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THE CANONICAL ENSEMBLE REDEFINED - I:

FORMALISM

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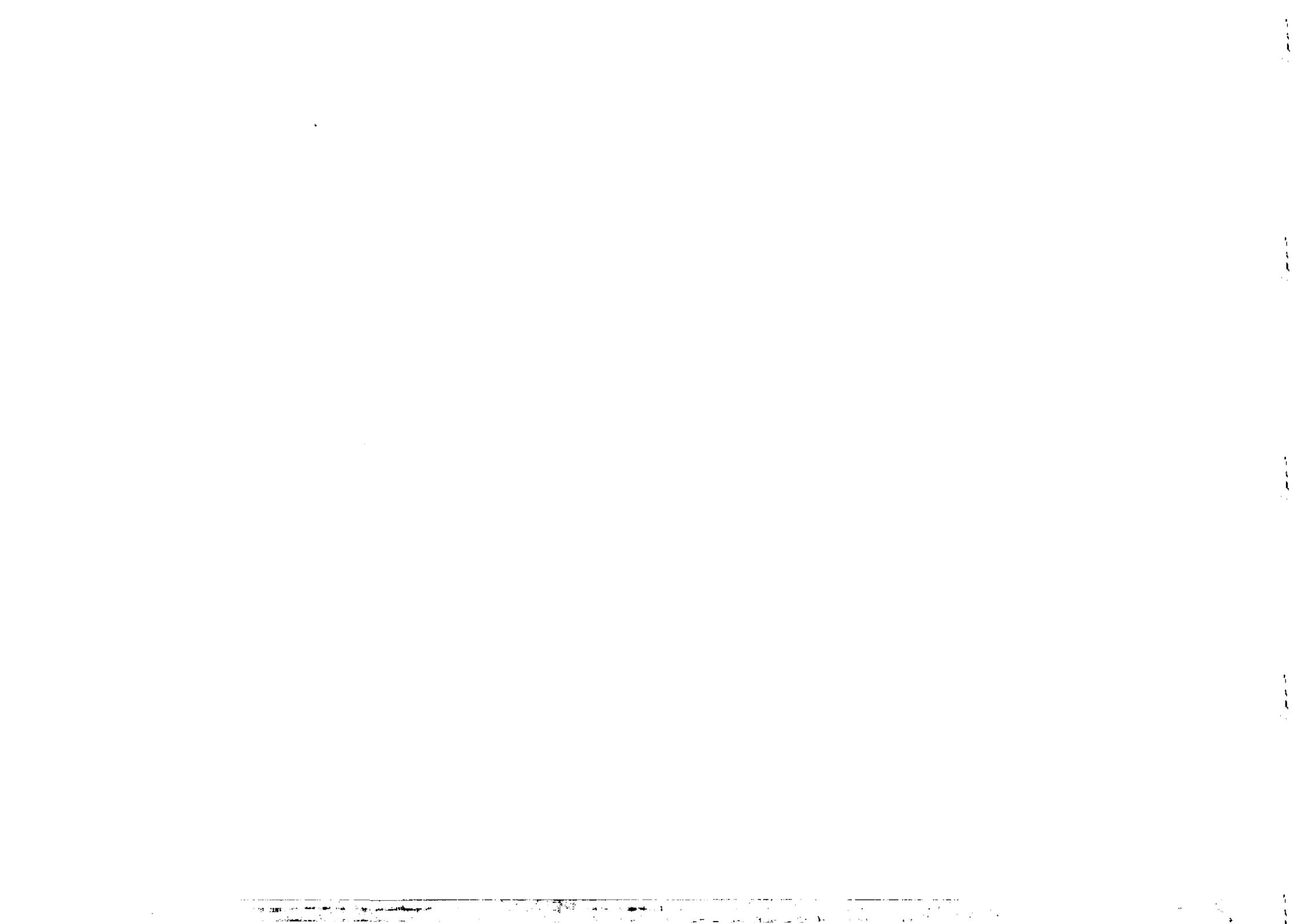


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THE CANONICAL ENSEMBLE REDEFINED - I:
FORMALISM *

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ABSTRACT

For studying the thermodynamic properties of systems we propose an ensemble that lies in between the familiar canonical and microcanonical ensembles. We point out the transition from the canonical to microcanonical ensemble and prove from a comparative study that all these ensembles do not yield the same results even in the thermodynamic limit. An investigation of the coupling between two or more systems with these ensembles suggests that the state of thermodynamical equilibrium is a special case of statistical equilibrium.

