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(M. S. Thesis)

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Classical Path Approximation for the Boltzmann Density Matrix*

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ABSTRACT

Using the classical-limit approximation for the quantum mechanical time evolution operator and the formal relation between time and reciprocal temperature ($t = -i\hbar\beta$, $\beta = 1/kT$), a "better-than-classical" approximation is obtained for the Boltzmann density matrix. The result involves classical trajectories in a potential which is the negative of the actual potential; it is seen that this effectively allows for some degree of tunneling. This new approximation gives exact quantum results in any region that the potential is quadratic and quite reasonable results for any potential, even in the limit of zero temperature.

I. INTRODUCTION

The formal relation between the time evolution operator, or propagator, $\exp[-iH(t_2-t_1)/\hbar]$ of quantum mechanics and the Boltzmann density operator $\exp[-\beta H]$ of statistical mechanics is well-known[1]; H is the (time-independent) Hamiltonian governing the system, (t_2-t_1) an increment in time, and β is related to the absolute temperature $\beta = (kT)^{-1}$. A common trick in statistical mechanics is to compute the time propagator for the system and then obtain the density operator by invoking the formal relation $\beta = i(t_2-t_1)/\hbar$. All equilibrium properties of the system are obtainable from the density operator; its diagonal matrix elements in a coordinate representation, for example, give the particle density

$$\rho_\beta(x) = \langle x|e^{-\beta H}|x\rangle, \tag{1}$$

the integral over which is the partition function

$$Z(\beta) = \int dx\ \rho_\beta(x). \tag{2}$$

When "the system" under consideration involves only the degrees of freedom of heavy particles (i.e., atoms and molecules, as opposed to electrons), a classical-limit approximation[2] to the propagator is often quite accurate; this has been found to be true for several examples dealing with atomic and molecular collision dynamics[3]. In this approximation matrix elements of the propagator are given by[2,4]

$$\langle x_2|e^{-iH(t_2-t_1)/\hbar}|x_1\rangle = \left[i\ \frac{\partial^2\phi(x_2,x_1)}{\partial x_2 \partial x_1}\ /2\pi\hbar \right]^{1/2}$$

$$\exp[i\phi(x_2,x_1)/\hbar], \tag{3}$$

where $\phi(x_2,x_1)$ is the classical action integral

$$\phi(x_2,x_1) = \int_{t_1}^{t_2} dt\ \tfrac{1}{2}m\dot{x}(t)^2 - V(x(t)), \tag{4}$$

computed along the path $x(t)$ determined by the classical equations of motion with the initial and final positions, x_1 and x_2, as boundary conditions. [For simplicity of presentation Eqs. (3) and (4) are written as though there were just one degree of freedom; this need not be the case.]

This paper explores the result one obtains for the density matrix,

$$\rho_\beta(x_2,x_1) \equiv \langle x_2|e^{-\beta H}|x_1\rangle, \tag{5}$$

by making the classical approximation to the propagator in time, as above, and then making the transcription to imaginary time

$$(t_2-t_1) = -i\hbar\beta. \tag{6}$$

Surprisingly, one does <u>not</u> obtain the usual classical approximation, which (for the diagonal elements) is

$$\rho_\beta^{CL}(x) = \left(\frac{2m}{\hbar^2}/4\pi\beta\right)^{\frac{1}{2}} e^{-\beta V(x)}. \tag{7}$$

This at first seems contradictory, for a classical-limit approximation should give the classical limit! The origin of the discrepancy lies in Eq. (6); i.e., in the classical limit, $\hbar \to 0$, one considers (t_2-t_1) to be a macroscopic quantity (of order $\hbar^0$) when dealing with the propagator, but considers β to be macroscopic when dealing with the density operator. The classical limit in statistical mechanics ($\beta \sim \hbar^0$), therefore, automatically implies short imaginary

times (of order $\hbar$); the classical limit in dynamics (real time), however, does not have a short time limit built into it. By making the classical approximation to the propagator one does not incorporate a small β, or high temperature limit in the resulting approximation for the density matrix; its validity is limited only by the ability of classical mechanics to describe the particle dynamics and is thus expected to be accurate at lower temperatures than the usual classical approximation. In the limit of high temperature (small β) one does recover Eq. (7).

