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SPECIFIC HEAT OF THE ANISOTROPIC RIGID ROTATOR

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ABSTRACT

The exact (numerical) thermal evolution of the specific heat C of the single anisotropic (not necessarily equal inertial momenta $I_x = I_y \equiv I_{xy}$ and I_z) quantum rigid rotator is calculated. For values of I_{xy}/I_z low enough, C presents an unexpectedly high maximum; for sufficiently high values of I_{xy}/I_z a second peak emerges. Also a quite rich $T \to 0$ asymptotic behaviour is exhibited.

I - INTRODUCTION

Very few quantum systems exist for which the exact energy spectrum is known. Among them we have the symmetric top or anisotropic rigid rotator associated with two different momenta of inertia ($I_x = I_y \equiv I_{xy}$ and I_z do not necessarily coincide). This is an important system as it can account, within a first approximation, for the rotational degrees of freedom of: (i) molecules associated with an oblate inertial ellipsoid ($I_{xy} > I_z$) such as the heteronuclear diatomic ones (e.g. HD, NO, HCℓ) or more complex linear ones (e.g. HCN, SCO); (ii) molecules associated with a prolate ellipsoid ($I_{xy} < I_z$) such as benzene (C_6H_6); and finally (iii) molecules which are spherical from the inertial standpoint ($I_{xy} = I_z$) such as methane (CH_4).

Once the complete set of energy levels corresponding to this type of rotator is available, and because of its usefulness in describing rarefied gases, the calculation of thermal quantities such as the associated specific heat appears as a natural task. However, surprisingly enough, this has not, as far as we know, been accomphished for all temperatures, excepting of course the $I_{xy}/I_z \to \infty$ limit which since long is a standard one [1]. The purpose of the present paper is to exhibit the influence of the ratio I_{xy}/I_z on the thermal behaviour of the specific heat, as well as to present its numerically exact values corresponding to typical temperatures T and ratios I_{xy}/I_z.

II - SPECIFIC HEAT

Let us consider the system characterized by the Hamiltonian

$$\mathcal{H} = \frac{L_x^2 + L_y^2}{2I_{xy}} + \frac{L_z^2}{2I_z}$$

$$= \frac{L^2}{2I_{xy}} + \frac{1}{2}\left(\frac{1}{I_z} - \frac{1}{I_{xy}}\right)L_z^2 \qquad (1)$$

where $L_i\,(i = x,y,z)$ and L respectively are the components and modulus of the angular momentum $\vec{L}$, $I_x = I_y \equiv I_{xy}$ and I_z being the corresponding momenta of inertia. The eingenvalues $E_{\ell,m}$ of this Hamiltonian are given [2] by

$$E_{\ell,m} = \frac{\hbar^2}{2}\left[\frac{\ell(\ell+1)}{I_{xy}} + \left(\frac{1}{I_z} - \frac{1}{I_{xy}}\right)m^2\right] \qquad (2)$$

where $\ell = 0,1,2,\ldots,$ and $m = \ell, \ell - 1, \ldots, -\ell$, each level presenting, because of the possible projections of $\vec{L}$ on the intrinsic rotation axis of the rotator, a $(2\ell + 1)$ degeneracy (see Ref. [3] for a discussion of the eigenvalues associated with the general case where all three $\{I_i\}$ are arbitrary). Notice that, in both particular cases $I_{xy}/I_z \to \infty$ (oblate) and $I_{xy}/I_z = 1$, the levels follow the $\ell(\ell + 1)$ law, but while the former presents a $(2\ell + 1)$ degeneracy, the latter presents a $(2\ell + 1)^2$ one. In the particular case $I_{xy}/I_z = 0$ (prolate) the levels are equidistant and present a relatively irregular degeneracy. The fundamental and few first excited levels are illustrated in Fig. 1.