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I. INTRODUCTION

In studying the thermodynamic properties of systems using statistical mechanics we restrict ourselves to a constant energy surface since we know that the energy of the system under consideration is constant. The basic assumption of ergodicity ¹⁾ which helps us replace the time average of physical observables by the corresponding phase averages, leads us, naturally, to a constant density on the energy surface given by

$$\rho = \text{constant} \quad \text{if } (E - \Delta E) \leq E \leq (E + \Delta E) \quad (1.1)$$

where $[\Delta E \ll E]$

= 0 otherwise .

The ensemble of systems represented by the above equation is called the microcanonical ensemble in which all the systems have the same energy E . For most physical systems the use of microcanonical ensemble turns out to be formidable. Gibbs also proposed the canonical ²⁾ ensemble. Starting from the two postulates viz. (i) for statistical equilibrium, the ensemble density ρ has to be a stationary state of Liouville's equation, i.e.

$$[\rho, H] = 0 \quad (1.2)$$

and that

$$\int \rho d\Gamma = 1 \quad (1.3)$$

where $d\Gamma$ is the volume element in phase space, he proposed

$$\rho = \exp(-\beta H) \quad (1.4)$$

"as the most simple form conceivable". He went ahead to identify β as $1/kT$ where T is the temperature and k is the Boltzmann constant, from the

structure of a Pfaff differential which is analogous to that of dF in thermodynamics. The ensemble of systems represented by equation (1.4) is called the canonical ensemble of Gibbs. It was only many years later that Jaynes³⁾ showed that both those ensembles can be derived from information theory. Starting from this theory we embark upon the redefined ensemble which lies in between the above-mentioned ensembles. It has the form

$$\rho = \exp(-\beta H - \gamma H^2) \quad (1.5)$$

In Section II we outline the method of information theory and derive all possible forms of density thereof. The main objective being the study of thermodynamic properties of systems we identify, in Section III, the coefficients β and γ in terms of the temperature and in that process understand the origin of the redefined ensemble. In Section IV we derive the analogous thermodynamical relations and suggest a recipe for calculating the thermodynamic properties. The coupling between two systems described by the redefined ensemble is investigated in Section V and the conditions for statistical and thermodynamical equilibria discussed. A comparative study of the mean energy and the fluctuations in all these ensembles is presented in Section VI and conclusive remarks comprise Section VII.

II INFORMATION THEORY AND ENSEMBLE DENSITIES

The method of information theory is but the method of most probable distribution involving Lagrange's undetermined multipliers. To find the most probable distribution ρ subject to the given set of constraints

$$\langle f_i \rangle = k_i \quad (2.1)$$

where k_i 's are constants, assign a statistical entropy to ρ defined by

$$S_\rho = -k \langle \ln \rho \rangle \quad (2.2)$$

In the above equations the brackets denote the averaging done with the density ρ and k in (2.2) is introduced for thermodynamical reasons. The least biased form of ρ is obtained by maximizing S_ρ or minimizing the information (negentropy) subject to the constraints (2.1). Introducing the normalization of ρ as one of the constraints, we have for any small variation

$$\delta \left[\int d\Gamma \rho \left[-k \ln \rho - \sum_i k_i f_i \right] \right] = 0 \quad (2.3)$$

which yields

$$\rho = \exp \left(-\sum_i \alpha_i f_i \right) \quad (2.4)$$

α_i 's are Lagrange's undetermined multipliers to be determined from (2.1).

If we now specify that we do not know anything about the system except that the particle number and energy are fixed then on the constant energy surface we get

$$\rho = \exp(-\alpha) \quad (2.5)$$

which defines the microcanonical ensemble. $\exp(\alpha)$ would be the possible number of states with the energy E . If on the other hand we want to define the ensemble in such a way that the average value of the energy of the ensemble alone is fixed we get

$$\rho = \exp(-\alpha - \beta H) \quad (2.6)$$

which is the canonical ensemble and

$$\rho = \exp(-\alpha - \beta H - \gamma H^2) \quad (2.7)$$

would correspond to that ensemble obtained by conserving $\langle H \rangle$ and $\langle H^2 \rangle$. This ensemble is a subset of Gibbs ensemble and it encompasses the micro-

canonical ensemble. By conserving higher and higher powers of the H we would approach the microcanonical ensemble.

$$\rho = \exp\left(-\sum_i \beta_i H^i\right) \quad (2.8)$$

would represent any intermediate ensemble.

