FIRST ORDER PHASE TRANSITIONS IN NANOSCOPIC SYSTEMS

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The problem of the first order phase transitions in nanoscopic systems is investigated in the framework of Hill’s nanothermodynamics. We obtain the equilibrium conditions and a generalized version of the Clapeyron-Clausius equation for a nanoscopic system which contains two phases. We will show that the equilibrium conditions obtained in the present paper are the same as the ones that result from the equivalence between Tsallis thermodynamics and Hill’s nanothermodynamics.

1. INTRODUCTION

In the last decade were published many theoretical articles [1–5] regarding the thermodynamical or statistical study of nanoscopic systems. We can mention in this context Hill’s nanothermodynamics, quantum thermodynamics and some applications of nonextensive thermostatistics in the mesoscopic domain. In the present paper, by taking into account Hill’s theory, we present an investigation of the first order phase transitions in nanoscopic systems. We will establish the equilibrium conditions for a nanoscopic system which contains two phases and the generalization of the Clapeyron-Clausius equation for nanoscopic systems. Contrary to the usual procedure we assume that the entropy is an extensive parameter only at macroscopic level. We will show that the correct equilibrium conditions can be obtained taking into account the equivalence between Tsallis thermodynamics and Hill’s nanothermodynamics.

2. THEORY

To establish the equilibrium conditions in the case of nanoscopic systems we will use Hill’s approach, i.e. we consider an ensemble of $N$ identical nanoscopic systems which represents a macroscopic system [1].
Let us consider a macroscopic system which contains two phases in thermodynamical equilibrium. Suppose that we divide each phase in identical nanoscopic systems. The differential of internal energy for the considered phases is given by [1]

\[ d\langle E_i^{(1)} \rangle = T^{(1)} dS_i^{(1)} - p^{(1)} d\langle V_i^{(1)} \rangle + \mu^{(1)} d\langle N_i^{(1)} \rangle + \mathcal{E}^{(1)} dN^{(1)} \]  

(1)

\[ d\langle E_i^{(2)} \rangle = T^{(2)} dS_i^{(2)} - p^{(2)} d\langle V_i^{(2)} \rangle + \mu^{(2)} d\langle N_i^{(2)} \rangle + \mathcal{E}^{(2)} dN^{(2)} \]  

(2)

In the above relations we have used the standard notations, i.e. \( T \)-temperature, \( S \)-entropy, \( p \)-pressure, \( V \)-volume, \( \mu \)-chemical potential and \( N \)-particle number. \( \mathcal{E} \) represents the energetic subdivision potential introduced by Hill and \( N \) signifies the number of nanoscopic systems in the ensemble. The indexes (1) and (2) refer to the considered phases while the index “\( t \)” signifies the fact that the respective quantity regards the “total” (\( t \)) ensemble of identical nanoscopic systems. \( \langle X \rangle \) represents the statistical mean (expected) value of the random variable \( X \).

The thermodynamical equilibrium state is given by the maximum of the entropy, which lead to the following extremum condition

\[ \delta S_t = \delta S_t^{(1)} + \delta S_t^{(2)} = 0 \]  

(3)

The above relation is valid because in the case of macroscopic systems the entropy is an extensive parameter. We must mention that equation (3) does not hold for a nanoscopic system which contains two phases because of the nonextensive behavior of the entropy.

Taking into account the relations (1), (2) and (3) one obtains

\[ \frac{1}{T^{(1)}} \delta \langle E_i^{(1)} \rangle + \frac{1}{T^{(2)}} \delta \langle E_i^{(2)} \rangle + \frac{\mu^{(1)}}{T^{(1)}} \delta \langle V_i^{(1)} \rangle + \frac{\mu^{(2)}}{T^{(2)}} \delta \langle V_i^{(2)} \rangle - \]  

\[ -\frac{\mathcal{E}^{(1)}}{T^{(1)}} \delta \langle N_i^{(1)} \rangle - \frac{\mathcal{E}^{(2)}}{T^{(2)}} \delta \langle N_i^{(2)} \rangle - \frac{\mathcal{E}^{(1)}}{T^{(1)}} \delta N^{(1)} - \frac{\mathcal{E}^{(2)}}{T^{(2)}} \delta N^{(2)} = 0 \]  

(4)

As the global system is isolated, one finds the conditions:

\[ \langle E_i \rangle = \langle E_i^{(1)} \rangle + \langle E_i^{(2)} \rangle = \text{const.}; \quad \delta \langle E_i^{(1)} \rangle = -\delta \langle E_i^{(2)} \rangle \]  

\[ \langle V_i \rangle = \langle V_i^{(1)} \rangle + \langle V_i^{(2)} \rangle = \text{const.}; \quad \delta \langle V_i^{(1)} \rangle = -\delta \langle V_i^{(2)} \rangle \]  

\[ \langle N_i \rangle = \langle N_i^{(1)} \rangle + \langle N_i^{(2)} \rangle = \text{const.}; \quad \delta \langle N_i^{(1)} \rangle = -\delta \langle N_i^{(2)} \rangle \]  

\[ N = N^{(1)} + N^{(2)} = \text{const.}; \quad \delta N^{(2)} = -\delta N^{(1)} \]  