The canonical partition function Z associated with the spectrum (2) is given by

$$Z(t) = \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-\ell(\ell+1)/t} \sum_{m=-\ell}^{\ell} e^{-(I_{xy}/I_z - 1)m^2/t} \tag{3}$$

where

$$t \equiv 2 I_{xy} k_B T/\hbar^2 \tag{4}$$

If by $<\ldots>$ we denote the canonical thermal average, then the specific heat is given by

$$C \equiv \frac{d}{dt} <\mathcal{H}> = \frac{1}{k_B T^2}\left[<\mathcal{H}^2> - <\mathcal{H}>^2\right] \tag{5}$$

hence

$$\frac{C}{k_B} = \frac{1}{t^2}\left[\frac{V}{Z} - \left(\frac{W}{Z}\right)^2\right] \tag{6}$$

where Z is given by Eq. (3),

$$V \equiv \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-\ell(\ell+1)/t} \sum_{m=-\ell}^{\ell} \left[\ell(\ell + 1) + \left(\frac{I_{xy}}{I_z} - 1\right)m^2\right]^2 e^{-(I_{xy}/I_z - 1)m^2/t} \tag{7}$$

and

$$W \equiv \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-\ell(\ell+1)/t} \sum_{m=-\ell}^{\ell} \left[\ell(\ell + 1) + \left(\frac{I_{xy}}{I_z} - 1\right)m^2\right] e^{-(I_{xy}/I_z - 1)m^2/t} \tag{8}$$

We have used Eq. (6) to numerically calculate C: the results are presented in Fig. 2 and Table I (to calculate, within the desired precision, the value of C/k_B corresponding to let us say

$I_{xy}/I_z = 0$ and $t = 10$, it has been necessary to compute terms up to $\ell \simeq 200$). We notice in Fig. 2 that, for all ratios I_{xy}/I_z, a peak (whose abcissa and ordinate will be noted t_M and C_M respectively) is present which becomes unexpectedly pronounced for low I_{xy}/I_z; its evolution with I_{xy}/I_z is presented in Fig. 3 and Table II. For $I_{xy}/I_z > 8.06513$ a lower peak (whose abcissa and ordinate will be noted t_m and C_m respectively) emerges which presents almost no evolution with I_{xy}/I_z: for $I_{xy}/I_z = 8.06513$, 10 and higher than 25 we have respectively $(t_m, C_m/k_B) = (0.8968, 1.10723)$, $(0.81303, 1.09795)$ and $(0.80717, 1.09762)$. We also remark that, for any finite I_{xy}/I_z, $\lim_{T\to\infty} C/k_B = 3/2$ (classical equipartition associated with 3 degrees of freedom), whereas $\lim_{T\to\infty} \lim_{J_{xy}/J_z\to\infty} C/k_B = 1$ (classical equipartition associated with only 2 degrees of freedom). Finally let us mention that, in the limit $T \to 0$,

$$\frac{C}{k_B} \sim \frac{6}{t^2}\left[\left(\frac{I_{xy}}{I_z}+1\right)^2 e^{-(I_{xy}/I_z+1)/t} + 2e^{-2/t}\right], \tag{9}$$

consequently the leading terms are given by

$$\frac{C}{k_B} \sim \begin{cases} \dfrac{6(I_{xy}/I_z+1)^2}{t^2}\, e^{-(I_{xy}/I_z+1)/t}, & \text{if } 0 \le \dfrac{I_{xy}}{I_z} < 1; \quad (10.a) \\[2ex] \dfrac{36}{t^2}\, e^{-2/t}, & \text{if } \dfrac{I_{xy}}{I_z} = 1; \quad (10.b) \\[2ex] \dfrac{12}{t^2}\, e^{-2/t}, & \text{if } \dfrac{I_{xy}}{I_z} > 1 \quad (10.c) \end{cases}$$

which exhibit interesting non uniform convergences.

III - CONCLUSION

Let us conclude by recalling that the present calculation of the specific heat C of the single anisotropic ($I_x = I_y \equiv I_{xy}$ and I_z might be different) quantum rigid rotator is a <u>numerically exact</u> one.

The most remarkable feature of the influence of the ratio I_{xy}/I_z on the thermal evolution of C is the existence, for all values of I_{xy}/I_z, of an important peak which becomes sharper and sharper while I_{xy}/I_z decreases; in the extreme prolate limit ($I_{xy}/I_z = 0$) its height almost attains $k_B 5/2$. On the other hand for I_{xy}/I_z high enough, a second and smaller peak emerges which, in the extreme oblate limit ($I_{xy}/I_z = \infty$), becomes the well known small bump detectable through standard calculation [1]. Also it has been exhibited how, through non uniform convergence, the high temperature classical k_B 3/2 limit associated with 3 degrees of freedom, becomes a k_B limit when one of those degrees is maintained frozen. Finally a quite rich picture (once more associated with non uniform convergences) emerges in the very low temperature region.

