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Partition Function of Noble Gas Trimers

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Temperature dependences of the partition function, Gibbs function, enthalpy and heat capacity for the trimers Ar_3, Kr_3 and Xe_3 are described.

Calculation of the partition function for noble gas dimers is not complicated, since the values of energy levels are obtained from the one-dimensional Schrodinger equation, the solution of which can be found both numerically and analytically by the WKBJ method.[1] However, noble gas trimers are a special case. Classical dynamics of such systems are chaotic even at small excitation energies (about the energy of the ground quantum state[2]), thus excluding the use of normal mode methods and making the calculation of energy levels very elaborate. On the other hand, owing to the large number of bound states of trimers, an approximate quasi-classical form of the density of levels can be obtained. This form can be used for the calculation of the partition function. Successful results of the semiclassical calculations of density of states for H_3^+ have been reported in ref. 3.

This article presents temperature dependencies of the Gibbs function, enthalpy and heat capacity for the Ar, Kr and Xe trimers obtained by the above-mentioned method.

Noble gas trimers may be considered as bound states of a system of similar particles with Hamiltonian (1),

$$H=\sum_{i=1}^{3}\frac{\vec{p}_i^{\,2}}{2m}+\sum_{i<j}^{3}U_{LJ}(r_{ij}) \qquad (1)$$

where m is the particle mass, $\vec{p}_i$ and $\vec{r}_i$ are vectors of moment and position, $r_{ij}=|\vec{r}_i-\vec{r}_j|$ and $U_{LJ}(r)$ is the pairwise Lennard–Jones interaction potential, eqn. (2).

$$U_{LJ}(r)=4U_0\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right] \qquad (2)$$

The parameters of such a potential are currently determined to high accuracy and are easily accessible.[4] For a pair of atoms Ar $U_0=1.67\times10^{-21}$J, $\sigma=0.34$ *nm*, for Kr $U_0=2.27\times10^{-21}$J, $\sigma=0.38$ *nm*, for Xe $U_0=3.07\times10^{-21}$J, $\sigma=0.41$ *nm*.[5] In the system where U_0, m, σ are units (dimensionless), values of the Planck constant are $\hbar$ (Ar)$=2.93\times10^{-2}$, $\hbar$ (Kr)$=1.55\times10^{-2}$, $\hbar$ (Xe)$=9.9\times10^{-3}$. Small values of $\hbar$ allow the calculation of the density of levels $\rho(E)$ with the help of the quasi-classical Weyl formula, eqn.(3),[6]

$$\rho_w(E)=\frac{1}{(2\pi\hbar)^N}\frac{d\Omega(E)}{dE}\xi \qquad (3)$$

where $\Omega(E)$ is the volume of the part of the classical phase space with energy less than E and N is the number of degrees of freedom. On the assumption that our system consists of identical bosons, it follows that the symmetry factor is $\xi=\frac{1}{6}$. The phase volume of internal degrees of freedom for the trimer can be represented by the formula (4),

$$\Omega(E)=\frac{1}{27}\int_{H<E}\prod_{i=1}^{n}d\vec{p}_i\prod_{i=1}^{n}d\vec{r}_i\Theta(E-H), \qquad (4)$$

where $\Theta(x)$ is a unit step function, and values of $\vec{r}_3$ and $\vec{p}_3$ in H are determined by the equations $\vec{r}_3=-\vec{r}_1-\vec{r}_2, \vec{p}_3=-\vec{p}_1-\vec{p}_2$. The numerical coefficient before the integral arises from the transition into the centre of mass reference frame and equals n^{-3}, where $n=3$ is the number of particles in the system. The procedure for the $\Omega(E)$ calculation by the Monte Carlo method has been outlined in the authors' previous work.[7] Quasi-classical density state values are plotted in Fig. 1.

The values of $\rho_w(E)$ are not sensitive to the precise form of the interaction potential. We have repeated our calculations for the trimer Ar_3, replacing the Lennard–Jones potential (2) by the modified Buckingham potential with eight parameters, taken from ref. 8. The changes in the density of levels which have resulted from this replacement can be described briefly as the multiplication of $\rho_w(E)$ by the factor 0.924.

The partition function is determined by the expression (5),

$$Z=\int\rho(E)\exp(-E/kT)dE \qquad (5)$$

where T is the absolute temperature and k is the Boltzman constant.

For an analysis of experimental data on the formation of clusters in a supersonic flow, the value $Z(E)$ and the thermodynamic functions in the temperature range T from 1 to 100 K are of special interest.[9,10] In the lower part of this range, for $T\leqslant7-10$ K, we can neglect the excitation of vibrational states. For such temperatures the main contribution to the integral (5) comes from the vicinity of the ground state (with energy E_0), where the quasi-classical formula (3) is ineffective, but one can use the rotational approximation (6).[11]

