copolymers (see Table 3). This fact also justify the random phase approximation for block copolymers.

Acknowledgements. This work was indebted to the Korea Science and Engineering Foundation, was also partially supported by the Center for the Theoretical Physics and Chemistry. The authors acknowledge helpful discussions with Dr. C.H. Kim.

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Calculation of Thermodynamic Properties Through the Use of two New Analytical Expressions for the Partition Function of the Morse Oscillator

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The entropy and heat capacity are calculated for the Morse oscillator model in order to test the quality of the partition function recently deduced by two of us. It is found that these analytical expressions are more reliable than the usually accepted one and give better results in the calculation of thermodynamic properties.

1. Introduction

The calculation of thermodynamic propeties in statiscal mechanics is usually made through known or estimated structural and spectroscopic parameters, by means of the analytical expression for the partition function of the system under consideration. Usually, the rigid rotorharmonic oscillator model is unsatisfactory, so it is neccesary to use more realistic models. The Morse potential is generally chosen as a model of a one–dimensional anharmonic oscillator[1]. The partition function corresponding to this model can be calculated exactly in a numerical way, because there is only a finite number of energy eigenvalues[2,3].

However, in the study of certain physical–chemistry properties, it is mandatory to take recourse to analytical expressions for the partition function, even though they give only approximate results. For instance, isotope effects on the equilibrium constants are of theoretical and experimental interest in connection with isotope separation. It has been suggested that in the approximation of the harmonic oscillator–rigid rotator the isotopic mass dependence of the dissociation equilibrium constant of diatomic molecules changes sign at high temperatures[2]. It is necessary to calculate molecular partition function which is customarily done in the framework of the Born–Oppenheimer approximation. The rotation–vibration energy levels can be calculated by direct integration of the Schrödinger equation so that precise partition functions are available by numerical sumation of Boltzmann factors[4].

For a qualitative discussion numerical partition functions are not well suited, so that analytical partition functions are neccesary for the general discussion of the effect mentioned above. Unfortunately, analytical expressions can only be found in certain approximations.

The usual way to obtain those approximate analytical exppressions consists in taking into account the partition function of the Morse oscillator:

$$Q(N, u) = A(u) \sum_{n=0}^{N} \exp(-u(n - n(n+1)\chi)) \qquad (1)$$

and replacing the upper limit of the sum by $\infty^{2.5}$, where

$$u = \hbar\omega/kT \qquad (2)$$

and

$$A(u) = \exp(-u/2 + u\chi/4) \qquad (3)$$

with ω the vibrational frecuency in wave numbers, $\chi = \hbar\omega/(4D)$, and D is the dissociation energy from the potential minimum. The exponential series that is obtained clearly diverges because of the term $un\chi^2$ in the exponential factor.

In order to avoid this difficulty, it is customary to consider an expansion of $Q(\infty, u)$ in power series of χ and to retain only a finite number of terms.

After performing that expansion, the following expression is obtained[2,5]:

$$Q(\infty, u, M) = A(u) \sum_{s=0}^{M} \sum_{n=0}^{\infty} (s!)^{-1} (u\chi n(n+1))^s e^{-nu} \qquad (4)$$

If only the first term in χ is considered, we arrive at the well-known expression[2,5]:

$$Q(\infty, u, l) = A(u)(1-\alpha)^{-1}(1 + 2u\chi\alpha(1-\alpha)^{-2}) \qquad (5)$$

with

$$r = e^{-u}$$

Although the expression (5) gives good results, the way that leads to it is mathematically wrong, because $Q(\infty, u)$ is divergent.

Recently, two new analytical expressions for the partition function of the Morse oscillator have been given, and they were obtained via a mathematical procedure that is wholly correct. By means of it, the previous formal errors were amended[6]. These two new analytical formulations gave better results than those obtained using less elaborate expressions. With the purpose to verify the validity of application of such formulations, in the present work we have calculated two thermodynamic properties: the entropy S and the heat-capacity, C over a wide range of temperatures.