The present numerical and analytical results could possibly be of utility for testing theoretical non exact procedures for calculating specific heats, as well as for high precision analysis of experimental data on rarefied gases.

We acknowledge stimulating comments from S.I.Zanette.

REFERENCES

[1] J.E.Mayer and M.G.Mayer,"Statistical Mechanics", second edition, Chap. 7 (John Wiley, 1977)

[2] P.R.Bunker, "Molecular Symmetry and Spectroscopy", Chap.8 (Academic, New York, 1979)

[3] A.O.Caride and S.I.Zanette, J.Chem. Phys. 76, 1179 (1982)

CAPTION FOR FIGURES AND TABLES

Fig. 1 - Reduced energetic levels of the fundamental ($\ell = 0$) and few first excited ($\ell = 1,2,3,\ldots$) states as functions of the ratio I_{xy}/I_z.

Fig. 2 - Reduced specific heat C/k_B as a function of the reduced temperature $t \equiv 2\, I_{xy} k_B T/\hbar^2$ for typical values of I_{xy}/I_z (numbers parametrizing the curves).

Fig. 3 - I_{xy}/I_z-dependences of: (a) the reduced temperature t_M at which the big peak of Fig. 2 occurs; (b) the corresponding value C_M/k_B.

Table 1 - Values of C/k_B associated with typical ratios I_{xy}/I_z and reduced temperatures $t \equiv 2\, I_{xy} k_B T/\hbar^2$. At the (∞,∞) position a double result appears because

$$\lim_{I_{xy}/I_z \to \infty} \lim_{t \to \infty} C/k_B = 3/2, \text{ whereas } \lim_{t\to\infty} \lim_{I_{xy}/I_z \to \infty} C/k_B = 1.$$

Table 2 - t_M and C_M/k_B (respectively abcissa and ordinate of the big peak appearing in Fig. 2) for typical values of I_{xy}/I_z.