Section II gives explicit expressions for the density matrix for the case of a single particle in a one dimensional potential well; several limiting cases are considered in Sec. III. It is observed that the classical path approximation gives the exact quantum result for the case of a harmonic potential, and that reasonable results are obtained even in the limit of zero temperature for any potential from which $V''(x) \neq 0$ at the potential minimum. Section IV presents the numerical results of several examples chosen to test the expressions derived.

II. EXPLICIT FORMULAS FOR A ONE DIMENSIONAL POTENTIAL WELL

The beginning point is the classical limit of the propagator as given in Eqs. (3) and (4); the classical equation of motion which determines the classical trajectory is

$$mx''(t) = - V'(x(t)), \tag{8}$$

which has the solution

$$t_2-t_1 = \int_{x_1}^{x_2} dx \left\{ \frac{2}{m}[E-V(x)] \right\}^{-\frac{1}{2}}, \tag{9}$$

where E is an implicit function of x_1, x_2, and t_2-t_1.

If one switches to imaginary time $t= -i\tau$, then Eq. (8) becomes

$$mx''(\tau) = +V'(x(\tau)), \tag{10}$$

and with $t_2-t_1= - i\hbar\beta$, the implicit solution is

$$2\beta(\hbar^2/2m)^{\frac{1}{2}} = \int_{x_1}^{x_2} dx\ [E+V(x)]^{-\frac{1}{2}}. \tag{11}$$

The "classical path" in imaginary time, therefore, is of the same form as that for a path in real time <u>with the potential V(x) replaced by -V(x)</u>. If V(x) is a potential well, in which classical trajectories are oscillatory, then -V(x) is a potential barrier and the trajectory in imaginary time reflects from the barrier.

The classical path approximation for the density matrix is thus given by

$$\langle x_2|e^{-\beta H}|x_1\rangle = \left[- \frac{\partial^2\phi(x_2,x_1)}{\partial x_2 \partial x_1} /2\pi\hbar \right]^{\frac{1}{2}} \exp[-\phi(x_2,x_1)/\hbar], \tag{12}$$

where

$$\phi(x_2,x_1) = \int_0^{\hbar\beta} d\tau\ \frac{1}{2}mx'(\tau)^2 + V(x(\tau)); \tag{13}$$

using the classical equation for $x(\tau)$, the "phase" ϕ is found to be

$$\phi(x_2,x_1) = -\hbar\beta E + \int_{x_1}^{x_2} dx\{2m[E+V(x)]\}^{\frac{1}{2}}, \tag{14}$$

where E is determined implicitly in terms of x_1, x_2, and β by Eq. (11). Using Eqs. (11) and (14), one can differentiate implicitly and show that the normalization function is given by

$$\left[-\frac{\partial^2\phi(x_2,x_1)}{\partial x_2\partial x_1}\right]^{-1} = (2m)^{-\frac{1}{2}}[E+V(x_1)]^{\frac{1}{2}}[E+V(x_2)]^{\frac{1}{2}}$$

$$\times \int_{x_1}^{x_2} dx\ [E+V(x)]^{-\frac{3}{2}}. \tag{15}$$

Eqs.(12), (14), and (15), together with the defining relation in Eq. (11), are the complete expressions. It should be noted that these results can also be derived by applying a steepest descent approximation directly to evaluation of the path integral representation of the density matrix[1]. Identical expressions are obtained, so this approach will not be presented.

Since one is most often concerned with the diagonal elements (i.e., the particle density), we now specialize to this situation. In this case ($x_1=x_2\equiv x$) one seeks a classical trajectory on the potential $-V(x)$ which originates at x and returns to x in the prescribed finite time interval $\hbar\beta$. It is clear that this must be a trajectory which experiences a classical turning point; since $-V(x)$ is a potential barrier, one and only one such trajectory exists. The integral from x_1 to x_2 in Eq. (11) becomes twice the integral from x_o to x,

$$\beta(\hbar^2/2m)^{\frac{1}{2}} = \int_{x_o}^{x} dx'\ [V(x')+E]^{-\frac{1}{2}}, \tag{16}$$

where x_o is the classical turning point: $-V(x_o) = E$. Fig. 1 shows a sketch of the situation; the implicit relation is as follows: for given values of x and β one must choose E to be that value for which the time required to go from x to x_o and back to x is precisely $\hbar\beta$. Since this transit time can be made as small as desired by choosing E in the region of E_1 in Fig. 1 (i.e., close to $-V(x)$), or as large as desired by taking E in the vicinity of E_2 in Fig. 1 (i.e., close to zero), it is

clear that there is one value of E which satisfies Eq. (16) for any β between 0 and ∞.