2. Analytical expressions for the partition function, the entropy and heat-capacity.

The expressions that were deduced for the partition function are[6]:

$$Q(N, u) = A(u) \sum_{s=0}^{\infty} \sum_{j=0}^{s} \binom{s}{j}(s!)^{-1}(-1)^{s+j}u^s\chi^s f^{(s+j)}(u) \qquad (6)$$

and

$$Q(N, u) = A(u) \sum_{s=0}^{\infty} (s!)^{-1}(\chi/u)^s g^{(2s)}(u) \qquad (7)$$

where

$$f(u) = (1 - \alpha^{N+1})/(1-\alpha)$$

and

$$g(u) = (1 - \gamma^{N+1})/(1-\gamma)$$

with

$$f^{(i)}(u) = d^i f(u)/du^i$$

and

$$g^{(i)}(u) = d^i g(u)/d\chi^i$$

If we symbolize equation (6), summed up to the M-th power in χ as $Q(N, u, M)$, then we obtain:

$$Q(N, u, l) = A(u)(f(u)(1 + 2\alpha u\chi(1-\alpha)^{-2} - (N+1)u\chi(1-\alpha)^{-1}(N + 2(1-\alpha)^{-1}\alpha^{N+1}) \qquad (8)$$

In a similar way, from (7), we obtain;

$$Z(N, u, l) = A(u)(g(u)(1 + u\chi\gamma(1+\gamma)(1-\gamma)^{-2} - (N+1)u\chi(1-\gamma)^{-1}(N + (1+\gamma)(1-\gamma)^{-1}\gamma^{N+1}) \qquad (9)$$

where

$$\gamma = \exp(-u(1-\chi)) = \alpha e^u \chi$$

From expressions (8) and (9) and taking into account that the statistical expression for the entropy is[5]:

$$S = k(\ln Q - (\beta/Q)\partial Q/\partial\beta) \qquad (10)$$

and for the heat-capacity:

$$C = k\beta^2(Q^{-1}\partial^2 Q/\partial\beta^2 - Q^{-2}(\partial Q/\partial\beta)^2) \qquad (11)$$

the calculations of both thermodynamic properties are straightforward and they were done for a wide range of temperatures, similar to other calculations[3].

Taking into account that $\beta = (kT)^{-1}$ and $u = \hbar\omega/kT$, then $u = \hbar\omega\beta$ and since $\frac{\partial Q}{\partial\beta} = \frac{\partial Q}{\partial\mu}\frac{\partial\mu}{\partial\beta}$ and $\frac{\partial\mu}{\partial\beta} = \hbar\omega = u/\beta$, we arrive at the following formulae for S and C:

$$S = k(\ln Q - \frac{u}{Q}(dQ/du)) \qquad (12)$$

$$C = ku^2\left(Q^{-1}\frac{d^2Q}{du^2} - Q^{-2}(dQ/du)^2\right) \qquad (13)$$

Therefore, evaluating analytically the first and second derivatives of Q with respect to u and replacing them in expressions (12) and (13), the values of the thermodynamic properties were determined. Similar calculations have been done for $Z(N, u, l)$.

3. Results and discussion

In Table 1, the results of the calculation of the entropy from the expressions (5), (8), and (9) are displayed for different values of u and χ. The results are compared with the exact ones[3]. In Table 2 we give the results of the calculation of the heat-capacity. Instead of using (u, χ), we have employed $(v, v = u/4\chi)$ as variables in order to compare our results with those given by Amorebieta and Colussi[3].

The numerical values for the entropy in Table 1 lead us to the following conclusions:

(i) The results obtained for the entropy using $Q(N, u, l)$ or $Z(N, u, l)$ are closer to the exact values than those obtained from $Q(\infty, u, l)$.

(ii) The behaviour of $S_{Q(N, u, l)}$ and $S_{Z(N, u, l)}$ are similar to the function $S_{Q(N, u)}$, if it is considered as depending on v, that is, for a fixed u value. They show a maximum value when $v = 3.0$. On the other hand, $S_{Q(\infty, u, l)}$ has not this behaviour, and besides it is a monotonously

TABLE 1: Entropy of a Morse Oscillator (J k^{-1}mol^{-1}) for Several u and v Values ($u=\hbar\omega/kT$, $v = u/4\chi)h$. Results are Ordered as Follows: $Q(\infty,u,1)-S_{Q(M,u,1)}-S_{Z(N,u,1)}-S_{Q(N,u)}$

