sum_{\ell=0}^N \sigma_\ell = M, \quad \sum_{\ell=0}^N \ell \sigma_\ell = N \quad (7)$$

There is a (finite even in the limit $N \rightarrow \infty$) degeneracy: $M! / (\sigma_1! \cdot \sigma_2! \cdot \dots \sigma_N!)$ different n -configurations correspond to the same σ -configuration.

The potential energy for a given configuration is

$$U_n = -U_0 \sum_{i=1}^M n_i (n_i - 1) \quad (8)$$

or

$$U_\sigma = -U_0 \sum_{\ell=0}^N \ell(\ell - 1) \sigma_\ell. \quad (9)$$

The integration over configuration space can be written as^{1,4)}

$$\int_V d^3x_1 \int_V d^3x_2 \dots \int_V d^3x_N = N! V_0^N \sum_n \left(\prod_{i=1}^M n_i! \right)^{-1}, \quad (10)$$

where the sum extends over all n -configurations $n = (n_1, n_2, \dots, n_M)$ compatible with Eq. (6). From this one easily derives the analogous expression

$$\int_V d^3x_1 \int_V d^3x_2 \dots \int_V d^3x_N = N! M! V_0^N \sum_\sigma \left[\prod_{\ell=0}^N \sigma_\ell! (\ell!)^{\sigma_\ell} \right]^{-1}, \quad (11)$$

where the sum extends over all σ -configurations $\sigma = (\sigma_0, \sigma_1, \dots, \sigma_N)$ compatible with Eq. (7).

We are now prepared to study the microcanonical and the canonical ensembles.

3. THE MICROCANONICAL ENSEMBLE

The volume of phase space $\Omega(E)$ below the energy shell is

$$\begin{aligned}
 \Omega(E) &= \int d^{3N}p \int_V d^{3N}x \, \theta\left(E - \frac{1}{2m} \sum_{k=1}^N \vec{p}_k^2 - U\right) \\
 &= (2m\pi)^{3N/2} \frac{1}{\left(\frac{3N}{2}\right)!} \int_V d^{3N}x \, \theta(E - U) (E - U)^{3N/2} \\
 &= (2m\pi)^{3N/2} \frac{N! V_0^N}{\left(\frac{3N}{2}\right)!} \sum_n \frac{\theta(E - U_n) (E - U_n)^{3N/2}}{\prod_{i=1}^M n_i!} \\
 &= (2m\pi)^{3N/2} \frac{N! M! V_0^N}{\left(\frac{3N}{2}\right)!} \sum_{\sigma} \frac{\theta(E - U_{\sigma}) (E - U_{\sigma})^{3N/2}}{\prod_{\ell=0}^N \sigma_{\ell}! (\ell!)^{\sigma_{\ell}}} \quad (12)
 \end{aligned}$$

where the sums extend over all admissible n and σ -configurations, respectively.

For large N the sums can be replaced by the largest term [this statement can easily be made mathematically rigorous⁵⁾], the configuration to which it corresponds will be denoted by n or σ , respectively. We then obtain for the entropy per particle

$$\begin{aligned}
 \frac{S}{N} &= \frac{1}{N} \log \frac{\Omega}{N!} = \text{const} + \frac{1}{2} \log (U_0^3 V_0^2 N) + \chi \\
 \chi &= \frac{3}{2} \log \left[\epsilon - 1 + \sum_{i=1}^M \left(\frac{n_i}{N} \right)^2 \right] - \sum_{i=1}^M \left(\frac{n_i}{N} \right) \left(\log \frac{n_i}{N} - 1 \right) \\
 &= \frac{3}{2} \log \left[\epsilon - 1 + \sum_{\ell=0}^N \sigma_{\ell} \left(\frac{\ell}{N} \right)^2 \right] - \sum_{\ell=0}^N \sigma_{\ell} \frac{\ell}{N} \left(\log \frac{\ell}{N} - 1 \right), \quad (13)
 \end{aligned}$$

where $\epsilon = 1 + E/N^2 U_0$. We have applied Stirling's formula for $n_i!$ and $l!$ and dropped all terms of order N^{-1} .