TABLE 1

t \ I_{xy}/I_z	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	2	3	4	5	10	25	∞
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.1	0.02724	0.01213	0.00531	0.00229	0.00098	0.00042	0.00018	0.00007	0.00003	0.00001	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
0.2	0.98854	0.72793	0.53453	0.38791	0.27864	0.19892	0.14183	0.10155	0.07347	0.05409	0.04083	0.01403	0.01362	0.01362	0.01362	0.01362	0.01362	0.01362
0.3	2.13002	1.83177	1.61899	1.43061	1.25274	1.08555	0.93265	0.79693	0.67959	0.58026	0.49761	0.19534	0.17011	0.16850	0.16841	0.16840	0.16840	0.16840
0.4	2.45910	2.22306	2.11379	2.03785	1.96608	1.88542	1.79188	1.68705	1.57519	1.46114	1.34919	0.66136	0.51189	0.48921	0.48625	0.48585	0.48585	0.48585
0.5	2.38486	2.16258	2.10030	2.08425	2.08689	2.09390	2.09521	2.08427	2.05799	2.01622	1.96078	1.24417	0.90811	0.81856	0.79882	0.79398	0.79398	0.79398
0.6	2.24233	1.99879	1.94106	1.93290	1.94853	1.97789	2.01406	2.05074	2.08232	2.10455	2.11481	1.70682	1.25860	1.07197	1.01225	0.98935	0.98933	0.98933
0.7	2.13422	1.86069	1.79567	1.77991	1.78692	1.80843	1.84058	1.88018	1.92369	1.96731	2.00752	1.95212	1.52531	1.25623	1.14041	1.07647	1.07629	1.07629
0.8	2.06909	1.76832	1.69668	1.67323	1.67036	1.67993	1.69904	1.72634	1.76044	1.79950	1.84122	2.01660	1.70582	1.39913	1.22802	1.09846	1.09755	1.09755
0.9	2.03389	1.71126	1.63634	1.60845	1.59923	1.60035	1.60892	1.62405	1.64541	1.67252	1.70448	1.97780	1.81332	1.51731	1.30598	1.09265	1.08955	1.08955
1.0	2.01606	1.67633	1.60097	1.57147	1.55915	1.55559	1.55779	1.56477	1.57639	1.59277	1.61383	1.89768	1.86533	1.61567	1.38574	1.08089	1.07291	1.07291
1.2	2.00335	1.63899	1.56729	1.53899	1.52569	1.51927	1.51670	1.51674	1.51898	1.52351	1.53060	1.73498	1.86586	1.75190	1.54533	1.07428	1.04334	1.04334
1.4	2.00065	1.61886	1.55271	1.52744	1.51551	1.50937	1.50621	1.50478	1.50456	1.50536	1.50727	1.62504	1.80256	1.81047	1.67543	1.10300	1.02622	1.02621
1.6	2.00012	1.60479	1.54413	1.52186	1.51155	1.50625	1.50342	1.50194	1.50128	1.50119	1.50159	1.56323	1.72638	1.81090	1.75670	1.16255	1.01722	1.01714
1.8	2.00002	1.59364	1.53796	1.51827	1.50937	1.50487	1.50247	1.50118	1.50054	1.50029	1.50033	1.53116	1.65920	1.77810	1.79133	1.24290	1.01245	1.01211
2.0	2.00000	1.58440	1.53312	1.51562	1.50788	1.50402	1.50198	1.50090	1.50035	1.50011	1.50006	1.51525	1.60738	1.73181	1.79130	1.33352	1.01018	1.00905
2.5	2.00000	1.56685	1.52455	1.51112	1.50545	1.50272	1.50131	1.50058	1.50021	1.50004	1.50000	1.50289	1.53594	1.62281	1.71941	1.54998	1.01404	1.00512
3	2.00000	1.55450	1.51898	1.50834	1.50400	1.50196	1.50094	1.50041	1.50015	1.50003	1.50000	1.50094	1.51122	1.55638	1.63434	1.69667	1.03630	1.00331
4	2.00000	1.53851	1.51237	1.50520	1.50242	1.50117	1.50055	1.50024	1.50008	1.50002	1.50000	1.50039	1.50140	1.50990	1.53824	1.77014	1.15072	1.00171
5	2.00000	1.52881	1.50872	1.50355	1.50162	1.50077	1.50036	1.50015	1.50005	1.50001	1.50000	1.50024	1.50048	1.50181	1.50927	1.70481	1.32849	1.00105
6	1.99999	1.52244	1.50649	1.50258	1.50117	1.50055	1.50025	1.50011	1.50004	1.50001	1.50000	1.50016	1.50030	1.50054	1.50224	1.62556	1.50695	1.00071
7	1.99999	1.51800	1.50502	1.50196	1.50088	1.50041	1.50019	1.50008	1.50003	1.50001	1.50000	1.50012	1.50022	1.50030	1.50067	1.56902	1.64380	1.00051
8	1.99999	1.51478	1.50400	1.50154	1.50068	1.50032	1.50015	1.50006	1.50002	1.50000	1.50000	1.50009	1.50016	1.50021	1.50031	1.53551	1.72695	1.00038
9	1.99999	1.51237	1.50327	1.50125	1.50055	1.50025	1.50012	1.50005	1.50002	1.50000	1.50000	1.50007	1.50013	1.50016	1.50020	1.51749	1.76297	1.00030
10	1.99999	1.51051	1.50272	1.50103	1.50045	1.50021	1.50009	1.50004	1.50001	1.50000	1.50000	1.50006	1.50010	1.50013	1.50015	1.50836	1.76515	1.00024
∞	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2,1

TABLE II

I_{xy}/I_z	t_M	C_M/k_B
0	0.41328	2.46206
0.1	0.42274	2.23255
0.2	0.44026	2.14512
0.3	0.45831	2.10802
0.4	0.47662	2.09509
0.5	0.49534	2.09425
0.6	0.51446	2.09884
0.7	0.53387	2.10500
0.8	0.55345	2.11052
0.9	0.57312	2.11421
1	0.59286	2.11550
2	0.80028	2.01660
3	1.09333	1.87841
4	1.49708	1.81635
5	1.89573	1.79480
10	3.82142	1.77258
25	9.56126	1.76553
∞	∞	3/2

