THERMODYNAMIC PROPERTIES OF THE SYSTEMS WITH HETEROGENEOUS MASSES

Ljiljana Maksimović, R. Maksimović and Bratislav Tošić

1 Faculty of Sciences, Institute of Physics, Novi Sad, Yugoslavia
2 Police Academy, Belgrade, Yugoslavia

ABSTRACT

Thermodynamic properties of a system with heterogeneous masses in the discrete approximation were analyzed in the temperature range 300-400 K. Qualitative agreement with experimental results is achieved. Special attention was payed to the peaks arising in the entropy of system, internal energy, specific heat and free energy. The position and height of these peaks fit well the experimental data.

1. INTRODUCTION

The techniques of the synthesis of new materials have made an exceptional progress during the last years. Composite and polymer materials are more often synthesized from the molecules of different masses, which on the other hand makes the theoretical analysis of the physical properties of such structures rather difficult. Several attempts were made in that direction [1-4].

The aim of this paper is the application of the statistical methods in order to obtain comparatively simple criteria for the estimate of the thermodynamic characteristics of the materials composed of different molecules.

Since our aim is to formulate the model valid at low temperatures, the model energy will be the energy of the system of coupled oscillators averaged over the Debye sphere. It is known that Debye $\hbar k_D$ momentum corresponds to the temperature of order 150 K ( $k_D \approx \frac{\pi}{a}$, $a$ - the lattice constant). So we start with

$$ E_{\text{mod}} = \frac{h\nu}{4} \int d^3 k = \frac{3}{4} \hbar k_D \nu $$  \hspace{1cm} (1.1)

where $\nu$ is the velocity of sound in the material.

We shall assume that the masses can all be expressed as an integer multiple of the proton mass $m_p$:

$$ M_n = nm_p, \quad n = 1, 2, \ldots, N $$ \hspace{1cm} (1.2)

so the model energy can be written as:
where $C_p$ is Hooke's elastic constant of the material. One should stress here that (1.2) the masses continually change in steps of $m_0$, which is definitely an idealization and in the certain sense leads only to qualitative results.

2. STATISTICAL DISTRIBUTION

Let us denote the total number of the molecules by $N$, and the number of the molecules with the mass $M_0$ by $N_0$. The statistical probability of the system is then given by:

$$P = \frac{N!}{N_0! N^{N-N_0}}$$

(2.1)

The law of the particle and energy conservation state:

$$\sum_{n=1}^{N} N_n = N = \text{const} ; \quad \sum_{n=1}^{N} E_n N_n = U = \text{const}$$

(2.2)

It is well known that the most probable distribution is obtained by varying the functional:

$$\Phi = \ln P - \alpha \ln N - \beta U = \ln N + \sum_{n=1}^{N} (N_n \ln N_n + \alpha N_n + \beta E_n N_n)$$

(2.3)

and equating the variation (2.3) to zero.

It this way we obtain:

$$N_n = e^{-(\alpha + 1)} e^{-\beta E_n}$$

(2.4)

Substituting (2.4) into (2.3), we obtain:

$$\frac{N_n}{N} W_n = e^{-\beta E_n} ; \quad \beta = \frac{1}{k_B T}$$

(2.5)

The expression for $E_n$ includes $\frac{1}{\sqrt{n}}$ which complicates the calculations considerably. For this reason we shall approximate, using the trapezoidal rule, the function $\frac{1}{\sqrt{n}}$ by a linear function: $\frac{1}{\sqrt{n}} = b - an$.

The coefficients $a$ and $b$ follow from the conditions: $b - a N = \frac{1}{\sqrt{N}}$ and $b - a = 1$, giving:

$$a = \frac{1}{\sqrt{N} (1 + \sqrt{N})} ; \quad b = 1 + a$$

(2.6)

Substituting (2.6) into the expression for the probability, we obtain:

$$E_n = E_0 N_0 \frac{1}{\sqrt{N}} = E_0 (1 + a)$$

and the expression for energy turns into:

$$E_n = E_0 N \frac{1}{\sqrt{N}} = E_0 (1 + a)$$

3. THERMODYNAMICS CHARACTER

The entropy of the system equals:

$$S = \ln P = N \ln N - \sum_{n=1}^{N} N_n \ln N_n$$

$$S = N S_0$$

where

$$S = \sum_{n=1}^{N} e^{\alpha n} e^{-\beta n}$$

A brief calculation gives:

$$S = Z \left( \frac{1}{1 - e^{\alpha}} \right) \left( \frac{1}{1 - e^{\beta}} \right)$$