We must now find the configuration of Eq. (13) which maximizes χ , i.e. the point $\alpha_i = n_i/N$ ($i = 1, 2, \dots, M$) on the simplex

$$1 \geq \alpha_i \geq 0, \quad \sum_i \alpha_i = 1$$

for which

$$\chi = \frac{3}{2} \log \left(\epsilon - 1 + \sum_i \alpha_i^2 \right) - \sum_i \alpha_i (\log \alpha_i - 1)$$

is maximal.

Consider the set K of points in the simplex where

$$\epsilon - 1 + \sum_i \alpha_i^2 \geq 0.$$

This set is compact. χ can be considered as a continuous mapping of K into the extended real line and hence has a maximum (which is actually $< \infty$). Since this is not assumed on the boundary of K (either $\chi \rightarrow -\infty$ or a partial derivative $\chi, i \rightarrow +\infty$ if α tends towards the boundary of K) the maximum will be attained in the interior of K where χ is differentiable. Therefore

$$\delta\chi = \sum_i \delta\alpha_i \left\{ \frac{3}{2} \frac{2\alpha_i}{\epsilon - 1 + \sum_j \alpha_j^2} - \log \alpha_j \right\} \quad (14)$$

has to vanish for a displacement compatible with $\sum_i \delta\alpha_i = 0$. We conclude that all brackets in Eq. (14) have to be independent of i , i.e. a constant.

However, the equation

$$\frac{2\alpha}{\theta} - \log \alpha = \text{const} \quad (15)$$

with

$$\frac{3}{2} \vartheta = \epsilon - 1 + \sum_{j=1}^M \alpha_j^2 \quad (16)$$

has two solutions μ and ν , $\mu \leq \nu$, only. Introducing their ratio

$$b = \frac{\mu}{\nu}, \quad 0 \leq b \leq 1$$

we find

$$\mu = -\frac{\vartheta}{2} b \frac{\log \frac{1}{b}}{1-b} \quad (17)$$

$$\nu = -\frac{\vartheta}{2} \frac{\log \frac{1}{b}}{1-b}.$$

Note that ϑ is essentially the temperature:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{1}{NU_0} \frac{\partial \chi}{\partial \epsilon} = \frac{1}{NU_0} \left\{ \frac{1}{\vartheta} + \sum_i \chi_{,i} \frac{\partial \alpha_i}{\partial \epsilon} \right\}.$$

Since $\chi_{,i}$ is independent of i and $\sum (\partial \alpha_i / \partial \epsilon) = 0$, we obtain

$$T = NU_0 \vartheta. \quad (18)$$

with ϑ of Eq. (16).

χ is stationary if, and only if, $M - g$ cells are occupied by $N\mu$ particles each and g cells by $N\nu$ particles each, μ and ν being related by Eq. (17).

We must now investigate whether this stationary point

$$\alpha = (\underbrace{\mu, \mu, \dots, \mu}_{M-g}; \underbrace{\nu, \nu, \dots, \nu}_g)$$

corresponds to a local maximum of χ . The condition for this is

$$\delta^2 \chi = \frac{1}{2} \sum_{i,k} \chi''_{ik} \delta \alpha_i \delta \alpha_k < 0$$

for a displacement compatible with $\sum_i \delta \alpha_i = 0$. The matrix of second derivatives is

$$\chi''_{ik} = \chi_{,ik} = \left(\frac{2}{\vartheta} - \frac{1}{\alpha_i} \right) \delta_{ik} - \frac{8}{3} \frac{\alpha_i \alpha_k}{\vartheta^2}. \quad (19)$$

