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SEMICLASSICAL STATISTICAL MECHANICS OF HARD WALL POTENTIALS VIA THE TRANSFORMED POTENTIAL APPROACH

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Semiclassical Statistical Mechanics of Hard Wall Potentials via the Transformed Potential Approach

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Abstract

A non-perturbative technique for treating the semiclassical statistical mechanics of hard wall systems based on the WKB quantization condition modified for a non-infinite interval is proposed. Application to some simple cases shows that the method is an improvement over a previous non-perturbative approach.

I. Introduction

In spite of their apparently fictitious nature, hard wall potentials (such as hard spheres, square wells, and Sutherland potentials) have become one of the mainstays of the statistical mechanics of classical fluids. This is due almost entirely to their simplicity of form. Hard spheres, for example, readily lend themselves to analytical expressions for virial coefficients and equations of state as well as to economical Monte Carlo calculations. Moreover, it turns out that hard sphere fluids have a structure which is extremely similar to more realistic fluids.[1]

Yet, the very features which make hard wall potentials attractive for classical studies make the incorporation of quantum effects difficult. The standard perturbative approach, the Wigner-Kirkwood expansion,[2,3] is meaningless for nonanalytic potentials because it explicitly involves derivatives of the potential. More recently, an alternative perturbative approach[4,5] was developed which was based on an expansion with Ursell functions[6] to specific powers in $\hbar$. This latter technique and an extension employing Mayer functions has been successfully applied to the statistical mechanics of hard sphere fluids in a series of papers by Y. Singh, J. Ram, S. K. Sinha, and B. H. Singh.[7-10] In addition, a modified Wigner-Kirkwood expansion using hard sphere basis functions instead of free particle basis functions has been given by E. J. Derderian and W. A. Steele.[11]

All of these approaches, however, may be characterized as being perturbative in nature. This does not necessarily decrease their usefulness but it does tend to obscure the distinction between classical many body effects and purely two body quantum effects by blending the two together at varying levels of approximation. A perturbative approach also has the (possibly useful) property of obscuring certain interesting questions about the applicability of semiclassical approximations.

One way to avoid these difficulties, (the way which will be discussed in the article), is to employ the so-called "phase space sampling" method.[12] In this formulation the quantum mechanical propagator in imaginary time (temperature) is replaced by its stationary phase approximation. This has the effect of enabling all the results to be cast into a modified but non-perturbative classical form. For example, the semiclassical partition function may be written,

$$Q^{SC} = h^{-3N} \int \cdots \int \exp\{- \frac{2}{\hbar} \int_0^{\hbar\beta/2} H[\underset{\sim}{p}(\tau),\underset{\sim}{q}(\tau)]d\tau\} d\underset{\sim}{p}_0 d\underset{\sim}{q}_0 \tag{1.1}$$

where

$$\underset{\sim}{p}_0 = \underset{\sim}{p}(\tau=0) \qquad \underset{\sim}{q}_0 = \underset{\sim}{q}(\tau=0)$$

as compared to the classical partition function

$$Q^{CL} = h^{-3N} \int \cdots \int \exp\{-\beta H(\underset{\sim}{p},\underset{\sim}{q})\} d\underset{\sim}{p}\, d\underset{\sim}{q} \quad . \tag{1.2}$$

It is not entirely clear how to apply this formalism to hard wall potentials. In fact, there is some question as to whether such an application would be meaningful in view of the use of the stationary phase approximation--which appears to rely on a slowly varying potential.[13] As a first step toward answering these questions, the original discussion of the phase space sampling method[12] employed what might be termed the trajectory restriction approach to examine a particle in a box. With this technique any sampling trajectory, $(\underset{\sim}{p}(\tau), \underset{\sim}{q}(\tau))$, crossing an infinite potential discontinuity would be assumed to have zero action and therefore zero contribution. This would immediately restrict the integration range $(\underset{\sim}{p}_0, \underset{\sim}{q}_0)$ to only those trajectory starting points which did not allow the trajectories to wander into forbidden areas of phase space.

