

Partition Functions for Partly Classical Systems

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tively corroborates Labrouste's results in three dimensions.

List of possible singular areas

It has been noticed that *some of the characteristic areas corresponding to higher order transitions in phases which exist at higher temperatures are precisely those which correspond to ordinary phase transition of the first order at lower temperatures.*

The Table III summarizes this general relation. Areas corresponding to discontinuities of the first order (ordinary change of phase) are printed in heavy type. Those referring to higher order discontinuities are printed in ordinary type.

CONCLUSIONS

(1) From the fact that different substances give different types of isotherms conclusions are frequently drawn on the influence of molecular constitution on the force area characteristics. This is likely to lead to erroneous results unless care is taken to compare the monolayers in corresponding physical states.

(2) We are naturally led to inquire whether there exist, *in three dimensions*, relations analogous to those illustrated by Table III. That such relations do in fact exist is confirmed by the data of Schroer⁴³ on the compressibility of ether over a wide range of temperature including the critical temperature. Discontinuities of higher order appear at temperatures well above the critical, when the volume reaches values near the critical volume. Furthermore x-ray analysis indicates traces of organization in the same region.⁴⁴

Published data on the compressibility of three-dimensional liquids are unfortunately not sufficient to show up corresponding discontinuities in the neighborhood of the triple point volume.

I wish to express my sincere thanks to Professor E. K. Rideal for much help and criticism during the writing of this paper.

⁴³ Schroer, *Zeits. f. physik. Chemie* **140**, 381 (1929).

⁴⁴ Cybotactic condition. See W. Noll, *Phys. Rev.* **42**, 336 (1932); R. D. Spangler, *Phys. Rev.* **46**, 698 (1934); Benz and Stewart, *Phys. Rev.* **46**, 703 (1934).

Partition Functions for Partly Classical Systems

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A method is described for calculating the partition function of systems whose Hamiltonian operator separates into three terms of the following types. The first and second terms are functions of different sets of coordinates while the third is a small coupling term. The energy levels of the first term by itself are widely spaced compared to kT while those of the second are closely spaced. In the result given, the partition function becomes a sum over the widely spaced levels and a phase integral for the contribution of the other levels, as in the case with no coupling term, but here the effect of the coupling term is included in the integral. As an illustration it is shown that the coupling of rotational and vibrational angular momentum in a polyatomic molecule has no appreciable effect on the thermodynamic properties even though it has a marked effect on the energy levels.

IN many systems it is possible to separate the Hamiltonian operator into two terms, each involving different coordinates, such that one term leads to closely spaced and the other to widely spaced energy levels. The partition function for a separable system can be written as a product of two factors and in this case the factor involving closely spaced energy levels can often

be accurately approximated by an integral related to the classical phase integral.

In other cases, however, the Hamiltonian contains a third term, small but not negligible, which is a function of both sets of coordinates so that a strict separation cannot be carried out. It is the purpose of this note to show how such cases may be handled, retaining the phase integral ap-

proximation but bringing in the effect of the coupling term by a perturbation method.

PERTURBATION TECHNIQUE

Suppose that the Hamiltonian operator or matrix is

$$\mathbf{H} = \mathbf{H}' + \mathbf{H}'' + \epsilon \mathbf{H}''', \quad (1)$$

where \mathbf{H}' leads to widely spaced energy levels, \mathbf{H}'' to closely spaced levels, and $\epsilon \mathbf{H}'''$ is the coupling term, ϵ being a parameter of smallness. In giving the elements of \mathbf{H} it is convenient to use the wave functions of the unperturbed problem $\mathbf{H}' + \mathbf{H}''$ as basis functions so that two sets of quantum numbers, v (from H') and r (from H''), will be employed as indices. Then the only terms in \mathbf{H} nondiagonal in v will be of order ϵ , arising from $\epsilon \mathbf{H}'''$. In this case Van Vleck has shown¹ that \mathbf{H} may be transformed so that the terms off-diagonal in v are reduced to order ϵ^2 ; they can then be neglected if energies accurate to terms in ϵ^3 are desired. Van Vleck's result is that the new matrix \mathfrak{H} has the elements