Let us choose the following base of mutually orthogonal vectors:

$$\begin{aligned} \alpha^{(1)} &= (\underbrace{1, -1, 0, \dots, 0}_{M-g}; \underbrace{0, \dots, 0}_g) \\ \alpha^{(2)} &= (1, 1, -2, 0, \dots, 0; 0, \dots, 0) \\ \vdots \\ \alpha^{(M-g-1)} &= (1, 1, \dots, 1, 1+g-M; 0, \dots, 0) \\ \alpha^{(M-g)} &= (g, g, \dots, g; g-M, g-M, \dots, g-M) \\ \alpha^{(M-g+1)} &= (0, \dots, 0; 1, -1, 0, \dots, 0) \\ \alpha^{(M-g+2)} &= (0, \dots, 0; 1, 1, -2, 0, \dots, 0) \\ \vdots \\ \alpha^{(M-1)} &= (0, \dots, 0; 1, 1, \dots, 1-g) \\ \text{and} \\ \alpha^{(M)} &= \left(\frac{1}{M}, \frac{1}{M}, \dots, \frac{1}{M}; \frac{1}{M}, \frac{1}{M}, \dots, \frac{1}{M} \right). \end{aligned}$$

Any vector belonging to the simplex can be written in the form

$$\alpha_i = \sum_{r=1}^{M-1} a^{(r)} \alpha_i^{(r)} + \alpha^{(M)},$$

therefore the most general displacement is

$$\delta \alpha_i = \sum_{r=1}^{M-1} \delta a^{(r)} \alpha_i^{(r)}.$$

It is easy to check that

$$\sum_k \chi''_{ik} \alpha_k^{(r)} = \left(\frac{2}{\vartheta} - \frac{1}{\mu} \right) \alpha_k^{(r)} \quad (r = 1, 2, \dots, M-g-1)$$

$$\sum_k \chi''_{ik} \alpha_k^{(r)} = \left(\frac{2}{\vartheta} - \frac{1}{\nu} \right) \alpha_k^{(r)} \quad (r = M-g+1, \dots, M-1).$$

At least $(M - 2)$ basis vectors are eigenvectors of χ'' . Therefore

$$\delta^2 \chi = \sum_{r=1}^{M-1} \lambda^{(r)} \left(\delta a^{(r)} \right)^2$$

holds with

$$\lambda^{(r)} = \sum_{i,k} \chi''_{ik} a_i^{(r)} a_k^{(r)} \quad (r = 1, 2, \dots, M - 1) . \quad (20)$$

We conclude that the configuration $\alpha = (\mu, \dots, \mu; \nu, \dots, \nu)$ corresponds to a local maximum if all $\lambda^{(r)}$ are negative.

We distinguish between three cases:

I. Homogeneous distribution of particles
($g = 0$ or $b = 1$; $\mu = 1/M$)

The energy-temperature relation (16) reads

$$\frac{3}{2} \vartheta = \epsilon - 1 + \frac{1}{M} . \quad (21)$$

All $\lambda^{(r)}$ are equal: $\lambda^{(r)} = (2/\vartheta) - M$, thus we have a local maximum of χ if $\vartheta > 2/M$, i.e. if $\epsilon > 1 + (2/M)$.

II. One cluster and homogeneous distribution
of particles ($g = 1$, $b < 1$)

The energy-temperature relation is given in parametric form, the parameter being b = ratio of smaller/larger density

$$\nu(b) = \frac{1}{1 + b(M - 1)}$$

$$\mu(b) = b\nu(b)$$

(22)

$$\vartheta(b) = \frac{2\nu(b)(1 - b)}{\log \frac{1}{b}}$$

$$\epsilon(b) = 1 + \frac{3}{2} \vartheta(b) - (M - 1)[\mu(b)]^2 - [\nu(b)]^2 .$$

We find for the λ 's of Eq. (20):

$$\lambda^{(r)} = \frac{2}{\vartheta} - \frac{1}{\mu} = \frac{1}{\mu} \left(\frac{b \log \frac{1}{b}}{1-b} - 1 \right) < 0 \quad (r = 1, 2, \dots, M-2)$$

and

$$\lambda^{(M-1)} = (M-1) \left\{ \left(\frac{2}{\vartheta} - \frac{1}{\mu} \right) + (M-1) \left(\frac{2}{\vartheta} - \frac{1}{\nu} \right) - \frac{8}{3} \frac{(M-1)(\nu - \mu)^2}{\vartheta^2} \right\}. \quad (23)$$