One can see (3.3) that equilibrium is satisfied. This could be understood from:

The total internal energy is given by:

$$U = \sum_{n=1}^{N} E_n W_n$$

where

$$U = \sum_{n=1}^{N} (\alpha + 1) E_n W_n$$

Taking into account (2.5) and

$$U = \sum_{n=1}^{N} (\alpha + 1) E_n W_n$$

leading to:

$$U = E_0 \left[ 1 + \frac{1}{\sqrt{N} (1 + \sqrt{N})} \right]$$
\[ W_n = \frac{e^{n_0}}{\sum_{n=1}^{N} e^{n_0}} \]  
(2.7)

and the expression for energy turns into:

\[ E_n = E_0 n^2 + E_0 (1 + \alpha) - E_\alpha \alpha n \]  
(2.8)

3. THERMODYNAMICS CHARACTERISTICS

The entropy of the system equals by definition to the logarithm of the statistical probability \( S_\nu \):

\[ S_\nu = \ln P = N \ln N - \sum_{n=1}^{N} N_n \ln N_n, \]  
(3.1)

where

\[ S = -\sum_{n=1}^{N} \frac{e^{n_0} \ln e^{n_0}}{F}, \quad F = e^{n_0} e^{n_0} - 1 \]  
(3.2)

A brief calculation gives

\[ S = Z \left( \frac{1}{1 - e^x} - \frac{N}{1 - e^x} \right) + \ln \frac{e^{n_0} - 1}{e^x - 1} \]  
(3.3)

One can see from (3.3) that entropy vanishes at absolute zero, meaning that Nernst's theorem is satisfied. This could be understood from the fact that entropy is calculated from discrete variables \( \alpha \).

The total internal energy is given by:

\[ U_\nu = \sum_{n=1}^{N} N_n E_n = NU \]  
(3.4)

where

\[ U = \sum_{n=1}^{N} E_n W_n \]  
(3.5)

Taking into account (2.5) and (2.8), we can write also

\[ U = \sum_{n=1}^{N} (\alpha + 1) E_0 W_n - \frac{\sum_{n=1}^{N} E_n \alpha e^{n_0}}{\sum_{n=1}^{N} e^{n_0}} \]  
(3.6)

leading to

\[ U = E_0 \left[ 1 + \frac{1}{\sqrt{N(1 + \sqrt{N})}} \left( \frac{e^x - \frac{N e^{n_0}}{1 + \sqrt{N}}} {e^x - 1} \right) \right] \]  
(3.6)
At $\Theta = 0K$, the internal energy is:

$$U(0) = \left(1 - \frac{N - 1}{N + \sqrt{N}}\right)E_0$$

Specific heat can be obtained as the derivative of the internal energy over temperature (in energy units $\Theta$). In this way we obtain:

$$C_v = -\frac{\partial U}{\partial \Theta} = N^2 \frac{e^{\alpha \Theta} - e^{\Theta}}{(e^{\alpha \Theta} - 1)^2}$$

(3.7)

Specific heat vanishes in both limiting cases, $\Theta = 0$ and $\Theta \rightarrow \infty$, so it must have a maximum.

Finally, using the expression for the entropy and internal energy, we can obtain the expression for the free energy $F$:

$$F = U - TS = E_0 \ln \frac{e^{\alpha \Theta} - 1}{e^{\Theta} - 1}$$

(3.8)

The plot of free energy shows that it becomes negative rather soon, meaning that the system becomes thermodynamically stable with the rise of the influence of smaller masses in the physical processes.

4. CONCLUSION

The statistical analysis of the system with heterogeneous masses in the discrete approximation is in principle valid for the temperature range from absolute zero up to Debye temperatures. It turned out, after the comparison with experiments, that the temperature range can increased up to 400K.

The general theory was made on the basis of the successive mass increase ($M_1 = mn_0$) and gives qualitatively correct results for a series of thermodynamic characteristics (7-10).

Generally speaking, the approach is mathematically simple and the calculation of various quantities based on it seems to be reliable.

REFERENCES