FERMIONIC OSCILLATORS AND THEIR CONNECTION WITH THE ISOKINETIC TEMPERATURE

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Abstract. The behavior of a molecular architecture into an isotropic heat field was analyzed considering the thermodynamic properties of fermionic oscillators. Beginning with the grand canonical ensemble and the thermodynamic potential we could describe two major contributions: a trigonometric function responsible for selective energy accumulation under resonance conditions and a hyperbolic function which describes the suppression of the specific activation.

In a rather good approximation, the thermal induced phenomena under non-isothermal conditions have a behavior equivalent with a gas of fermions.

Key words: isokinetic temperature; vibrational energy transfer; specific heat; chemical potential.

1. INTRODUCTION

In some previous papers [1, 2] the relationship between the isokinetic temperature T_i in a series of similar thermal induced decompositions and the wave number of the thermally activated bond was established.

This relationship was applied in a series of earlier experimental data [3].

The behaviour of the chemical potential and specific heat, using the evaluation of the thermodynamic grand-canonical potential characterizing relativistic fermionic oscillators as the basic starting point is analyze and are obtained approximate analytical and numerical results.

The solid is assimilated to a system of harmonic oscillators that was studied applying the Fermi-Dirac statistics [4]. In addition the grand canonical distribution has to be used [5] with the thermodynamic potential Ω as potential.

An important consequence, a correlation between the isokinetic temperature and the spectroscopic wave number of the activated bond, is illustrated by a number of decomposition reactions under non-isothermal conditions.

The thermodynamic properties of fermionic oscillators, in detail the behavior of specific heat as dependence by temperature, is studied analytical and numerical in this work, given the relevant contributions to the understanding of the behavior of a molecular architecture into an isotropic heat field.

2. SIGNIFICATION OF ISOKINETIC TEMPERATURE

The thermodynamic functions provided by the vibrational partition function, *i.e.* the enthalpy, is given by [6]:

$$H = k_B \cdot T^2 \frac{\partial \ln Z}{\partial T}. \tag{1}$$

The statistics of an ideal gas of identical diatomic molecules, modeled by N oscillators, in thermodynamic equilibrium with a reservoir of temperature T is described by the vibrational partition function Z, using Fermi-Dirac distribution [5]:

$$Z = \frac{1}{1 + e^{\frac{\hbar\omega - \mu}{k_B T}}}, \tag{2}$$

where ω is the pulsation, k_B, the Boltzmann and h the Planck constants, respectively, $\hbar = h/2\pi$ and μ is the chemical potential, N is the number of particles.

Considering an activation process due to a vibrational energy transfer from an homogeneous and isotropic field of thermic oscillators to the solid state oscillator, the thermodynamic functions are in the relationship [7–10]:

$$dH = TdS, \tag{3}$$

where S is the entropy.

If the number of particles is constant, we could apply the canonical distribution with the free energy F, as the thermodynamic potential:

$$F = H - T \cdot S, \tag{4}$$

$$F = -k_B T \ln Z. \tag{5}$$

Using Eqs. (1), (4) and (5) the entropy can be express by vibrational partition function as:

$$S = k_B \left[\ln Z + T \frac{\partial \ln Z}{\partial T} \right]. \tag{6}$$

Taking into account the definitions of *H* and *S* from Eq. (1) and Eq. (6) by means of the partition function, the Eq. (3) becomes equivalent with:

$$T_i = \frac{\hbar\omega}{k_B},\tag{7}$$

where T_i is the isokinetic temperature that is assimilated with the characteristic temperature, c is the speed of the light in vacuum, ϖ is the wave number expressed in cm^{-1}.

The isokinetic temperature is the temperature at which all the decomposition reaction of similar solids would have the same rate constant. Also the same bond would be activated/broken, it means that the isokinetic temperature can be assimilated with the characteristic temperature of the activated vibration.

Therefore a correspondence between a kinetic parameter like the isokinetic temperature, T_i, and a calculated vibrational parameter ϖ is possible.