Like the canonical ensemble the redefined ensemble (2.7) can also be derived by the method of mean values (Darwin Fowler method). Having derived the formal expression (2.7) for ρ we now have to identify the coefficients B and γ .

III. IDENTIFICATION OF B and γ

The transition from statistical mechanics to thermodynamics is effected in one step where the statistical entropy of the microcanonical ensemble is identified as the thermodynamical entropy (S). From (2.2)

$$S = S_{MCE} = k \ln (\text{No. of possible states with the energy } E) \quad (3.1)$$

Once this identification is made the Lagrangian multipliers can be calculated. With this objective let us apply the principle of microcanonical ensemble to the system and the rest of the system. Let E_S, E_R and N_S, N_R denote the energy and particle number of the system and the rest of the system such that $E_S + E_R = E$. The density for the system would be directly proportional to the number of possible states $\omega'_R(E_R)$ for the rest of the system

$$\rho_S \propto \omega'_R(E_R) \quad (3.2)$$

$$S_{MCE}(E_R) = S_R(E) - E_S \left(\frac{\partial S_R}{\partial E_R}\right)_{E_R=E} + \frac{E_S^2}{2} \left(\frac{\partial^2 S_R}{\partial E_R^2}\right)_{E_R=E} \quad (3.3)$$

by Taylor expansion. On the right-hand side of (3.3) $S_{\rho}(E_R)$ has been replaced by S_R because of (3.1). From thermodynamics,

$$\left(\frac{\partial S_R}{\partial E_R}\right)_{E_R=E} = \frac{1}{T} \quad (3.4)$$

$$\left(\frac{\partial^2 S_R}{\partial E_R^2}\right)_{E_R=E} = -\frac{1}{T^2 C_V}$$

where T and C_V refer to the rest of the system. Using Eqs.(3.1) to (3.4) we get

$$\rho_S = \exp\left(\frac{S_R(E)}{k} - \frac{E_S}{kT} - \frac{E_S^2}{2kT^2 C_V} \dots\right) \quad (3.5)$$

Dropping the subscript S and replacing E_S by the Hamiltonian H , we have

$$\rho = \exp\left(-\beta H - \gamma H^2 \dots\right) \quad (3.6)$$

where $B = 1/kT$ and $\gamma = k\beta^2/2C_V$. In this equation whereas the first exponent varies as N_S the second varies as N_S^2/N_R . In the limit when N_S/N_R goes to zero the second and the higher order terms in H would vanish thus yielding Gibbs ensemble. This limit defines the concept of an infinite reservoir which is the requirement of an experimentalist. When he measures the temperature of the system he should do it in such a way that the system itself is not in the least disturbed and hence the need for putting the system in equilibrium with an infinite heat bath. Needless to say that it need not be and should not be used in the theoretical definition of equilibrium, for, if the system is in equilibrium every macroscopic subsystem should be in equilibrium with every other macroscopic subsystem. It must be added that Gibbs brings in the infinite heat bath only while interpreting $\exp(-\beta H)$ and not for defining the equilibrium state.

Thus when we relax the condition $N_S/N_R \rightarrow 0$, the higher order terms in H would no longer be negligible. For convenience let us set $N_S/N_R = a = 1$ and $C_V = N_S C_I = N C_I$.

$$\rho = \exp(-\beta H - \gamma/N H^2) \quad (3.7)$$

where $\gamma = k_B^2/2C_I$. Thus the redefined ensemble has an additional input parameter C_I the specific heat per particle of the system besides the temperature. The justification (or the lack of it) for neglecting the higher order terms in H (whose multipliers involve the derivatives of C_I) in ρ would depend upon the temperature. But one can speculate at this juncture that the effect of higher order terms in H would be more pronounced at low temperatures.