It is actually more convenient to replace E by $-V(x_o)$ and regard x_o as the implicitly defined function of the independent variables x and β:

$$\beta(\hbar^2/2m)^{\frac{1}{2}} = \int_{x_o}^{x} dx' \; [V(x') - V(x_o)]^{-\frac{1}{2}}. \tag{17}$$

The "phase" function of Eq. (14) becomes, with $x_1=x_2=x$ and $E = -V(x_o)$,

$$\phi_\beta(x) = \hbar\beta V(x_o)+2\int_{x_o}^{x} dx'\{2m[V(x')-V(x_o)]\}^{\frac{1}{2}}. \tag{18}$$

The normalization function of Eq. (15) actually requires slightly more care, for the singularity of the integrand at a classical turning point is not integrable. Thus one needs to re-do the implicit differentiation of $\phi(x_2,x_1)$, always integrating a reciprocal square root appearing in an integrand by parts before differentiating it. The result one obtains is formally the same as integrating Eq. (15) by parts and discarding the infinite surface terms, and is

$$\left[-\frac{\partial^2\phi(x_2,x_1)}{\partial x_2\partial x_1}\bigg|_{x_1=x_2=x}\right]^{-1} \equiv D_\beta(x)$$

$$= 2(2/m)^{\frac{1}{2}}\Big\{[V(x) - V(x_o)]^{\frac{1}{2}}/V'(x) + [V(x) - V(x_o)]$$

$$\times\int_{x_o}^{x} dx' \; V''(x') \; V'(x')^{-2}[V(x') - V(x_o)]^{-\frac{1}{2}}\Big\}. \tag{19}$$

The particle density is then given by

$$\rho_\beta(x) = [2\pi\hbar D_\beta(x)]^{-\frac{1}{2}} \exp[-\phi_\beta(x)/\hbar]; \tag{20}$$

Eqs. (17)-(20) are the final expressions for the particle density.

In concluding this section it is interesting to note the physical meaning of the "trajectory in imaginary time from x to x_o and back". Fig. 1b indicates the situation with the actual potential V(x) rather than -V(x). A trajectory in imaginary time means a path through a classically forbidden region, so that one is actually allowing for tunneling from the classically forbidden position x to the turning point x_o and back. If the "time" $\hbar\beta$ is short (high temperature), then the distance over which tunneling takes place is short; for long "times" (low temperature) the particle is allowed to tunnel large distances.

III. APPROXIMATE EXPRESSIONS

As a first limiting case, suppose that x is in a region where the potential is roughly linear. From Fig. 1 it is clear that this will always be the case for sufficiently small β; it may not be necessary to require that β be small, however. Expanding V(x') and $V(x_o)$ in Eqs. (17)-(19) linearly about x, one readily finds that Eq. (20) for the particle density becomes

$$\rho_\beta(x) = \left(\frac{2m}{\hbar^2}/4\pi\beta\right)^{\frac{1}{2}} \exp\{-\beta[V(x)-\hbar^2\beta^2V'(x)^2/24m]\}; \qquad (21)$$

for β sufficiently small the usual classical result [Eq. (7)] is recovered.

Eq. (21) may be viewed as the usual classical expression with the "effective potential"

$$V(x) - \hbar^2\beta^2V'(x)^2/24m;$$

this effective potential, which is clearly attractive, should not be confused with that which appears in the "first quantum

correction" which is discussed in ref. 1[5]; this latter correction term appears in an integral expression for the partition function, but the integrand in this case is not the particle density.

A more accurate, but still closed-form approximation is obtained by expanding the potential quadratically about x in Eqs. (17)-(19). In this case Eq. (20) gives

$$\rho_\beta(x) = \left(\frac{2m}{\hbar^2}/4\pi\beta\right)^{\frac{1}{2}} [u/\sinh(u)]^{\frac{1}{2}}$$

$$\exp\left\{-\beta\left[V(x) + \frac{V'(x)^2}{2V''(x)}\left(\frac{2\tanh(\frac{u}{2})}{u} - 1\right)\right]\right\}, \tag{22a}$$

with

$$u = \hbar\beta[V''(x)/m]^{\frac{1}{2}}; \tag{22b}$$

as $u \to 0$, Eq. (21) is recovered. The "effective potential" in this case is also attractive

$$V(x) + \frac{V'(x)^2}{2V''(x)}\left[\frac{2\tanh[\frac{u}{2}]}{u} - 1\right],$$

and the pre-exponential factor is also modified from the ordinary classical expression. [Note that Eq. (22) applies equally well if $V''(x) < 0$, the hyperbolic functions of imaginary argument becoming circular functions in the usual manner.]