The specific activation is possible due to more that one quantum because the breaking bond has an anharmonic behaviour, so the assigned spectroscopic wave number ϖ_{spectr} for the activated/broken bond will be in correlation with ϖ calculated by Eq. (7) using a natural number *n*:

$$\varpi_{spectr} = n\varpi, \; n = 1, 2, 3, \ldots\tag{8}$$

Some examples of the data processing are systematized in Table 1.

Table 1

Correspondence between T_i and ϖ_{spectr} for some reactions under non-isothermal conditions

Reaction	Compounds	T_i(K)	ϖ (cm^{-1})	n	$n\varpi$ (cm^{-1})	Assignment[8,9] for ϖ_{spectr} (cm^{-1})
Dehydration	Formates Acetates Propionates (of d and f metals)	308 315	214 219	16 16	3424 3504	Water loss 3400-3500
Decomposition	$Na_2S_2O_5$ $K_2S_2O_5$	286 415	200 288	5 3	1000 866	Absorption by bysulphite anion 900-1000
	$Na(CH_3COO)$ $K(CH_3COO)$	286 625	200 434	7 3	1400 1303	(C=O) *vs* by carboxyl anions 1330-1440
	Citric acid	379	263	6 7 12	1580 1844 3424	(C=O) v by sat. carbox. : 1700 OH in carboxylic group: 3500-3550

Table 1 (continued)

						Ester of arom. acids 1250-1300 C=C and C-H stretch 1580-1650 (C-CH3) *vs* 1370-1385 (C-CH3) *vs* 1435-1470
	Nifedipine	491	341	4 5	1364 1705	

Thermodynamic parameters for compounds were calculated through the kinetic parameters [11].

3. BEHAVIOUR OF SPECIFIC HEAT FOR FERMIONS OSCILLATORS

We will use the grand canonical distribution [4] with the thermodynamic potential Ω:

$$\Omega = -k_B T \ln Z .$$ (9)

The specific heat is defined as [4]:

$$C_V = \left. \frac{\partial U}{\partial T} \right|_{N,\omega} ,$$ (10)

where U is the internal energy

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}, \quad \beta = \frac{1}{k_B T} ,$$ (11)

with

$$Z = \frac{e^{-3\beta\omega}}{\left(1 - e^{-\beta\omega}\right)^3}$$ (12)

For a high number of particle N of the system, the specific heat has a linear dependence with temperature that could be written as [13]:

$$C_V \cong \frac{\pi^2}{\sqrt[3]{6\omega}} N^{2/3} T .$$ (13)

This linear dependence with temperature appears in metals at low values of temperature and is represented in Fig. 1. The same representation we can meet in the case of metals at low temperature.
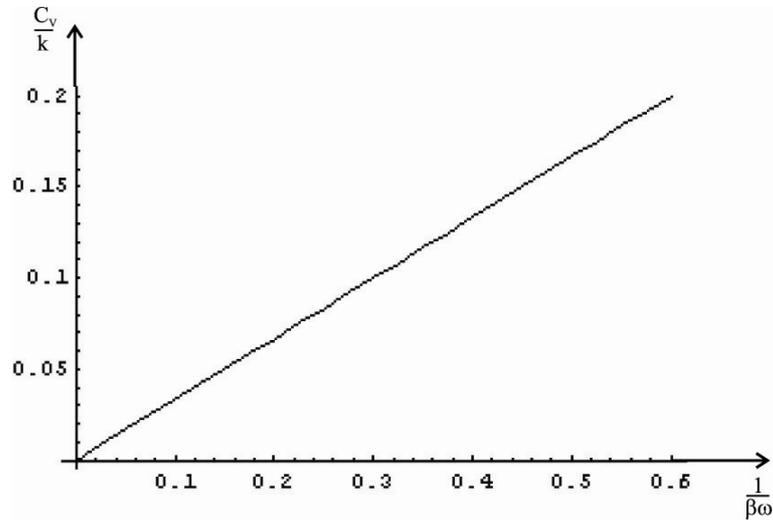
Fig. 1 – The linear dependence of specific heat with temperature.