v	u										
	0.10	0.15	0.20	0.30	0.40	0.50	0.60	0.80	1.00	2.00	5.00
0.2	43.82	40.46	38.08								
	11.53	9.15	5.77								
	11.52	9.14	5.76								
	11.51	9.12	5.73								
0.3	40.82	37.45	35.07	31.73							
	14.91	11.54	9.14	5.77							
	14.89	11.52	9.12	5.75							
	14.86	11.49	9.12	25.74							
0.4	38.83	35.46	33.08	29.74	27.38						
	17.30	13.38	11.53	9.17	5.77						
	17.28	13.36	11.51	9.13	5.74						
	17.23	13.32	11.46	9.08	5.73						
0.5	37.38	34.02	31.64	28.29	5.94	24.13					
	19.14	16.19	13.38	9.11	9.20	5.77					
	19.12	16.16	13.35	9.08	9.13	5.72					
	19.05	16.08	13.31	9.06	9.04	5.70					
0.6	36.28	32.92	30.53	27.19	24.83	23.02	21.55				
	20.63	17.26	14.87	11.50	9.11	5.72	5.76				
	20.61	17.23	14.84	11.46	9.06	5.69	5.70				
	20.52	17.15	14.77	11.40	9.00	5.68	5.69				
0.7	35.42	32.04	29.66	26.31	23.95	22.14	20.67				
	21.86	18.19	16.11	13.33	11.51	9.10	5.70				
	21.85	18.16	16.08	13.29	11.45	9.04	5.66				
	21.75	18.08	15.98	13.20	11.34	8.97	5.65				
0.8	34.70	31.33	28.95	25.60	23.24	21.42	19.95	17.68			
	22.92	19.81	17.16	13.25	11.41	9.02	9.07	5.71			
	22.90	19.79	17.13	13.22	11.32	8.98	9.01	5.64			
	22.80	19.68	17.03	13.15	11.30	8.93	8.91	5.60			
0.9	34.11	30.74	28.36	25.01	22.64	20.83	19.36	17.08			
	23.82	20.45	18.06	14.70	13.20	11.36	8.98	5.65			
	23.81	20.44	18.04	14.67	13.17	11.32	8.93	5.65			
	23.71	20.34	17.95	14.59	13.05	11.23	8.87	5.56			
1.0	33.61	30.24	27.86	24.51	22.14	20.32	18.85	16.57	14.85		
	24.60	21.03	18.84	15.88	13.10	11.27	8.91	8.94	5.62		
	24.59	21.01	18.83	15.87	13.08	11.23	8.87	8.91	5.56		
	24.50	20.93	18.74	15.78	13.01	11.16	11.17	8.83	5.52		
1.5	31.93	28.57	26.18	22.83	20.47	18.64	17.17	14.88	13.15		
	27.25	23.88	21.50	18.14	16.21	13.94	12.45	10.58	8.36		
	27.26	23.90	21.52	18.17	16.26	13.98	12.49	10.66	8.40		
	27.34	23.97	21.59	18.23	16.36	14.01	12.51	10.67	8.37		
2.0	30.98	27.61	25.23	21.88	19.51	17.69	16.21	13.92	12.19	7.27	
	28.58	25.27	22.82	19.33	17.10	15.27	14.04	11.48	9.73	4.65	
	28.60	25.31	22.87	19.39	17.18	15.38	14.19	11.63	9.90	4.83	
	28.99	25.72	23.22	19.70	17.49	15.67	14.56	11.84	10.08	4.85	
3.0	29.93	26.57	24.18	20.83	18.46	16.64	15.16	12.86	11.13	6.21	
	29.35	25.98	23.60	20.24	17.88	16.05	14.57	12.41	10.53	5.59	
	29.38	26.03	23.66	20.34	18.00	16.20	14.75	12.67	10.82	6.06	
	30.40	27.03	24.64	21.29	18.91	17.09	15.61	13.67	11.55	6.49	
40.	29.37	26.00	23.61	20.26	17.89	16.07	14.59	12.29	10.56	5.65	
	29.24	25.87	23.49	20.14	17.77	15.94	14.45	12.17	10.43	5.52	
	29.27	25.91	23.54	20.22	17.87	16.07	14.60	12.37	10.68	5.97	
	30.52	27.13	24.77	21.47	19.04	17.22	15.65	13.43	11.72	6.74	
5.0	29.01	25.64	23.26	19.90	17.54	15.71	14.23	11.94	10.20	5.31	1.05
	28.99	25.62	23.23	19.88	17.51	15.69	14.21	11.92	10.18	5.28	1.01
	29.01	25.65	23.27	19.94	17.59	15.79	14.33	12.07	10.36	5.63	1.76
	30.16	26.81	24.39	21.03	18.70	16.86	15.44	13.18	11.34	6.44	2.22