From Eqs. (22) one can deduce

$$\left(\frac{2}{\vartheta} - \frac{1}{\mu} \right) + (M-1) \left(\frac{2}{\vartheta} - \frac{1}{\nu} \right) = - \frac{d\vartheta}{d\mu} \times \frac{2(\nu - \mu)}{\vartheta^2} \quad (24)$$

and

$$\left(\frac{2}{\vartheta} - \frac{1}{\mu} \right) + (M-1) \left(\frac{2}{\vartheta} - \frac{1}{\nu} \right) - \frac{8}{3} \frac{(M-1)(\nu - \mu)^2}{\vartheta^2} = - \frac{2}{3} \frac{d\epsilon}{d\mu} \times \frac{2(\nu - \mu)}{\vartheta^2}. \quad (25)$$

From Eqs. (23) and (25) we conclude that the configuration $\alpha = (\mu, \mu, \dots, \mu, \nu)$ locally maximizes χ as long as ϵ increases monotonically with b (hence with μ). It can be easily shown that there is a b_1 such that

$$\frac{d\epsilon(b_1)}{db_1} = \frac{d\epsilon(b_1)}{d\mu(b_1)} = \frac{d\epsilon(b_1)}{d\vartheta(b_1)} = 0, \quad \lambda^{(M-1)} < 0 \quad \text{for} \quad 0 \leq b < b_1, \quad (26)$$

and thus there is a local maximum for

$$0 \leq \epsilon \leq \epsilon(b_1).$$

III. Many clusters and homogeneous distribution of particles ($1 < g < M$, $0 \leq b < 1$)

In this case at least one λ of Eq. (20) is positive,

$$\lambda^{(M-1)} = \frac{2}{\vartheta} - \frac{1}{\nu} = \frac{1}{\nu} \left(\frac{\log \frac{1}{b}}{1-b} - 1 \right) > 0,$$

therefore configurations $\alpha = (\mu, \dots, \nu, \nu)$ do not even locally maximize χ .

We are thus left with phase I and phase II, a phase corresponding to a local maximum of χ . There is a region of energy

$$1 + \frac{2}{M} < \epsilon < \epsilon(b_1) = \epsilon_1$$

where both phases coexist.

At a certain b_2 ($b_2 \leq b_1$) the equality $\chi_I = \chi_{II}$ will be fulfilled with

$$\begin{aligned} \chi_I &= \frac{3}{2} \log \left(\epsilon_2 - 1 + \frac{1}{M} \right) - \left(\log \frac{1}{M} - 1 \right), \\ \chi_{II} &= \frac{3}{2} \log [\epsilon_2 - 1 + (M-1) \mu_2^2 + \nu_2^2] - (M-1) \mu_2 (\log \mu_2 - 1) - \\ &\quad - \nu_2 (\log \nu_2 - 1), \end{aligned} \quad (27)$$

$$\epsilon_2 = \epsilon(b_2) \text{ of Eq. (22), etc.}$$

Thus, for $\epsilon < \epsilon_2$ the points (ϑ, ϵ) on phase II [Eqs. (22)], for $\epsilon > \epsilon_2$ the points (ϑ, ϵ) on phase I [Eq. (21)] maximize χ . At energy ϵ_2 the transition between the two phases (between points 2 and 3 of Figs. 1 to 4) occurs.

From Eqs. (24) and (25) one easily deduces that there is a $\bar{b}_1 < b_1$ such that

$$\frac{d\vartheta(\bar{b}_1)}{d\epsilon(\bar{b}_1)} = 0, \quad \frac{d\vartheta(b)}{d\epsilon(b)} < 0 \quad \text{for} \quad \bar{b}_1 < b < b_1. \quad (28)$$

Since the (microcanonical) transition energy turns out to be larger than $\bar{\epsilon}_1 = \epsilon(\bar{b}_1)$ we encounter a region of negative specific heat.

We demonstrated the existence of two distinct phases by finding the n-type configuration which maximizes χ . Although for phase II the solution is M-fold degenerate (since any of the M boxes can be occupied with higher density), the entropy per particle is altered by $N^{-1} \log M$ only which vanishes for $N \rightarrow \infty$. For a direct evaluation on a computer of the sum in Eq. (12), the formulation in terms of σ -configurations is, however, essential. It is remarkable that already a system of 20 particles has statistical properties which approximate those for $N \rightarrow \infty$ to within a few per cent.