Unfortunately, as noted in the original paper and elsewhere,[14] trajectory restriction exhibits only qualitative agreement with quantum mechanical results. Clearly a different method is needed. This article proposes a method based on the WKB approximation which, nonetheless, still fits within the phase space sampling framework. Some simple examples are then discussed in the light of this development.

II. Transformed Potential Formalism

In order to use the WKB approximation to write expressions involving semiclassical statistical mechanics, it is helpful to review the relationship between WKB and classical statistical mechanics. A quantum mechanically exact partition function may always be written

$$Q = \int_0^\infty e^{-\beta E}\ \rho(E)dE \qquad (2.1)$$

where $\rho(E)$, the density of states, is a series of delta functions at the energy eigenvalues. This can be approximated by allowing $\rho(E)$ to be a continuous distribution, $\frac{dn(E)}{dE}$, with n equal to the number of states.

$$Q = \int_0^\infty e^{-\beta E}\ (\frac{dn(E)}{dE})dE \qquad (2.2)$$

Using this expression it is then easy to show that the WKB density of states gives precisely the classical partition function.

Starting from the Bohr-Sommerfeld (WKB) quantization condition for a symmetric potential

$$\frac{h}{2}(n + \frac{1}{2}) = 2 \int_0^{x_>} [2\mu(E-V(x))]^{1/2}dx \qquad (2.3)$$

and differentiating with respect to E yields

$$\frac{dn}{dE} = \frac{2}{h}(2\mu)\int_0^{x_>} [2\mu(E-V(x))]^{-1/2}dx \qquad (2.4)$$

Note that the term involving the energy derivative of the turning point ($x_>$) vanishes since it involves the integrand evaluated at the turning point and since $E = V(x_>)$. Now substituting into (2.2) and interchanging integration order

$$Q = \frac{2}{h}(2\mu) \int_0^{\infty} \int_{V(x)}^{\infty} e^{-\beta E} \, [2\mu(E-V(x))]^{-1/2} dE \, dx \tag{2.5}$$

However we may transform integration variables to (x,p) instead of (x,E) by remembering that

$$\left(\frac{\partial E}{\partial p}\right)_x = \frac{p}{\mu} = \frac{1}{\mu} \, [2\mu(E-V(x))]^{1/2} \tag{2.6}$$

Thus taking advantage of the symmetry of the potential we obtain

$$Q = \frac{4}{h} \int_0^{\infty} \int_0^{\infty} \exp\{-\beta H(p,x)\} dp \, dx$$

$$Q = \frac{1}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\{-\beta H(p,x)\} dp \, dx \tag{2.7}$$

which is the classical partition function.

To be rigorously correct one should only employ the WKB quantization condition, Eq. (2.3), for potentials defined on an infinite interval ($-\infty \leq x \leq \infty$) because of the boundary conditions the WKB condition implicitly assumes. This is clearly a nontrivial consideration since it automatically precludes hard wall systems such as hard spheres and particles in boxes. Fortunately, the situation can be corrected without undue hardship.

Adams and Miller[15] have discussed the problem in some depth and they show that Langer's[16] trick of transforming coordinates so as to map the desired interval onto $(-\infty,\infty)$ merely has the effect of adding a uniquely defined potential, ΔV, to the potential in Eq. (2.3). In other words transforming to a coordinate system which obviates the difficulty is equivalent to just adding a ΔV which depends only on the original interval to the potential. For a hard sphere or Sutherland potential system, an (a,∞) interval, ΔV is given by[15]

$$\Delta V = \left(\frac{\hbar^2}{8\mu}\right) \frac{1}{(x-a)^2} \tag{2.8a}$$

which is just the usual Langer modification if a is set equal to zero, whereas for an infinitely high walled box, an $(-a/2,a/2)$ interval, ΔV becomes

$$\Delta V = \left(\frac{\hbar^2}{8\mu}\right)\left(\frac{\pi}{a}\right)^2 \sec^2\left(\frac{\pi x}{a}\right) \tag{2.8b}$$