Not only does Eq. (22) give the result of Eqs. (17)-(20) in any region in which V(x) can be approximated as a quadratic, it also gives the exact quantum result in such regions. This is true because of the fact that the classical approximation to the propagator is exact if the potential is quadratic[6]. Eq. (22) is exact, for example, for the harmonic oscillator. Since most physically meaningful potentials can be well represented by a quadratic over fairly wide regions, Eq. (22)

is expected to be accurate for most reasonable potentials.

An important feature is that Eq. (22) is just as applicable at low temperatures (large β) as at high temperatures. In the limit of large β, Eq. (22) gives

$$\rho_\beta(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{2}} \exp\left\{-\beta\hbar\omega/2 - \beta[V(x) - V'(x)^2/2V''(x)] - \frac{V'(x)^2}{V''(x)}/\hbar\omega\right\}, \tag{23}$$

where

$$\omega = \omega(x) = [V''(x)/m]^{\frac{1}{2}}.$$

If the minimum of $V(x)$ is at $x=0$, then for x near 0 one has

$$\rho_\beta(x) = \left(\frac{m\omega_o}{\hbar\pi}\right)^{\frac{1}{2}} \exp[-\beta\hbar\omega_o/2 - m\omega_o x^2/\hbar], \tag{24}$$

with

$$\omega_o = [V''(0)/m]^{\frac{1}{2}}.$$

This result is of the exact quantum form

$$\rho_\beta(x) = |\phi_o(x)|^2 e^{-\beta E_o},$$

where $\phi_o(x)$ and E_o are the lowest eigenfunction and eigenvalue of a harmonic oscillator of frequency ω_o:

$$\phi_o(x) = \left(\frac{m\omega_o}{\hbar\pi}\right)^{\frac{1}{4}} e^{-m\omega_o x^2/2\hbar}$$

$$E_o = \tfrac{1}{2}\hbar\omega_o.$$

Since most potentials are harmonic near their minima, one sees that Eq. (22) gives valid results even in this low temperature limit for which the ordinary classical expression is completely useless.

IV. NUMERICAL EXAMPLES

It has already been observed that the exact classical path expression [Eqs. (17)-(20)] and the approximation to it obtained by expanding the potential as a quadratic about x [Eq. (22)] both give the exact quantum mechanical result if the potential is a polynomial of order two or less. As a more stringent test the pure quartic potential,

$$V(x) = ax^4,$$

has been considered and the partition function computed via Eq. (2).

Fig. 2 shows the partition function versus the dimensionless temperature $t = kT(2m/\hbar^2 a^{\frac{1}{2}})^{\frac{2}{3}}$ for the two approximations, compared to the ordinary classical result and the exact quantum values; only the low temperature region is shown, for all the approximations become accurate at high temperature. It is seen that both the exact classical path approximation, and the quadratic approximation to it are significantly more accurate than the ordinary classical results. For this example the quadratic path approximation [Eq. (22)] is actually somewhat more accurate than the exact classical path [Eqs. (17)-(20)]; although this comparison may be different for other examples, it probably indicates that the quadratic approximation to the path [and thus Eq. (22)] is as accurate a description as is warranted by the overall procedure.

In conclusion, it is hoped that it will be possible to make use of these more accurate semiclassical procedures in more complicated systems in which classical trajectory methods are commonly employed.

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†Alfred P. Sloan Fellow.