4. THE CANONICAL ENSEMBLE

We have to calculate

$$Q(T) = \frac{1}{N!} \int d^3N_p \int_{V^N} d^3N_x e^{-T^{-1}[(1/2m) \sum_{k=1}^N \vec{p}_k^2 + U]} \quad (29)$$

for which we obtain with Eqs. (10) or (11)

$$\begin{aligned}
 Q(T) &= (2\pi T)^{3N/2} V_0^N \sum_n \frac{e^{T^{-1} U_0 \sum_{i=1}^M n_i (n_i - 1)}}{\prod_{i=1}^M n_i!} \\
 &= (2\pi T)^{3N/2} V_0^N M! \sum_{\sigma} \frac{e^{T^{-1} U_0 \sum_{\ell=0}^N \sigma_{\ell} \ell(\ell-1)}}{\prod_{\ell=0}^N \sigma_{\ell}! (\ell!)^{\sigma_{\ell}}} .
 \end{aligned} \tag{30}$$

If we again replace the sum by the largest term (it corresponds to a configuration denoted by n), we obtain for the free energy $F = -T \log Q$ the following expression:

$$\frac{F}{N} = \psi = -\frac{3}{2} \vartheta \log \vartheta - \sum_{i=1}^M \alpha_i^2 + \vartheta \sum_{i=1}^M \alpha_i (\log \alpha_i - 1) , \tag{31}$$

where we have again dropped a constant and terms of order N^{-1} . ϑ and α_i have the same meaning as in Section 3.

Our task is to find the configuration α_i which minimizes ψ . It is easily seen that the same equations are obtained as in the case of the microcanonical ensemble. However, when investigating whether the stationary points of case II correspond to a maximum of ψ one has to inspect

$$\bar{\lambda}^{(M-1)} = (M-1) \left(\frac{2}{\vartheta} - \frac{1}{\mu} \right) + (M-1)^2 \left(\frac{2}{\vartheta} - \frac{1}{\nu} \right)$$

instead of Eq. (23), since the matrix of second derivatives here is

$$\psi''_{ik} = \psi_{,ik} = \left(-2 + \frac{\vartheta}{\alpha_i} \right) \delta_{ik} .$$

Equation (24) assures that the points (ϑ, ϵ) , on phase II of Section 3, also minimize ψ as long as ϑ increases monotonically with b . Recall that

$$\frac{d\vartheta(\bar{b}_1)}{d\epsilon(\bar{b}_1)} = 0 , \quad \frac{d\epsilon(b_1)}{d\vartheta(b_1)} = 0$$

with $0 < \bar{b}_1 < b_1$.

Thus the points (ϑ, ϵ) of Eq. (22)

- locally minimize ψ for $0 < b < \bar{b}_1$,
- locally maximize χ for $0 < b < b_1$,
- lead to negative specific heat in the microcanonical ensemble for $\bar{b}_1 < b < b_1$.

For $M > 2$ there is a region of temperature ($\vartheta > 2/\mu$) where both phases coexist.

For a certain $\bar{b}_2$ the free energies on phase I and II will be equal: $\psi_I = \psi_{II}$ where

$$\begin{aligned}\psi_I &= -\frac{3}{2} \vartheta_2 \log \vartheta_2 - \frac{1}{M} + \vartheta_2 \left(\log \frac{1}{M} - 1 \right) \\ \psi_{II} &= -\frac{3}{2} \vartheta_2 \log \vartheta_2 - (M-1) \mu_2^2 - \nu_2^2 + \vartheta_2 [(M-1) \mu_2 (\log \mu_2 - 1) + \\ &\quad + \nu_2 (\log \nu_2 - 1)]\end{aligned}\tag{32}$$

and $\vartheta_2 = \vartheta(\bar{b}_2)$ of Eq. (22), etc.

Thus, for $\vartheta < \vartheta_2$ the points on phase II minimize ψ , for $\vartheta > \vartheta_2$ the points on phase I minimize ψ . At temperature ϑ_2 the (canonical) transition between the two phases (between points $\bar{2}$ and $\bar{3}$ of Figs. 1 to 4) occurs.