What this suggests is that one rederive the partition function from the new WKB quantization condition

$$\frac{h}{2}\left(n + \frac{1}{2}\right) = 2\int_0^{x_>} [2\mu(E-V(x)-\Delta V(x))]^{1/2} dx \tag{2.9}$$

by following the same steps as previously but now replacing $V(x)$, wherever it appears, by $V(x) + \Delta V(x)$. The result is what might be called a classical transformed potential formula

$$Q^{CL+\Delta V} = \frac{1}{h}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\{-\beta[H(p,x)+\Delta V(x)]\} dp\, dx \tag{2.10}$$

and is a useful semiclassical approximation.

Proceeding further it seems not unreasonable to start with the phase space sampling semiclassical partition function, Eq. (1.1), and to replace $V(x)$ by $V(x) + \Delta V(x)$ there also. This would give what could be termed a semiclassical transformed potential formula

$$Q^{SC+\Delta V} = \frac{1}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\{-\frac{2}{\hbar} \int_{0}^{\hbar\beta/2} [H(\tau)+\Delta V(\tau)]d\tau\}dp_0\, dq_0 \qquad (2.11)$$

Here the imaginary time equations of motion $(p(\tau), q(\tau))$ would be derived by treating $H + \Delta V$ as the effective Hamiltonian instead of H alone.

These two semiclassical approximations, (2.10) and (2.11), together with the appropriate ΔV (Eq. (2.8)), provide the desired expressions valid for hard wall potentials. As can be readily verified, both forms go to the correct classical limit because ΔV is explicitly proportional to $\hbar^2$. Moreover, both seem physically reasonable in that they replace the actual discontinuous potential by a qualitatively similar but a "softer" potential (see Figure 1).

III. Examples of Usage

A. Particle in a Box

Because this potential (Figure 1b) is so highly quantum mechanical it provides an interesting testing ground for semiclassical approaches. Accordingly classical (CL), quantum mechanical (QM), and three different semiclassical--trajectory restricted (TR), classical transformed potential (CL+ΔV), and semiclassical transformed potential (SC+ΔV)--calculations were performed for a particle of mass m in a box of length a. Of these, the classical, quantum mechanical and trajectory restricted partition function and ensemble average energy have already been reported[12] so they will merely be cited for comparison purposes in term of the dimensionless quantum parameter θ

$$\theta = \left(\frac{a}{\hbar}\right)\left(\frac{2m}{\beta}\right)^{1/2} \qquad (3.1)$$

$$Q^{CL} = (2\pi^{\frac{1}{2}})^{-1}\theta$$

$$Q^{QM} = \sum_{n=1}^{\infty} e^{-\pi^2 n^2/\theta^2}$$

$$Q^{TR} = (2\pi^{\frac{1}{2}})^{-1} \quad \theta\, \mathrm{erf}\theta + (2\pi)^{-1}(e^{-\theta^2}-1)$$

$$\langle E\rangle^{QM}/\langle E\rangle^{CL} = [\sum_{n=1}^{\infty} (2\pi^2 n^2/\theta^2)e^{-\pi^2 n^2/\theta^2}]/Q^{QM}$$

$$\langle E\rangle^{TR}/\langle E\rangle^{CL} = [(2\pi^{\frac{1}{2}})^{-1}\ \theta\, \mathrm{erf}\theta]/Q^{TR}$$

The transformed potential (CL+ΔV and SC+ΔV) results were obtained from Eq. (2.10) and Eq. (2.11) respectively, with ΔV as given in Eq. (2.8b). For the particular case of the particle in a box this allows the CL+ΔV computation to be worked out analytically

$$Q^{CL+\Delta V} = (2\pi^{\frac{1}{2}})^{-1}\theta[1-\mathrm{erf}(\frac{\pi}{2\theta})]$$

$$\langle E\rangle^{CL+\Delta V}/\langle E\rangle^{CL} = 1 + (\frac{1}{2}\, e^{-\pi^2/4\theta^2})/Q^{CL+\Delta V}$$

although the SC+ΔV calculation must be done numerically.[17] All of these computations are summarized in Figure 2 and Figure 3.