For $k_B T \leq \omega/100$ the specific heat will be zero, so there is an exponential dependence with temperature that could be written as:

$$C_V \cong e^{-\alpha\omega/T}, \alpha - \text{constant} . \tag{11}$$

For $k_B T > \omega/100$ the dependence of specific heat with temperature that could be written as:

$$C_v \cong \frac{\pi^2 T \mu^2}{6\omega^3}\left(1 + \Sigma_1 - 12\frac{\Sigma_2^2}{\Sigma_3}\right), \quad \text{with } \Sigma_1 \cong \frac{3\beta^3\omega^3\left(2\mu-1\right)^2}{16\cosh^2\left[\frac{\beta\omega}{4}\left(2\mu-1\right)\right]} - 1,$$

$$\Sigma_2 \cong \frac{\beta^2\omega^2\left(2\mu-1\right)}{16\cosh^2\left[\frac{\beta\omega}{4}\left(2\mu-1\right)\right]}; \quad \Sigma_3 \cong \frac{\beta\omega}{4\cosh^2\left[\frac{\beta\omega}{4}\left(2\mu-1\right)\right]}, \tag{14}$$

where $\beta = \dfrac{1}{k_B T}$ and μ is the chemical potential.

This dependence of temperature is in accord with Einstein model and is represented in Fig. 2. The first ascendant part of the graphic but and the saturation region are similar with the results obtained using the Debye approximation. A closed representation is known by Einstein model [14].
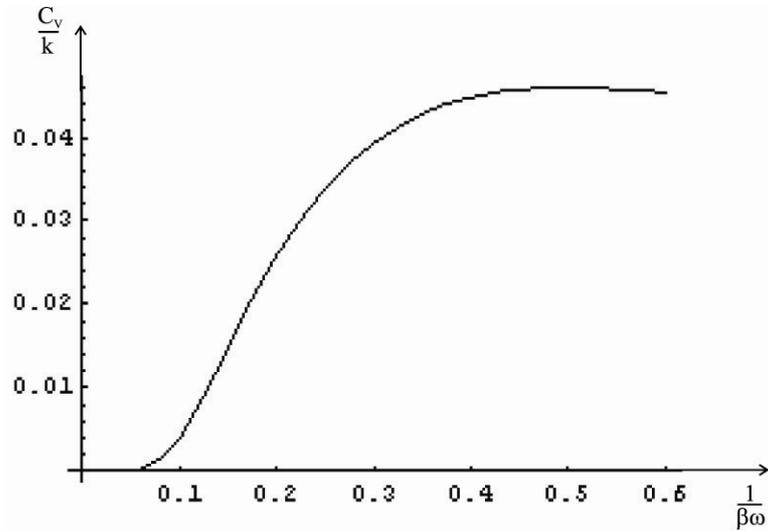
Fig. 2 – Dependence of specific heat with temperature for the case $k_B T > \omega/100$.