(5)

Then the relation (4) takes the following form
The above relation can be satisfied for arbitrary variations of $\langle E^{(1)}_i \rangle$, $\langle V^{(1)}_i \rangle$, $\langle N^{(1)}_i \rangle$ and $\mathcal{N}^{(1)}$ only if

$$T^{(1)} = T^{(2)} = T$$

$$p^{(1)} = p^{(2)} = p$$

$$\mu^{(1)}(T, p, N^{(1)}) = \mu^{(2)}(T, p, N^{(2)})$$

$$\mathcal{E}^{(1)}(T, p, \mu^{(1)}) = \mathcal{E}^{(2)}(T, p, \mu^{(2)})$$

The conditions (7)–(9) are well known from macroscopic thermodynamics. But we must mention that in the case of nanoscopic systems $T$, $p$ and $\mu$ are independent variables [4, 3]. We observe also that for nanoscopic systems we have a supplementary condition, given by the equality of Hill’s subdivision potentials $\mathcal{E}^{(1)}$ and $\mathcal{E}^{(2)}$ for the considered phases. In the case of macroscopic systems the condition (10) becomes the trivial equality $0 = 0$.

The equilibrium conditions can be obtained by using the differential equation for the entropy:

$$dS^{(i)} = \sum_{\alpha} \Phi^{(i)}_{\alpha} d\langle X^{(i)}_{\alpha} \rangle + \mathcal{J}^{(i)} d\mathcal{N}^{(i)}, \quad i = 1, 2$$

where $\Phi^{(i)}_{\alpha}$ and $X^{(i)}_{\alpha}$ signify the entropic intensive and extensive parameters respectively: $\Phi^{(i)}_{1} = 1/T^{(i)}$, $X^{(i)}_{1} = E^{(i)}$, $\Phi^{(i)}_{2} = p^{(i)}/T^{(i)}$, $X^{(i)}_{2} = V^{(i)}$, $\Phi^{(i)}_{3} = -\mu^{(i)}/T^{(i)}$, $X^{(i)}_{3} = N^{(i)}$. In the above relation $\mathcal{J}^{(i)}$ represents the entropic subdivision potential given by

$$\mathcal{J}^{(i)} = -\frac{\mathcal{E}^{(i)}}{T^{(i)}}$$

From the extremum condition (3) one obtains

$$\Phi^{(1)}_{\alpha} = \Phi^{(2)}_{\alpha}$$

$$\mathcal{J}^{(1)} = \mathcal{J}^{(2)}$$

One can observe easily that these conditions are equivalent with (7)–(10).
Because \( \langle E_i^{(1)} \rangle \) is a first order homogeneous function with respect to \( S_i^{(1)} \), \( \langle V_i^{(1)} \rangle \), \( \langle N_i^{(1)} \rangle \) and \( \mathcal{N}^{(1)} \), we have [4]

\[
\langle E_i^{(1)} \rangle = T^{(1)} S_i^{(1)} - p^{(1)} \langle V_i^{(1)} \rangle + \mu^{(1)} \langle N_i^{(1)} \rangle + \mathcal{E}^{(1)} \mathcal{N}^{(1)}
\]

(15)

Differentiating the above equation and taking into account the relation (1) one obtains

\[
\mathcal{N}^{(1)} d\mathcal{E}^{(1)} = -S_i^{(1)} dT^{(1)} + \langle V_i^{(1)} \rangle dp^{(1)} - \langle N_i^{(1)} \rangle d\mu^{(1)}
\]

(16)

On the other hand \( S_i^{(1)} = \mathcal{S}^{(1)} \mathcal{N}^{(1)} \), \( \langle V_i^{(1)} \rangle = \langle V \rangle \mathcal{N}^{(1)} \), \( \langle N_i^{(1)} \rangle = \langle N \rangle \mathcal{N}^{(1)} \).

So we obtain the following equation [4]

\[
d\mathcal{E}^{(1)} = -S^{(1)} dT^{(1)} + \langle V \rangle dp^{(1)} - \langle N \rangle d\mu^{(1)}
\]

(17)

where the quantities \( S^{(1)} \), \( \langle V \rangle \) and \( \langle N \rangle \) refer to one nanoscopic system.

The above equation represents a generalization of the Gibbs-Duhem equation from macroscopic thermodynamics.