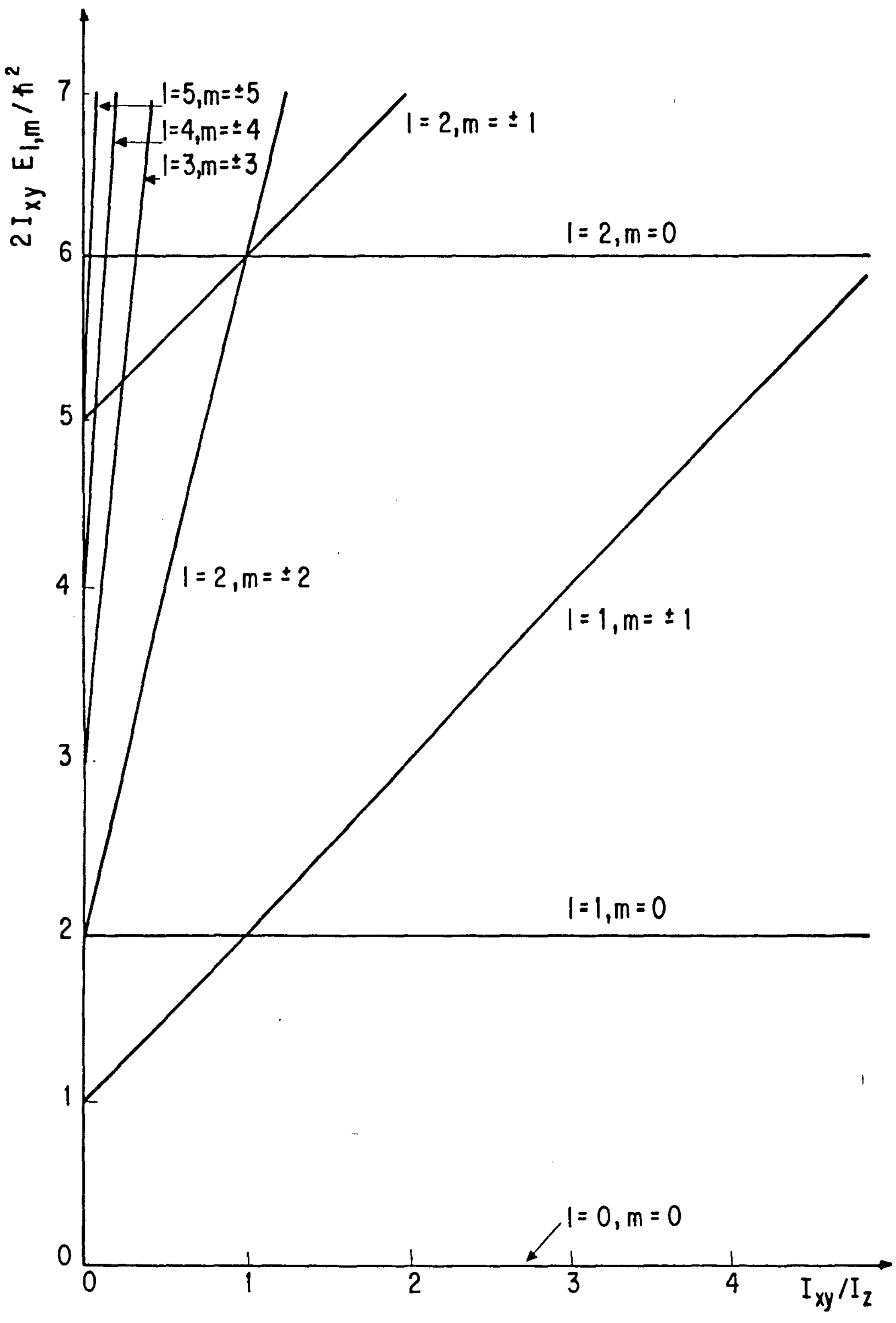
$2I_{xy}\ E_{l,m}/\hbar^2$
7
6
5
4
3
2
1
0
l=5,m=±5
l=4,m=±4
l=3,m=±3
l = 2,m = ± 1
l = 2,m = 0
l = 2,m = ± 2
l = 1,m = ± 1
l = 1,m = 0
l = 0,m = 0
0
1
2
3
4
I_{xy}/I_z