The dependence of specific heat as function of the particle number has an oscillation form but this oscillation attenuates in domain of high temperatures. This dependence is represented in Fig. 3 for different values of the product $\beta\omega$.
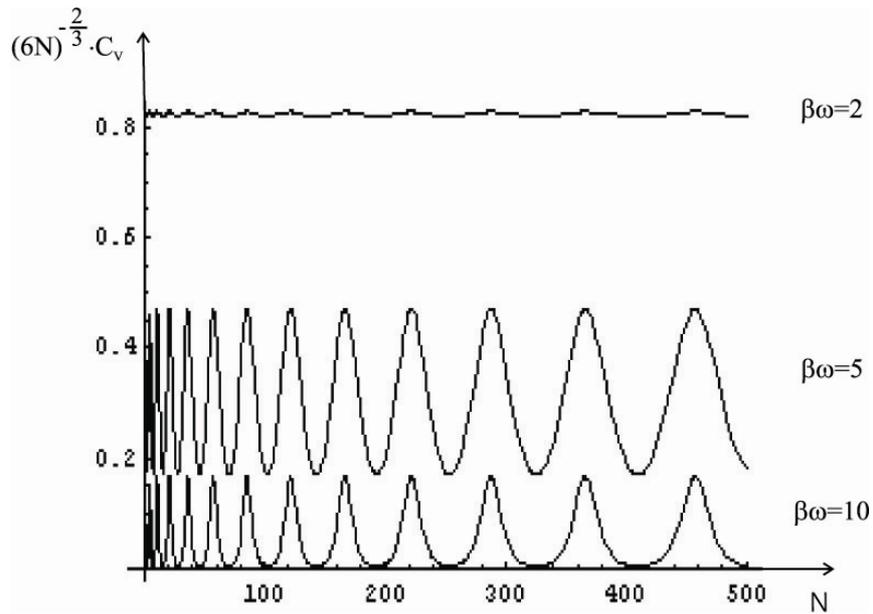

Fig. 3 – Dependence of specific heat with particle numbers N.

Graphics dependences on temperature for this system are similar with that of the tau-oscillator [12].

4. CONCLUSION

The behaviour of the the isokinetic temperature and specific heat, using the evaluation of the thermodynamic grand-canonical potential characterizing relativistic fermionic oscillators as the basic starting point, is analyze and are obtained approximative analytical and numerical results.

The isokinetic temperature can be assimilated with the characteristic temperature of the activated vibration.

The solid is assimilated to a system of harmonic oscillators with a Fermi-Dirac energy distribution.

Dependence of specific heat with temperature of this system is in accordance with others models as Einstein or Debye approximation for solid state.

REFERENCES

1. N. Pop, G. Vlase, T. Vlase, N. Doca, A. Mogos, A. Ioitescu, *Compensation effect as a consequence of vibrational energy transfer in homogeneous and isotropic heat field*, J. Therm. Anal. Cal., **92**, 313–317 (2008).
2. A. K. Galwey, M. E. Brown, *Application of the Arrhenius equation to solid state kinetics: can this be justified*?, Thermochimica ACTA, **386**, 91–98 (2002).
3. R. Larsson, *Isokinetic effects in ethane hydrogenolysis and their relation to the mechanism of the reaction*, Catal. Lett. **11**, 137–148 (1991).
4. R. K. Pathria, *Statistical Mechanics*, University of Waterloo, 1980.
5. A. L. Fetter, J. D. Walecka, *Quantum Theory of Many-particle Systems*, Mc Graw-Hill, New York, 1965.
6. A. Ben-Naim, *Statistical Thermodynamics for Chemists and Biologist*, Plenum Press, New York, 1992.
7. C. Kemball, Proc. R. Soc., London Ser. A, **207**, 539 (1951).
8. W. Good, J. Stone, Tetrahedron, **31**, 379 (1975).
9. M. M. Al Omari, M. B. Zughul, J. E. D. Davies, A. A. Badwan, J. Incl. Phenom. Macrocycl. Chem., **57**, 379 (2007).
10. V. Sajfert, N. Pop, M. Đurić, D. Popov, C. Hatiegan, *About some thermodynamical properties of cylindrical nanorods*, Rom. Rep. Phys., **64**, *4*, 1019–1027 (2012).
11. C. Danvirutai, P. Noisong , S. Youngme, *Some thermodynamic functions and kinetics of thermal decomposition of $NH_4MnPO_4 H_2O$ in nitrogen atmosphere*, J. Therm. Anal. Cal., **100**, 117–124 (2010).
12. V. Badescu, P. Landsberg, J. Phys. A, **35**, 591 (2002).
13. N. Pop, Math. Phys Sci. Bull.of "Politehnica" University, **50**, *64*, 73 (2005).
14. N. W. Ashesoft, N. D. Mermin, *Solid State Physics Sauders College*, Philadelphia, 1976.