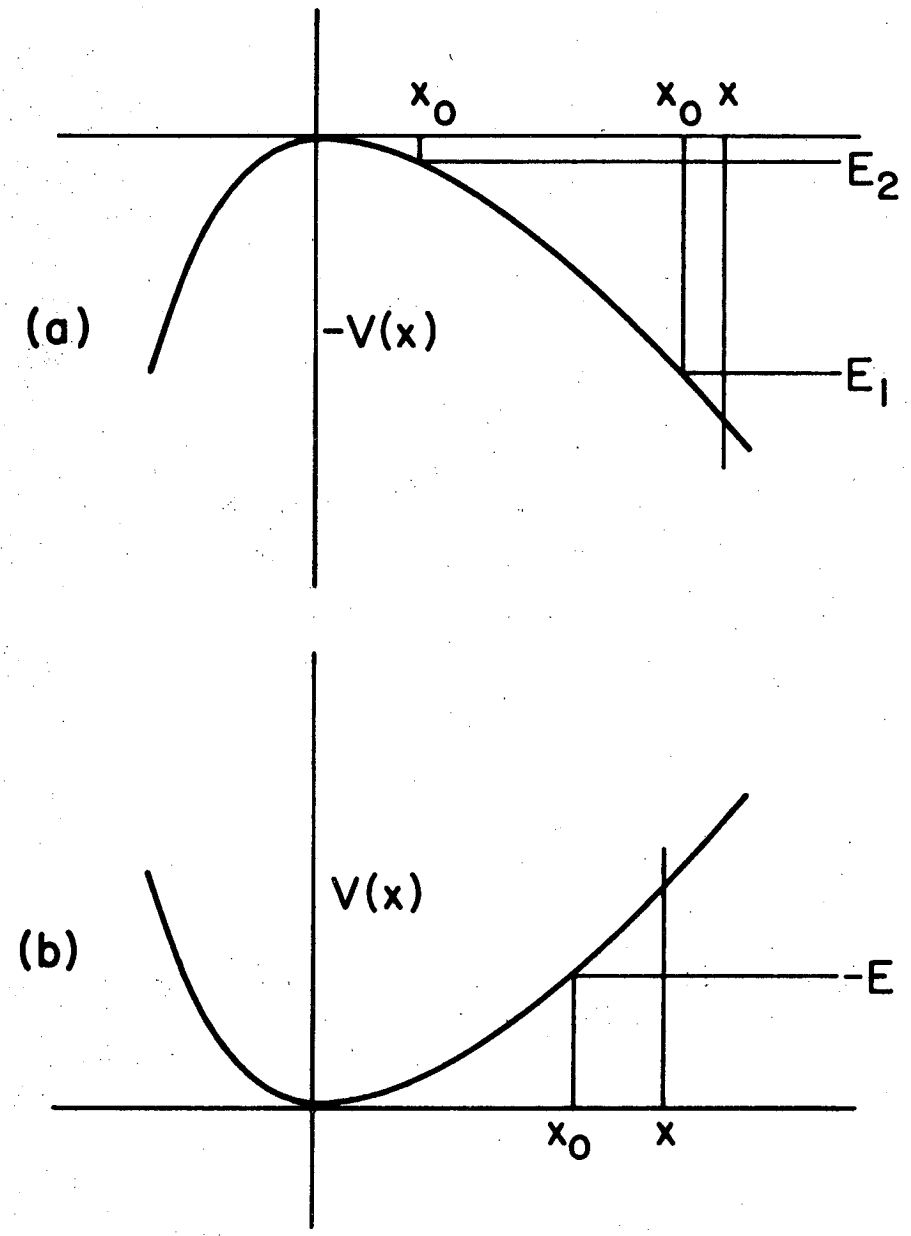
1. See, for example, R.P. Feynman and A.R. Hibbs, Quantum Mechanics and Path Integrals (McGraw-Hill, N.Y., 1965), pp. 273-279.
2. Ref. 1, p. 29.
3. W.H. Miller, J. Chem. Phys. **53**, 3578 (1970); Chem. Phys. Lett. **7**, 431 (1970); J. Chem. Phys. **54**, June (1971).
4. For the derivation of this form of the normalization, see W.H. Miller, J. Chem. Phys. **53**, 1949 (1970).
5. Ref. 1, pp. 279-282.
6. Ref. 1, pp. 62-64.

FIGURE CAPTIONS

1. (a) A sketch of the negative potential $-V(x)$. For given values of x and β there is one value of E between $-V(x)$ and 0 which satisfies Eq. (16).

   (b) A sketch of the actual potential $V(x)$; it is seen that the pertinent trajectory from x to x_o and back is through a classically forbidden region.

2. The partition function for the quartic potential $V(x) = ax^4$ versus the dimensionless temperature $t = kT(2m/\hbar^2 a^{\frac{1}{2}})^{\frac{2}{3}}$: solid line - exact quantum values; dashed line - Eq. (2) with the particle density given by the quadratic approximation, Eq. (22); dash-dot line - Eq. (2) with the particle density given by the exact classical path, Eqs. (17)-(20); dotted line - Eq. (2) with the particle density given by the ordinary classical approximation, Eq. (7). The arrow at $t = 1.060$ is the position of the lowest eigenvalue of this potential.