In all these discussions ϵ is essentially the mean energy since

$$E = F - T \frac{\partial F}{\partial T} = N^2 U_0 \left\{ \psi - \frac{\partial}{\partial \vartheta} \psi \right\} = N^2 U_0 (\epsilon - 1) .\tag{33}$$

Again the temperature dependence of the minimizing configuration gives no contribution.

The canonical transition temperature can also be calculated by a method analogous to that of Maxwell's line in the discussion of the van der Waals gas.

If ϵ_I is the energy corresponding to the canonical transition temperature ϑ_2 on phase I, ϵ_{II} the energy corresponding to ϑ_2 on phase II, then

$$\left(\int_{\epsilon_{II}}^{\epsilon_I} d\epsilon \frac{1}{\vartheta(\epsilon)} \right)_{\text{microcanonical ensemble}} = \frac{\epsilon_I - \epsilon_{II}}{\vartheta_2}\tag{34}$$

has to hold: the left-hand side is the entropy difference per particle as calculated in the microcanonical ensemble, the right-hand side is the same quantity as calculated in the canonical ensemble, and both must be equal. Thus in a $\vartheta^{-1}-\epsilon$ plot the straight line of the canonical ensemble cuts the microcanonical curve such that the areas above and below are equal (Fig. 4).

5. CONCLUDING REMARKS

The results of these investigations can be described as follows.

We study the entropy S [or $-(\text{free energy}) = -F$] in the microcanonical (or canonical) ensemble and find that for some values of energy E (or temperature T) there is only one relative maximum (apart from an inessential M -fold degeneracy), for others there are two, only one being the absolute maximum. These we called phases, and the phase transition occurs if one relative maximum becomes higher than the other.

In particular, in the microcanonical ensemble at high E there is only the maximum corresponding to homogeneous distribution of all particles. When lowering the energy at a certain value of E (point 1) the configuration with one cluster of condensed matter, the rest of the particles being homogeneously distributed, becomes also a relative maximum, its entropy S_{II} is, however, still below S_I . At the transition energy (points 2, 3) S_{II} becomes the larger of the two and there is a sudden change in density and an increase in temperature associated with it. This can be understood as follows. Since it is now statistically more favourable to have a cluster of larger density the potential energy becomes more negative and, since we stay at the same total energy, the kinetic energy and with it the temperature must increase. By decreasing the total energy further the density in the cluster becomes still larger, the potential even more negative and the temperature increases. This is the reason for the region of negative specific heat. If the energy is lowered too much, too large a fraction of particles form the cluster so that the specific heat will be that of an ideal gas again since the particles within a cluster do not exert forces on each other in this model.

In the canonical ensemble there is also a region of coexistence of the two phases with a transition point where one free energy overtakes the other. In a plot of S versus E (see Fig. 1) this means that the region of wrong curvature of S (negative specific heat C) is bridged by a straight line. This implies a finite change in S, E and the density at a certain fixed T and F . Thus the two ensembles are not identical in this region; as it must be C is always positive in the canonical ensemble, the $C < 0$ region being hidden in the phase transition. The physical reason for this is the instability of a system with negative specific heat in thermal contact with a heat bath^{1, 2)}.

The phase transitions in the two ensembles are of a somewhat unusual type. In the microcanonical ensemble we have a finite change in T at fixed E , thus there is not only no latent heat but also $C = 0$ at the transition point. In the canonical ensemble there is a latent heat, but this occurs for constant volume. The condensation encountered here differs from the condensation of an ordinary liquid where C_p but not C_v has a δ -like singularity.

We encounter a further peculiarity: the pressure, calculated in any ensemble, is just as if we had free particles: $P \cdot V = N \cdot T$. The reason for this is that the potential is not really translation invariant but fixed in space, therefore only the kinetic energy contributes to P .

Thus the phase transitions do not appear in a $P - V$ diagram, and the macro-canonical partition function is entire in the fugacity Z . It may seem paradoxical that the macrocanonical partition function $\exp(PV/T)$ is identical to the one for a system of free particles, but this is only the case when it is expressed in terms of T and N , not in T and Z .

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FIG.2

FIG.4