$$\mathfrak{H}_{vr, v'r'} = \text{order } \epsilon^2 (v \neq v')$$

$$\begin{aligned} \mathfrak{H}_{vr, vr'} &= W_v^0 + H''_{rr'} + \epsilon H'''_{vr, vr'} \\ &+ \epsilon^2 \sum_{v'', r''} H'''_{vr, v''r''} H'''_{v''r'', vr'} / (W_v^0 - W_{v''}^0), \end{aligned} \quad (2)$$

where $W_v^0 = H'_{vv}$ and the sum is over all states $v''r''$ except those with $v'' = v$. Let the coupling term H''' have the form

$$\mathbf{H}''' = \sum_i \mathbf{A}'_i \mathbf{A}''_i, \quad (3)$$

in which \mathbf{A}'_i is a function only of the variables of \mathbf{H}' and \mathbf{A}''_i is a function only of the variables of \mathbf{H}'' . Then the elements of \mathfrak{H} diagonal in v may be represented as submatrices:

$$\begin{aligned} \mathfrak{H}_{vv} &= W_v^0 \mathbf{E} + \mathbf{H}'' + \epsilon \sum_i \mathbf{A}'_{vv} \mathbf{A}''_i + \\ &\epsilon^2 \sum_{ij} \left\{ \sum_{v''} \mathbf{A}'_{vv''} \mathbf{A}'_{v''v} / (W_v^0 - W_{v''}^0) \right\} \mathbf{A}''_i \mathbf{A}''_j. \end{aligned} \quad (4)$$

Here \mathbf{E} is the unit matrix.

¹ J. H. Van Vleck, Phys. Rev. **33**, 484 (1929); O. M. Jordahl, *ibid.* **45**, 87 (1934). The terms of order ϵ^3 can also be found.

THE PARTITION FUNCTION

If W_{vr} is an energy level for the complete problem, the partition function Z is

$$Z = \sum_{v, r} \exp(-W_{vr}/kT), \quad (5)$$

where k is Boltzmann's constant and T the absolute temperature. In the case given here this may be approximated by the expression

$$(1/\sigma h^s) \sum_v \exp(-W_v^0/kT) \int \cdots \int \exp(-\mathfrak{H}''_v/kT) dq dp, \quad (6)$$

in which σ is the so-called symmetry number, h is Planck's constant, s is the number of coordinates involved in \mathbf{H}'' , q represents these coordinates, p represents the corresponding conjugate momenta, and \mathfrak{H}''_v is the classical analogue of the double-primed part of \mathfrak{H}_{vv} ; that is,

$$\begin{aligned} \mathfrak{H}''_v &= H'' + \epsilon \sum_i \mathbf{A}'_{vv} \mathbf{A}''_i + \\ &\epsilon^2 \sum_{ij} \left\{ \sum_{v''} \mathbf{A}'_{vv''} \mathbf{A}'_{v''v} / (W_v^0 - W_{v''}^0) \right\} \mathbf{A}''_i \mathbf{A}''_j. \end{aligned} \quad (7)$$

In using this, H'' and \mathbf{A}''_i are regarded as classical functions of q and p analogous to the operator functions $\mathbf{H}''(\mathbf{p}, \mathbf{q})$ and $\mathbf{A}''_i(\mathbf{p}, \mathbf{q})$. Since \mathfrak{H}''_v may be a function of v , it is necessary to include the integral inside the summation over v . In going over to Eq. (6) the sum over the quantum-mechanical levels determined by the matrix $\mathfrak{H}_{vv} - W_v^0 \mathbf{E}$ has been replaced by an integral involving a classical Hamiltonian function which is the classical analog of $\mathfrak{H}_{vv} - W_v^0 \mathbf{E}$.