FIG.1

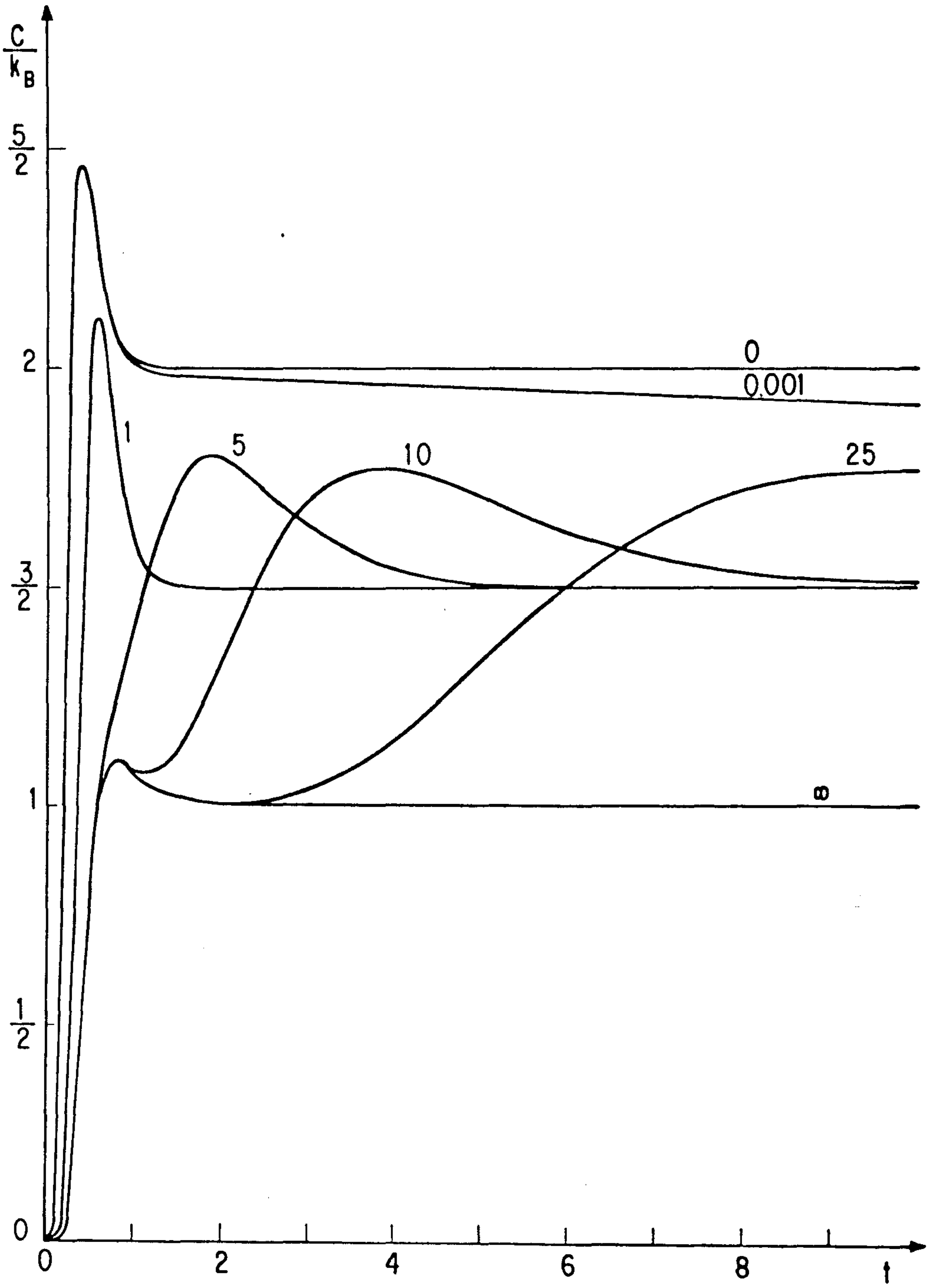

FIG. 2

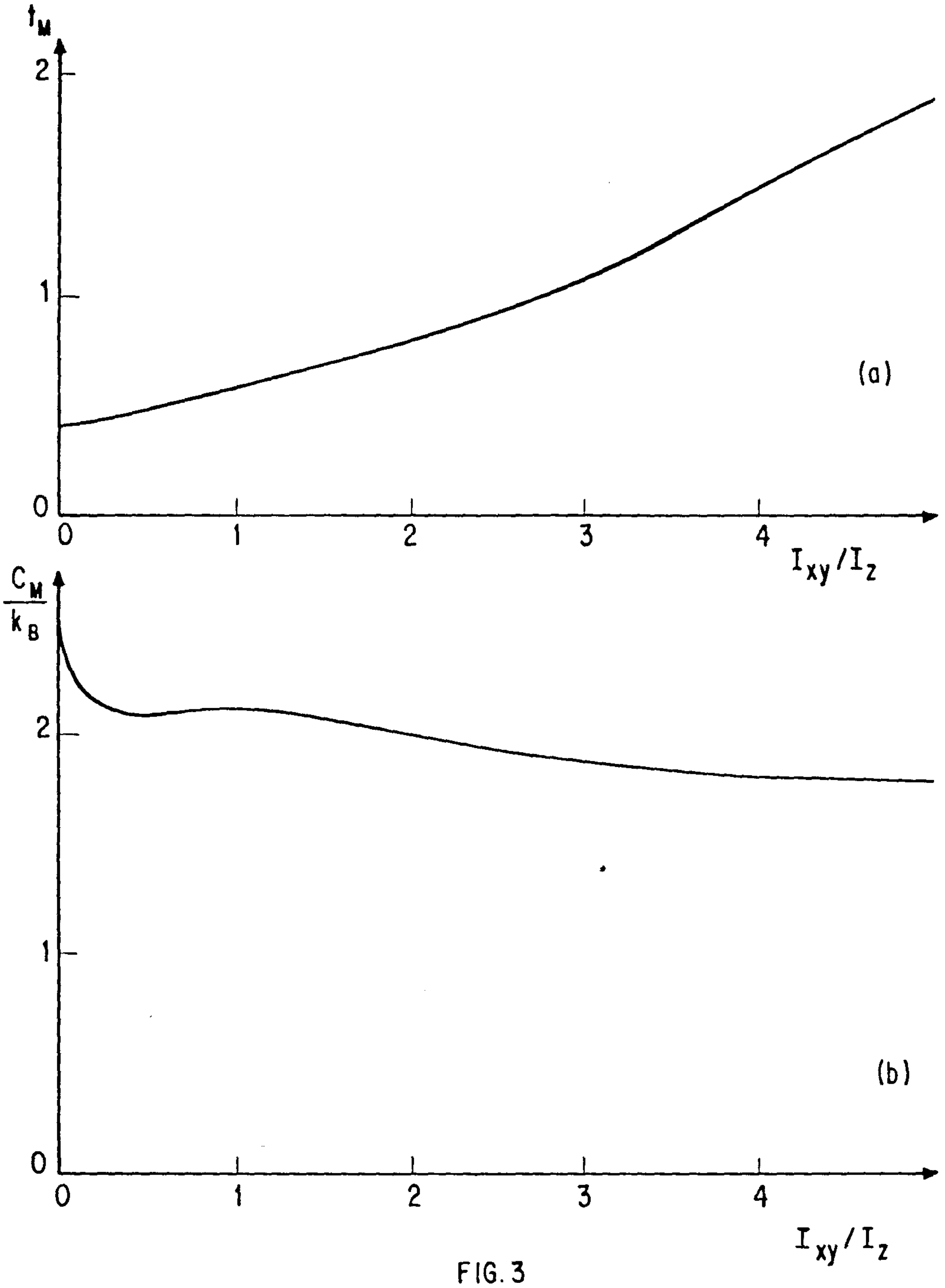

FIG. 3

TABLE I

t \ I_{xy}/I_z	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	2	3	4	5	10	25	∞
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.1	0.02724	0.01213	0.00531	0.00229	0.00098	0.00042	0.00018	0.00007	0.00003	0.00001	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
0.2	0.98854	0.72793	0.53453	0.38791	0.27864	0.19892	0.14183	0.10155	0.07347	0.05409	0.04083	0.01403	0.01362	0.01362	0.01362	0.01362	0.01362	0.01362
0.3	2.13002	1.83177	1.61899	1.43061	1.25274	1.08555	0.93265	0.79693	0.67959	0.58026	0.49761	0.19534	0.17011	0.16850	0.16841	0.16840	0.16840	0.16840
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0.8	2.06909	1.76832	1.69668	1.67323	1.67036	1.67993	1.69904	1.72634	1.76044	1.79950	1.84122	2.01660	1.70582	1.39913	1.22802	1.09846	1.09755	1.09755
0.9	2.03389	1.71126	1.63634	1.60845	1.59923	1.60035	1.60892	1.62405	1.64541	1.67252	1.70448	1.97780	1.81332	1.51731	1.30598	1.09265	1.08955	1.08955