6.0	28.77	25.40	23.01	19.66	17.29	15.47	13.99	11.69	9.96	5.07	0.93
	28.76	25.40	23.01	19.66	17.29	15.46	13.99	11.69	9.95	5.06	0.90
	28.78	25.42	23.04	19.70	17.35	15.54	14.07	11.80	10.09	5.32	1.39
	29.70	26.33	23.93	20.59	18.24	16.40	14.94	12.64	10.09	6.02	1.67
7.0	28.59	25.22	22.84	19.48	17.12	15.29	13.81	11.52	9.78	4.90	0.85
	28.59	25.22	22.84	19.48	17.12	15.29	13.81	11.52	9.78	4.89	0.85
	28.60	25.24	22.86	19.52	17.16	15.35	13.86	11.60	9.88	5.08	1.25
	29.29	25.92	23.56	20.19	17.82	16.00	14.52	12.26	10.50	5.61	1.80
10.0	28.26	24.90	22.51	19.10	16.79	14.97	13.49	11.19	9.45	4.58	0.70
	28.26	24.90	22.51	19.16	16.79	14.97	13.49	11.19	9.45	4.58	0.70
	28.27	24.91	22.52	19.17	16.81	14.99	13.52	11.23	9.50	4.67	0.87
	28.58	25.19	22.80	19.45	17.07	15.26	13.77	11.46	9.75	4.90	1.05
50.0	27.63	24.26	21.87	18.52	16.15	14.33	12.85	10.55	8.82	3.96	0.41
	27.63	24.26	21.87	18.52	16.15	14.33	12.85	10.55	8.82	3.97	0.41
	27.63	24.26	21.88	18.52	16.15	14.33	12.85	10.55	8.82	3.97	0.42
	27.66	24.27	21.88	18.53	16.15	14.34	12.84	10.54	8.83	3.98	0.42

diminishing function.

(iii) For v values less than 2.0, the results for S show the correct behaviour, that is they decrease as v decreases. On the contrary, $S_{Q(\infty, u, 1)}$ grows as v diminishes and the results ar very far from the exact ones.

Similar conclusions follow from the analysis of the results in Table 2 for C, with the difference that there are some values abnormally large for small u and v values, although for medium and large u and v values, the correct behaviour is observed. Another point that deserves special attention is that the C values have errors with respect to the exact ones, that are greater than those obtained for S.

4. Conclusions

In this work, two thermodynamical properties have been evaluated in order to test the validity of application of expressions (8) and (9). The results of Table 1 and 2 show that such analytical expressions lead to formulations for the entropy and heat capacity from which we obtain results that are close to the exact values. Moreover, they show the correct behaviour. This is not true when we consider the results obtained from expression (5), except when the u and v values lie in the neighborhood of one of the $S_{Q(N, u)}-S_{Q(\infty, u, 1)}$, and $C_{Q(N, u)}-C_{Q(\infty, u, 1)}$ crossings, or for v values greater than those belonging the corssings.

It is singificant that the results allow us to verify the usefulness of these formulations for small u and v values, and to date there are no correct values and all calculations have been done in the range where $Q(\infty, u, 1)$ gives correct results[2].

Then we conclude that the analytical formulations recently given[6], are more reliable than the usually accepted ones, they give better results and can be used for a range of temperatures, that up to now, had not been reported.

TABLE 2: Heat Capacity of a Morse Oscillator (J k^{-1}mol^{-1}) for Several u and v values ($u = \hbar\omega/kT$, $v = u/4\chi$). Results are Ordered as Follows: $C_{Q(\infty, u, 1)}-C_{Q(N, u, 1)}-C_{Z(N, u, 1)}C_{Q(N, u)}$

v	u									
	0.10	0.60	0.80	1.00	1.50	2.00	3.00	4.00	5.00	10 00
0.20	15.94									
	12.80									
	14.44									
	0.03									
0.60	14.15	13.88								
	1.46	1.44								
	1.42	1.16								
	0.29	0.17								
0.80	13.47	13.22	13.03							
	0.90	0.65	0.71							
	0.82	0.09	0.05							
	0.53	0.42	0.32							
1.00	12.93	12.68	12.50	12.29						
	1.02	0.84	0.91	0.60						
	0.94	0.39	0.05	−0.32						
	0.84	0.75	0.67	0.50						
1.50	11.94	11.71	11.53	11.32	10.73					
	2.56	2.33	2.47	1.96	1.40					
	2.47	1.84	1.76	1.19	0.32					
	1.91	1.72	1.67	1.46	1.02					