In a similar way we obtain

\[
d\mathcal{E}^{(2)} = -S^{(2)} dT^{(2)} + \langle V \rangle dp^{(2)} - \langle N \rangle d\mu^{(2)}
\]

(18)

The equilibrium conditions (7)–(10) with the relations (17) and (18) lead to the following equation

\[
-S^{(1)} dT + \langle V \rangle dp - \langle N \rangle d\mu = -S^{(2)} dT + \langle V \rangle dp - \langle N \rangle d\mu
\]

(19)

In the case of a nanoscopic system the quantities \( T, p \) and \( \mu \) are independent variables and the chemical potential \( \mu \) depends on \( T, p \) and \( \langle N \rangle \) [4, 3]. Note that in the case of macroscopic systems the chemical potential depends only on \( T \) and \( p \) [6].

Let us focus our attention on the case of nanoscopic systems, for which we have

\[
d\mu^{(i)} = \left( \frac{\partial \mu^{(i)}}{\partial T} \right)_{p, \langle N^{(i)} \rangle} dT + \left( \frac{\partial \mu^{(i)}}{\partial p} \right)_{T, \langle N^{(i)} \rangle} dp + \left( \frac{\partial \mu^{(i)}}{\partial \langle N^{(i)} \rangle} \right)_{T, p} d\langle N^{(i)} \rangle
\]

Introducing the expression of \( d\mu^{(2)} \) in relation (19) and taking into account the equilibrium condition (9) one obtains
This equation represents a generalization of the well known Clapeyron-Clausius equation from macroscopic thermodynamics.

### 3. CONNECTION WITH TSALLIS THERMODYNAMICS

The fundamental equations of Hill’s nanothermodynamics for one nanoscopic system are

\[
\sum_{\alpha} \Phi_{\alpha} d \langle X_{\alpha} \rangle = dS
\]

(21)

\[
\sum_{\alpha} \Phi_{\alpha} \langle X_{\alpha} \rangle = S - J
\]

(22)

\[
\sum_{\alpha} \langle X_{\alpha} \rangle d \Phi_{\alpha} = -dJ
\]

(23)

Based on the results from Ref. [7] the above equations are equivalent with the fundamental equations of Tsallis thermodynamics  \( \langle X_{\alpha} \rangle_q \) represents the q-mean value of the random variable \( X_{\alpha} \)

\[
\sum_{\alpha} \Psi_{\alpha} d \langle X_{\alpha} \rangle_q = dS^*
\]

(24)

\[
\sum_{\alpha} \Psi_{\alpha} \langle X_{\alpha} \rangle_q = \frac{1}{1-q} \left[ 1 + (1-q)S^* \right] \ln \left[ 1 + (1-q)S^* \right]
\]

(25)

\[
\sum_{\alpha} \langle X_{\alpha} \rangle_q d \Psi_{\alpha} = \ln \left[ 1 + (1-q)S^* \right] dS^*
\]

(26)

if we take  \( S \equiv S^* \),  \( \Psi_{\alpha} \equiv \Phi_{\alpha} \),  \( \langle X_{\alpha} \rangle \equiv \langle X_{\alpha} \rangle_q \) and

\[
J \equiv S^* - \left[ 1 + (1-q)S^* \right] \frac{\ln \left[ 1 + (1-q)S^* \right]}{1-q}
\]

(27)

In the above equation \( S^* \) represents the Tsallis entropy.
Let us consider a nanoscopic system which contains two phases, denoted by (1) and (2). These phases can be considered as two subsystems. The equilibrium conditions are [7, 8]

\[ \Psi^{(1)} = \Psi^{(2)} \]  

\[ S^{(1)} - \left[ 1 + (1-q)S^{(1)} \right] \ln \frac{1 + (1-q)S^{(1)}}{1-q} = S^{(2)} - \left[ 1 + (1-q)S^{(2)} \right] \ln \frac{1 + (1-q)S^{(2)}}{1-q} \]  

which are equivalent with (13) and (14). For a macroscopic system \( q = 1 \) (the entropy is an extensive parameter) and equation (29) becomes the trivial equality \( 0 = 0 \).

4. CONCLUSIONS

In the present work we have studied the problem of the first order phase transitions in nanoscopic systems from a thermodynamical point of view. We established the equilibrium conditions for a nanoscopic system which contains two phases, based on Hill’s theory. The fact that in the case of nanoscopic systems the quantities \( T, p \) and \( \mu \) are independent variables has some interesting consequences, one of them being a supplementary equilibrium condition, in addition to the ones known from macroscopic thermodynamics. This condition is connected with the subdivision potential \( \varepsilon \), introduced by Hill. We obtained also a generalized form of the Clapeyron-Clausius equation. We have shown that the equilibrium conditions are the same as the ones resulted from the equivalence between Tsallis thermodynamics and Hill’s nanothermodynamics.

REFERENCES