AN ILLUSTRATION: ROTATION-VIBRATION COUPLING

A good approximation for the Hamiltonian operator for the vibration and rotation of a symmetrical top molecule is²

$$\mathbf{H} = \mathbf{H}' + \mathbf{H}'' - (1/C) \mathbf{p}_z \mathbf{P}_z. \quad (8)$$

Where \mathbf{H}'' is the ordinary rotational operator for

² J. H. Van Vleck, Phys. Rev. **47**, 487 (1935); M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935); E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

a rigid symmetrical top, \mathbf{H}' is the vibrational operator, and $\mathbf{p}_z, \mathbf{P}_z$ are the components of vibrational and total angular momenta along the symmetry axis. C is the moment of inertia about the symmetry axis.

Applying the general method, one gets

$$\mathfrak{H}_v'' = H'' - (1/C)(p_z)_{vv}P_z + (1/C^2) \times \left\{ \sum_{v'''}' (p_z)_{vv'''}(p_z)_{v''v} / (W_v^0 - W_{v''}^0) \right\} P_z^2. \quad (9)$$

Since many of the vibrational energy levels $W_{v''}^0$ of a symmetrical top molecule are degenerate, the term in P_z^2 requires further discussion. It is necessary to use the proper linear combinations of the wave functions for a degenerate level in calculating $(p_z)_{vv''}$, the correct combinations being those which make $(p_z)_{vv''}$ zero when v and v'' represent the same energy level but different states. When this is done it is seen that the term in P_z^2 is probably quite small in ordinary cases. Its effect is to modify the moment of inertia C which would occur in the rigid case.

\mathbf{H}'' has the form

$$\mathbf{H}'' = \frac{1}{2A}(\mathbf{P}_x^2 + \mathbf{P}_y^2) + \frac{1}{2C}\mathbf{P}_z^2, \quad (10)$$

where A is the moment of inertia about the x and y axes (perpendicular to the symmetry axis z) and $\mathbf{P}_x, \mathbf{P}_y$ are the components of total angular momentum about these axes, so that

$$\mathfrak{H}_v'' = \frac{1}{2A}(P_x^2 + P_y^2) + \frac{1}{2C'}P_z^2 - \frac{1}{C}(p_z)_{vv}P_z, \quad (11)$$

where

$$\frac{1}{C'} = \frac{1}{C} + \frac{2}{C^2} \sum_{v'''}' (p_z)_{vv'''}(p_z)_{v''v} / (W_v^0 - W_{v''}^0). \quad (12)$$

This can be inserted directly in the phase inte-

gral if the volume element $8\pi^2 dP_x dP_y dP_z$ is used instead of $dq dp$, since P_x, P_y, P_z are momentoids, not true momenta.³ To evaluate the integral it is convenient to make a transformation which eliminates the linear term in P_z ; viz;

$$P_z = \mathcal{P}_z + (C'/C)(p_z)_{vv}. \quad (13)$$

The resulting integral is

$$(8\pi^2/\sigma h^3) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\mathcal{L}/kT} dP_x dP_y d\mathcal{P}_z, \quad (14)$$

with

$$\mathcal{L} = \frac{1}{2} \{ [(P_x^2 + P_y^2)/A] + (\mathcal{P}_z^2/C') - (C'/C^2)(p_z)_{vv}^2 \}.$$

The complete partition function is therefore

$$Z = (8\pi^2/\sigma h^3)(2\pi kT)^{3/2} A C'^{1/2} \sum_v \exp \{ -[W_v^0 - \frac{1}{2}(C'/C^2)(p_z)_{vv}^2]/kT \}. \quad (16)$$

The effect of the coupling term is twofold: first it changes C to C' and second it adds a small correction to some of the excited vibrational energy levels. In practice both these effects are probably negligible. Certainly if the best values available for W_v^0 are those calculated by a simple normal coordinate treatment, there will be other corrections to W_v^0 of the same or greater magnitude. However, it is interesting to show that the thermodynamic properties are not much affected even though this coupling term produces a major change in the observed rotational spacing, up to 300 percent, in fact, in methane.

I should like to thank Dr. Fred Stitt and Dr. B. L. Crawford, Jr. for reading the manuscript. Another application of this method has been made by Dr. Crawford to the problem of molecules having several attached symmetrical tops.

³ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932), p. 35.