IV. EVALUATION OF THERMODYNAMIC PROPERTIES

Define the new partition function

$$Z = \exp(\alpha) = \int d\Gamma \exp(-\beta H - \gamma/N H^2) \quad (4.1)$$

$$\begin{aligned} S_S &= -k \langle \ln \rho \rangle \\ &= k(\alpha + \beta \langle H \rangle + \gamma/N \langle H^2 \rangle) \end{aligned}$$

$$-kT \ln Z = U - T[S_S - k\gamma/N \langle H^2 \rangle] \quad (4.2)$$

For any intermediate ensemble defined by (2.8) we obtain

$$-kT \ln Z = U - T[S_S - k\beta_2 \langle H^2 \rangle - k\beta_3 \langle H^3 \rangle \dots] \quad (4.3)$$

Comparing (4.2) and (4.3) with the thermodynamical relation

$$F = U - TS \quad (4.4)$$

we get

$$F = -kT \ln Z \quad (4.5)$$

$$S = S_S - k\beta_2 \langle H^2 \rangle - k\beta_3 \langle H^3 \rangle \dots \quad (4.6)$$

(4.5) and (4.6) represent the average free energy^{*} and the thermodynamical entropy evaluated with respect to ρ . Other thermodynamical properties cannot in general be calculated as derivatives of the average free energy. The reason lies in the following. The thermodynamical relation

$$Tds = dE + \sum_i X_i dx_i \quad (4.7)$$

where x_i 's are the state variables and X_i 's the conjugate forces is a Micro Law valid for every member in the ensemble with a given energy E . Using the Ehrenfest⁴⁾ principle if want to calculate X_i from the relation

$$X_i = - \left(\frac{\partial E}{\partial x_i} \right)_{x_1, x_2, \dots, x_{i-1}, x_{i+1}, \dots, S} \quad (4.8)$$

we have to bear in mind that systems with a given energy E occur with a definite probability given by ρ . Hence (4.8) gets transformed into

$$X_i = \frac{\int d\Gamma \left[\left(-\frac{\partial E}{\partial x_i} \right)_{x_1, \dots, x_{i-1}, x_{i+1}, \dots, S} \right] \rho(H)}{\int d\Gamma \rho(H)} \quad (4.9)$$

^{*}) That $\exp(-\beta A)$ should always represent the partition function could be understood easily as the maximization of volume in phase space representing the minimization of free energy in an appropriate way.

and the constancy of S refers to nothing but the constancy of number of states at energy E . X_i need not in general satisfy the relation

$$X_i = \left(\frac{\partial u}{\partial x_i} \right)_{x_1, \dots, x_{i-1}, x_{i+1}, \dots, S} \quad (4.10)$$

where U is the average energy evaluated with $\rho(H)$. For example in the case of the redefined ensemble, pressure is given by

$$P = \frac{\int d\Gamma \left(-\frac{\partial E}{\partial V} \right)_S \exp(-\beta H - \sqrt{1/N} H^2)}{\int d\Gamma \exp(-\beta H - \sqrt{1/N} H^2)}$$

$$P = - \frac{\partial}{\partial V} [-kT \ln Z] \quad (4.11)$$

The recipe hence is to apply (4.7) to every microcanonical ensemble and use (4.5), (4.6) and (4.9) for evaluating the thermodynamical properties.

To complete the analogy between statistical mechanics and thermodynamics one has to show that the thermodynamic limit exists. In the redefined ensemble, the existence of the thermodynamic limit $\lim_{N \rightarrow \infty} \frac{1}{N} F$ for a hard core finite range attractive potential can be proved along the lines discussed in Thompson⁵⁾ for Gibbs ensemble.

The extension to grand ensemble is straightforward. The grand partition function is defined as

$$\Omega = \sum_{N_i=0}^{\infty} \beta^{N_i} \sum \exp(-\beta H - \sqrt{1/N_i} H^2) \quad (4.12)$$

where λ is a parameter to be eliminated from the equation for N , the average number of particles in a volume V at temperature T given by

$$N = \beta \frac{\partial}{\partial \beta} \ln \Omega \quad (4.13)$$

The average energy is given by

$$U = \frac{\sum_{N_i=0}^{\infty} \beta^{N_i} \sum H \exp(-\beta H - \sqrt{1/N_i} H^2)}{\sum_{N_i=0}^{\infty} \beta^{N_i} \sum \exp(-\beta H - \sqrt{1/N_i} H^2)} \quad (4.14)$$