2.00	11.30	11.06	10.89	10.68	10.08	9.44				
	4.64	4.75	4.21	3.98	4.20	2.62				
	4.56	4.29	3.63	1.71	3.07	1.37				
	3.34	3.26	2.97	2.76	2.48	1.63				
3.00	10.51	10.28	10.10	9.88	9.24	8.53	7.26			
	7.89	7.65	7.90	7.24	6.55	5.80	4.37			
	7.86	7.46	7.68	6.92	6.07	5.12	3.23			
	6.55	6.32	6.44	5.86	5.16	4.35	2.79			
4.00	10.05	9.82	9.64	9.42	8.75	8.00	6.47	5.32		
	9.25	8.92	8.83	8.61	7.67	7.16	6.07	4.37		
	9.25	8.91	8.84	8.62	7.60	7.13	6.17	4.05		
	9.16	8.74	8.70	8.45	7.28	6.82	5.78	3.49		
5.00	9.75	9.51	9.33	9.11	8.43	7.66	6.13	4.79	3.60	
	9.54	9.33	9.17	8.90	8.28	7.44	5.71	4.73	3.34	
	9.55	9.41	9.28	9.03	8.49	7.66	5.82	5.43	3.91	
	10.57	10.46	10.38	9.87	9.46	8.28	5.87	6.12	3.64	
6.00	9.54	9.30	9.12	8.90	8.21	7.41	5.82	4.44	3.25	
	9.49	9.25	9.07	8.85	8.16	7.36	5.77	4.38	3.02	
	9.50	9.33	9.17	8.98	8.35	7.61	6.12	4.89	3.49	
	10.98	10.75	10.54	10.33	9.61	8.74	7.04	5.55	3.43	
7.00	9.38	9.14	8.96	8.74	8.04	7.23	5.60	4.17	2.99	
	9.37	9.13	8.95	8.73	8.03	7.22	5.59	4.17	2.99	
	9.38	9.19	9.04	8.83	8.19	7.43	5.91	4.65	3.69	
	10.84	10.59	10 50	10 21	9.38	6.68	7.24	6.08	4.69	
10.00	9.08	8.84	8.66	8.44	7.73	6.89	5.18	3.70	2.53	0.19
	9.08	8.84	8.66	8.44	7.73	6.89	5.18	370	2.53	0.19
	9.09	8.88	8.71	8.49	7.81	7.00	5.34	3.93	2.87	0.73
	9.83	9.62	9.41	9.20	8.49	7.66	6.00	4.53	3.47	1.38
50.00	8.47	8.23	8.05	7.82	7.09	6.20	4.34	2.77	1.64	0.07
	8.47	8.23	8.05	7.82	7.09	6.20	4.34	2.77	1.64	0.07
	8.47	8.23	8.05	7.82	7.09	6.21	4.35	2.78	1.66	0.08
	8.49	8.24	8.08	7.82	7.10	6.23	4.36	2.79	1.67	0.08

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Reactions of Oxomolybdenum(V) with the 17-tungsto-2-phosphate Anion

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Reactions of MoOCl$_5^{2-}$ with α_2-[P$_2$W$_{17}$O$_{61}$]$^{10-}$ have been studied spectrophotometrically and several complexes have been identified. The transient species initially formed is probably [Mo$_2$O$_4$(P$_2$W$_{17}$O$_{61}$)$_2$]$^{18-}$. At pH $\leq$ 3 the visible spectrum changes gradually, indicating formation of a transient isomer of [P$_2$Mo^{V}W$_{17}$O$_{62}$]$^{7-}$, which again transforms into the stable isomer. The transient isomer absorbs light much more strongly than the stable isomer in the visible range. At pH $>$ 3 [P$_2$W^V W$_{16}$O$_{61}$]$^{11-}$ is formed probably via the transient isomer of [P$_2$Mo^{V}W$_{17}$O$_{61}$]$^{7-}$.

Introduction

Recently we have investigated reactions of MoO^{3+} with [PW$_{11}$O$_{39}$]$^{7-}$ and [SiW$_{11}$O$_{39}$]$^{8-}$ spectrophotometrically and found several transient complexes.[1] Now we have extended this work to the reaction of MoO^{3+} with [P$_2$W$_{17}$O$_{61}$]$^{10-}$,