XBL 714-6702

Figure 1

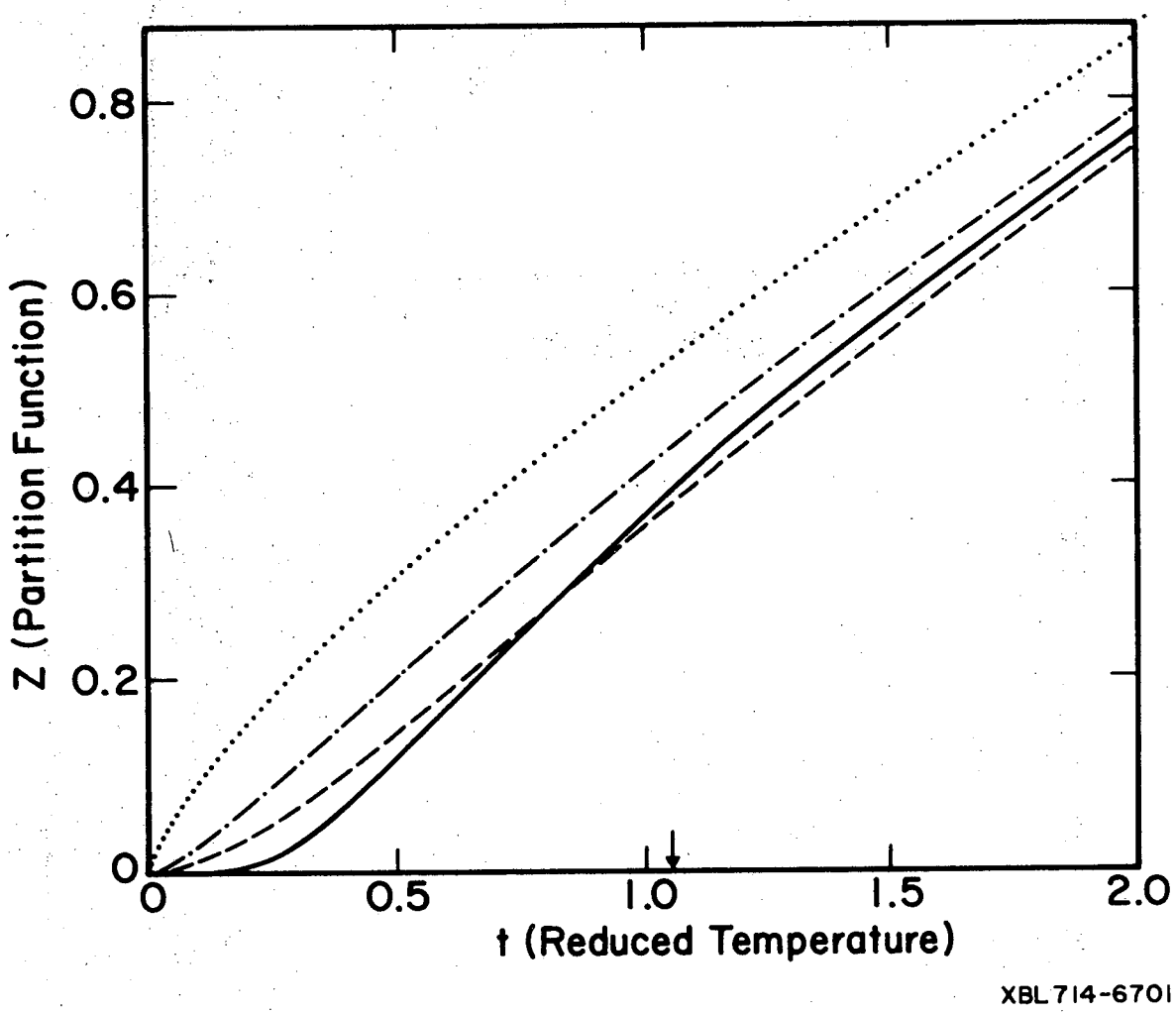

0.8
0.6
0.4
0.2
0
Z (Partition Function)
0
0.5
1.0
1.5
2.0
t (Reduced Temperature)
XBL 714-6701

Figure 2

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