Equations similar to (4.9) are used for evaluating the conjugate forces and from the equation the free energy can be calculated

$$F = -kT [\ln(\Omega/\beta^N)] \quad (4.15)$$

V. COUPLING BETWEEN REDEFINED ENSEMBLES

Consider two systems of energy E_1 and E_2 and particle number N_1 and N_2 respectively. The partition functions Z_i can be written in terms of the density of states $g_i(E_i)$ as

$$Z_i = \int_0^{\infty} dE_i g_i(E_i) \exp(-\beta_i E_i - \sqrt{1/N_i} E_i^2) \quad (5.1a)$$

Setting

$$\ln g_i(E_i) = \omega_i(E_i)/k \quad (5.1b)$$

one can solve (5.1a) by the saddle point method. The saddle point is given by

$$\frac{1}{k} \left(\frac{\partial \omega_i(E_i)}{\partial E_i} \right)_{E_i = \bar{E}_i} = \beta_i + 2 \sqrt{1/N_i} \bar{E}_i \quad (5.2)$$

If the two systems are coupled to form a composite system statistical equilibrium will be obtained when

$$\delta \left(\sum_i S_{P_i} \right) = 0 \quad (5.3)$$

Since the total energy is fixed

$$\sum_i \delta E_i = 0 \quad (5.4a)$$

Condition (5.3) corresponds to allowing maximum number of complexions for the composite system. Using the relation

$$S_{p_i} = \omega_i (\bar{E}_i) \quad (5.4b)$$

(to be proved in section VI) and (5.4a), (5.3) gets reduced to

$$(\beta_1 - \beta_2) + 2 \left[\frac{\gamma_1}{N_1} \bar{E}_1 - \frac{\gamma_2}{N_2} \bar{E}_2 \right] = 0 \quad (5.5)$$

This condition for statistical equilibrium ^{*} does not imply thermodynamical equilibrium. If the two systems are of the same nature then at thermodynamical equilibrium it further demands that $(\frac{\bar{E}_1}{N_1} - \frac{\bar{E}_2}{N_2})$ should vanish. This will be true by very definition for a thermodynamic system. If the two systems are described by microcanonical ensemble or canonical ensemble, the condition for statistical equilibrium is the same as thermodynamical equilibrium. But if the composite system is made up of three or more systems none of these ensembles stipulates thermodynamical equilibrium as the condition for statistical equilibrium. Equation (5.3) would be valid in general by the very existence of saddle point and the nature of the condition would depend upon what ensemble we use to describe the systems. Physically (5.5) would mean that if two systems at different temperatures are brought together, the composite system shielded from the surroundings would be in statistical equilibrium even when thermodynamical equilibrium is not obtained. Thus thermodynamical equilibrium is a special case of statistical equilibrium.

^{*} If in equations (4.2) and (4.3) any other grouping of terms to represent F and S had been chosen we would have ended up with the inconsistent result that the maximization of thermodynamical entropy does not imply thermodynamical equilibrium.

Finally at statistical equilibrium we should be able to cast the density for the composite system in the same form as ρ_i . This means that we have to find an effective β and γ/N in terms of β_1 and β_2 and γ_1/N_1 and γ_2/N_2 . Starting with the expression for total statistical entropy

$$\begin{aligned} S_p &= S_{p_1} + S_{p_2} \\ &= \beta_1 \bar{E}_1 + \beta_2 \bar{E}_2 + \frac{\gamma_1}{N_1} \bar{E}_1^2 + \frac{\gamma_2}{N_2} \bar{E}_2^2 \end{aligned} \quad (5.6)$$

and using the condition (5.5) for statistical equilibrium we cast S_p into the same form as S_{p_i} .

$$\begin{aligned} S_p &= (\beta_1 + \beta_2) / 2 \bar{E} \\ &+ \frac{1}{4} \left(\frac{\gamma_1}{N_1} + \frac{\gamma_2}{N_2} \right) \left[E^2 - (\bar{E}_1 - \bar{E}_2)^2 \right] \end{aligned}$$

$$S_p \approx (\beta_1 + \beta_2) / 2 \bar{E} + \frac{1}{4} \left(\frac{\gamma_1}{N_1} + \frac{\gamma_2}{N_2} \right) \bar{E}^2 \quad (5.7)$$

when $(\bar{E}_1 + \bar{E}_2) \gg (\bar{E}_1 - \bar{E}_2)$. The effective values of β and γ/N are given by (5.7) and

$$\rho = \exp \left[-(\beta_1 + \beta_2) / 2 H - \frac{1}{4} \left(\frac{\gamma_1}{N_1} + \frac{\gamma_2}{N_2} \right) H^2 \right] \quad (5.8)$$