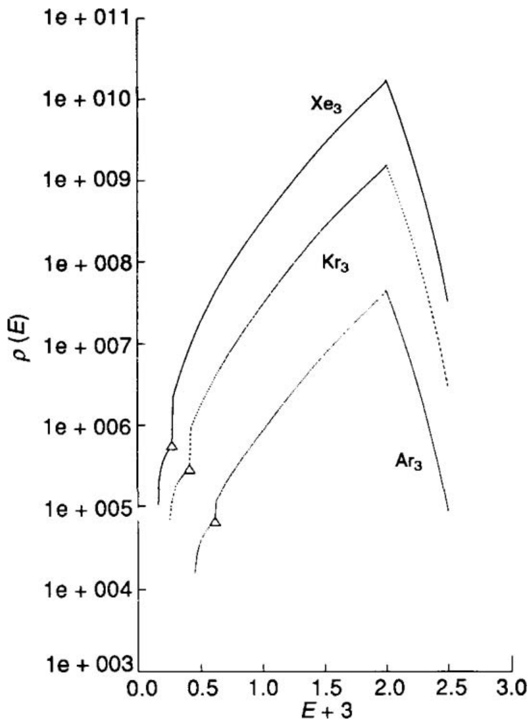

Fig. 1 Density of states used for numerical calculation of the partition function $Z(T)$. To the left of the shift Δ is the rotational approximation $\rho_r(E)$, and to the right, the quasi-classical $\rho_w(E)$ [$\rho_w(E)$ is in the natural system of units ($U_0=1$)].

$$\rho_r(E)=\frac{4}{\hbar^3}(E-E_0)^{1/2} \qquad (6)$$

This formula has been derived under the assumption that at a ground vibrational state the system is an equilateral triangle with the side length $a=\sigma2^{1/6}$.

Values of the expressions (3) and (6) are not essentially different in the region of the first vibrational state E_1. Therefore, it is possible to interpolate between the asymptotic expressions for $Z(T)$, by assuming $\rho(E)=(6)$ for $E<E_1$ and $\rho(E)=(3)$ for $E>E_1$ (Fig. 1). The subtle interpolation scheme that uses the rotational approximation near each of the several first excited vibrational states, will slightly change the value of $Z(T)$.

Partition function (5), at different temperatures, gives the temperature dependence of the thermodynamic function *i.e.*, the reduced Gibbs function $\phi^i(T)$, eqn. (7.1),

$$\frac{\phi^i(T)}{R}=\ln Z(T) \qquad (7.1)$$

where R is the universal gas constant.

The enthalpy $H^i(T)$ is given by eqn. (7.2),

$$\frac{H^i(T)-H^i(0)}{RT}=T\frac{\partial\ln Z(T)}{\partial T} \qquad (7.2)$$

where $H^i(0)$ is the energy of a ground vibrational state, measured from the depth of the potential well, and the heat capacity C_p^i by eqn. (7.3).

$$\frac{C_p^i}{R}=T^2\frac{\partial^2\ln Z(T)}{\partial T^2}+2T\frac{\partial\ln Z(T)}{\partial T} \qquad (7.3)$$

In Table 1 the numerical values of the reduced Gibbs function, enthalpy and heat capacity (in a dimensionless form) are represented in the temperature interval $5\ \mathrm{K}\leqslant T\leqslant150$ K. It can be noted that the calculations have been computated more precisely, although Table 1 consists of only three significant digits according to accepted standards.[12]

Table 1 Thermodynamic properties of Ar, Kr, Xe trimers.

T/K	Φ^i/R			$\frac{H^i(T) - H^i(0)}{RT}$			$\frac{C_p^i}{R} \cdot 10^2$		
	Ar_3	Kr_3	Xe_3	Ar_3	Kr_3	Xe_3	Ar_3	Kr_3	Xe_3
5	5.58	7.20	8.52	1.61	1.86	2.34	228	321	420
10	7.04	9.12	10.8	2.25	2.87	3.17	367	465	491
15	8.19	10.6	12.4	2.92	3.55	3.83	499	579	616
20	9.18	11.8	13.8	3.37	4.00	4.28	480	558	594
25	9.98	12.8	14.8	3.44	4.05	4.32	361	421	449
30	10.6	13.5	15.6	3.30	3.86	4.10	253	294	316
35	11.1	14.1	16.2	3.08	3.59	3.81	176	205	218
40	11.5	14.6	16.8	2.85	3.31	3.51	126	146	155
45	11.9	15.0	17.2	2.64	3.05	3.24	91.7	106	113
50	12.1	15.3	17.5	2.44	2.82	2.99	68.8	79.5	84.5
55	12.8	15.6	17.8	2.26	2.61	2.77	52.8	60.9	64.6
60	12.6	15.8	18.0	2.11	2.43	2.58	41.4	47.5	50.4
65	12.7	16.0	18.2	1.98	2.27	2.41	33.0	37.8	40.0
70	12.7	16.1	18.4	1.85	2.13	2.26	27.6	31.0	32.3
75	13.0	16.3	18.5	1.74	2.01	2.12	22.0	25.0	26.4
80	13.1	16.4	18.7	1.65	1.89	2.00	18.3	20.7	21.8
85	13.2	16.5	18.8	1.56	1.79	1.89	15.4	17.3	18.3
90	13.3	16.6	18.9	1.48	1.70	1.80	13.1	14.7	15.4
95	13.4	16.7	19.0	1.41	1.62	1.71	11.2	12.5	13.2
100	13.4	16.8	19.1	1.34	1.54	1.63	9.66	10.8	11.3
110	13.6	16.9	19.2	1.23	1.41	1.50	7.35	8.14	8.52
120	13.7	17.0	19.3	1.13	1.30	1.37	5.74	6.31	6.58
130	13.7	17.1	19.4	1.05	1.20	1.27	4.77	4.98	5.18
140	13.8	17.2	19.5	1.00	1.12	1.18	3.70	4.01	4.16
150	13.9	17.3	19.6	0.92	1.05	1.11	3.04	3.27	3.38

The values obtained can be used for investigation of the $A + A_2 \leftrightarrows A_3$ equilibrium near a nozzle during the process of supersonic expansion of noble gases into a vacuum, *i.e.*, an essential part of the theory describing cluster formation under the conditions allowed by modern experiments.

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