1.0	2.01606	1.67633	1.60097	1.57147	1.55915	1.55559	1.55779	1.56477	1.57639	1.59277	1.61383	1.89768	1.86533	1.61567	1.38574	1.08089	1.07291	1.07291
1.2	2.00335	1.63899	1.56729	1.53899	1.52569	1.51927	1.51670	1.51674	1.51898	1.52351	1.53060	1.73498	1.86586	1.75190	1.54533	1.07428	1.04334	1.04334
1.4	2.00065	1.61886	1.55271	1.52744	1.51551	1.50937	1.50621	1.50478	1.50456	1.50536	1.50727	1.62504	1.80256	1.81047	1.67543	1.10300	1.02622	1.02621
1.6	2.00012	1.60479	1.54413	1.52186	1.51155	1.50625	1.50342	1.50194	1.50128	1.50119	1.50159	1.56323	1.72638	1.81090	1.75670	1.16255	1.01722	1.01714
1.8	2.00002	1.59364	1.53796	1.51827	1.50937	1.50487	1.50247	1.50118	1.50054	1.50029	1.50033	1.53116	1.65920	1.77810	1.79133	1.24290	1.01245	1.01211
2.0	2.00000	1.58440	1.53312	1.51562	1.50788	1.50402	1.50198	1.50090	1.50035	1.50011	1.50006	1.51525	1.60738	1.73181	1.79130	1.33352	1.01018	1.00905
2.5	2.00000	1.56685	1.52455	1.51112	1.50545	1.50272	1.50131	1.50058	1.50021	1.50004	1.50000	1.50289	1.53594	1.62281	1.71941	1.54998	1.01404	1.00512
3	2.00000	1.55450	1.51898	1.50834	1.50400	1.50196	1.50094	1.50041	1.50015	1.50003	1.50000	1.50094	1.51122	1.55638	1.63434	1.69667	1.03630	1.00331