is a stationary state of Liouville's equation. In (5.8) β_1 and β_2 do not

refer to the temperatures at which the systems are brought together but instead to the instantaneous temperatures of these. For instance, if a block of ice is added to a cup of boiling water the resulting equilibrium temperature would not be given by $(\beta_1 + \beta_2)/2$. But if the two systems attain the same temperature, the temperature of the composite system is correctly given by $(\beta_1 + \beta_2)/2$. It is beyond the scope of statistical mechanics and even thermodynamics to predict how temperature equilibrium is effected. In the absence of information on instantaneous T_1 and T_2 equation (5.8) can be used to study only the thermodynamical equilibrium state of the composite system.

VI. AVERAGE ENERGY AND FLUCTUATIONS

Taylor expanding the exponent in the partition function (5.1a) about the saddle point we obtain

$$\begin{aligned} & \omega(E)/k - \beta E - \gamma/N E^2 \\ &= \omega(\bar{E})/k - \beta \bar{E} - \gamma/N \bar{E}^2 \\ &+ \frac{(E - \bar{E})^2}{2} \left[\frac{\partial^2}{\partial E^2} \left\{ \frac{\omega(E)}{k} - \beta E - \gamma/N E^2 \right\} \right]_{E = \bar{E}} \\ & \dots \end{aligned} \tag{6.1}$$

Retaining terms upto second order in $(E - \bar{E})$,

$$Z = \exp(\omega(\bar{E})/k - \beta \bar{E} - \gamma/N \bar{E}^2) \times \int_0^{\infty} dE \exp\left[-\frac{(E - \bar{E})^2}{2kT^2 N C_c}\right] \tag{6.2}$$

where C_c is given by

$$\frac{1}{C_c} = \frac{1}{C_R} + \frac{1}{C_I} \tag{6.3}$$

and C_R is the specific heat obtained from the redefined ensemble. From the above equation we could infer that the distribution in energy is a Gaussian as in Gibbs ensemble but with a smaller width $(kT^2 C_c N)^{1/2}$. As we include higher and higher powers of H in ρ the width would continue to decrease and the distribution would approach a δ function in the limit of micro-canonical ensemble. From (6.2) neglecting terms of order $\ln N$ in the thermodynamic limit, we obtain the relation

$$-kT \ln Z = \bar{E} - T \left[\omega(\bar{E})/k - k\gamma/N \bar{E}^2 \right] \tag{6.4}$$

Comparing (6.4) with (4.2) we realize

$$S_p = \omega(\bar{E}) \tag{6.5}$$

The saddle point relation

$$\frac{1}{k} \left[\frac{\partial \omega(E)}{\partial E} \right]_{E = \bar{E}} = \beta + 2\gamma/N \bar{E} \tag{6.6}$$

shows that the mean energy is smaller than that in the Gibbs ensemble. Since the density of states is fixed the saddle point \bar{E} shifts towards the left as higher powers of H are included in the ensemble. Though the relation

$$F = U - TS \quad (6.7)$$

is obtained for all the ensembles for a given temperature T , we attribute a lower and lower value of U as we approach the microcanonical ensemble or alternatively a higher temperature for a given energy. It can be seen from the saddle point equation that the shift in \bar{E} is not one of mere scaling. Thus even in the thermodynamic limit all these ensembles do not give the same results. (6.7) is the result of neglecting terms of order $\ln N$ in the thermodynamic limit and the equation

$$\frac{\langle E - \bar{E} \rangle^k}{\langle E \rangle^k} \propto \frac{1}{N^{k-1}} \quad (6.8)$$

only reflects on the sharpness of the saddle. (6.7) and (6.8) do not imply that all these ensembles give the same results. Applications of the redefined ensemble which will be discussed in future communications would elucidate this further.

The final question to be answered is how many powers of H should be conserved over the ensemble to do a microcanonical calculation. And the indirect answer is that if the number of powers conserved is the same as the number of possible states at the energy $E = U$ then \mathcal{S} would represent a microcanonical ensemble.

VII. CONCLUSION

From a detailed study of the redefined ensemble it is proved that the state of thermodynamical equilibrium is a special case of statistical equilibrium. The saddle point equation for the various ensembles reveals that the dependence of average energy on temperature is different for different ensembles and that all these ensembles do not after all yield the same results even in the thermodynamic limit.

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