4	2.00000	1.53851	1.51237	1.50520	1.50242	1.50117	1.50055	1.50024	1.50008	1.50002	1.50000	1.50039	1.50140	1.50990	1.53824	1.77014	1.15072	1.00171
5	2.00000	1.52881	1.50872	1.50355	1.50162	1.50077	1.50036	1.50015	1.50005	1.50001	1.50000	1.50024	1.50048	1.50181	1.50927	1.70481	1.32849	1.00105
6	1.99999	1.52244	1.50649	1.50258	1.50117	1.50055	1.50025	1.50011	1.50004	1.50001	1.50000	1.50016	1.50030	1.50054	1.50224	1.62556	1.50695	1.00071
7	1.99999	1.51800	1.50502	1.50196	1.50088	1.50041	1.50019	1.50008	1.50003	1.50001	1.50000	1.50012	1.50022	1.50030	1.50067	1.56902	1.64380	1.00051
8	1.99999	1.51478	1.50400	1.50154	1.50068	1.50032	1.50015	1.50006	1.50002	1.50000	1.50000	1.50009	1.50016	1.50021	1.50031	1.53551	1.72695	1.00038
9	1.99999	1.51237	1.50327	1.50125	1.50055	1.50025	1.50012	1.50005	1.50002	1.50000	1.50000	1.50007	1.50013	1.50016	1.50020	1.51749	1.76297	1.00030
10	1.99999	1.51051	1.50272	1.50103	1.50045	1.50021	1.50009	1.50004	1.50001	1.50000	1.50000	1.50006	1.50010	1.50013	1.50015	1.50836	1.76515	1.00024
∞	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2	3/2,1