In both the energy and partition function plots it is evident that the transformed potential curves are a significant improvement over the trajectory restricted curves. This is especially noticeable as the systems becomes less quantum mechanical (θ increases). More quantitatively, consider the first quantum corrections predicted by each of the methods. In terms of the thermal wavelength $\lambda = 2\pi^{1/2}(a/\theta) = (2\pi\hbar^2\beta/m)^{1/2}$

$$Q^{CL} = \frac{a}{\lambda}$$

$$Q^{TR} = Q^{CL}[1 - \frac{1}{2\pi}\,(\frac{\lambda}{a}) + \ldots]$$

$$Q^{CL+\Delta V} = Q^{CL}[1 - \frac{1}{2}\,(\frac{\lambda}{a}) + \ldots]$$

$$Q^{QM} = Q^{CL}[1 - \frac{1}{2}\,(\frac{\lambda}{a}) + \ldots]$$

Note that the transformed potential approach differs from the trajectory restricted version in that it implies the exact first quantum correction.

It is also interesting to compare the semiclassical and classical formulations which use the transformed potential. At small θ (the quantum limit), the semiclassical expression seems to be a marked improvement and, as expected, both expressions converge smoothly to the quantum curve for large θ (the classical limit). However there appears to be a distinct intermediate region in which the classical version does slightly better. Why this is so is not well understood at present.

B. Hard Sphere Radial Distribution Function

Choosing a one dimensional hard sphere example (Figure 1a) is a convenient way of illustrating the validity of the transformed potential technique for a semi-infinite interval. Thus, as before, the classical, quantum mechanical and three different semiclassical formulations were evaluated as a function of a reduced variable, ξ

$$\xi = (x-a)\left(\frac{4m}{\hbar^2\beta}\right)^{1/2}$$

This time however it is the two particle (density independent) radial distribution function, g(r),[18] which is calculated

$$g^{CL}(\xi) = 1$$

$$g^{QM}(\xi) = 1 - e^{-\frac{1}{2}\xi^2}$$

$$g^{TR}(\xi) = \frac{1}{2} + \frac{1}{2}\,\mathrm{erf}\,(2^{-\frac{1}{2}}\xi)$$

Again using Eq. (2.10) and (2.11), but with ΔV as given in Eq. (2.8a), it is possible to analytically compute the classical transformed potential g

$$g^{CL+\Delta V}(\xi) = e^{-(1/2\xi^2)}$$

and to numerically obtain the corresponding semiclassical g.

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The resulting curves (Figure 4) exhibit a behavior quite similar to that of the particle in a box case in that the transformed potential curves are both definitely superior to the trajectory restricted one (especially since the latter has a discontinuity at $\xi = 0$). Since ξ acts as measure of quantum effects (large ξ implying a classical limit and vice versa) it can be observed that the SC+ΔV version performs very well in the highly quantum mechanical region near the hard wall.

Still, by the same token, it might be noted that both ΔV plots differ from the exact curve noticeably at large distances. What is probably occuring is that the Langer type $1/r^2$ correction is overcompensating for the hard sphere potential. In passing, it might also be pointed out that the CL+ΔV curve crosses the exact curve in spite of displaying only a qualitative agreement with it. This suggests that the intermediate region of good agreement between the CL+ΔV and QM plots displayed in the previous section might be just a coincidence.

IV. Concluding Remarks

There are two difficulties which should be mentioned at this point. To begin with, the transformed potential formalism does not lend itself to rough estimates, such as a quantum correction expansion, because the ΔV term is not small even though it is proportional to $\hbar^2$. The trajectory restricted approach, on the other hand, readily allows one to derive an expression by the expedient of differentiating the restricted limits of integration with respect to $\hbar$. Secondly, neither approach will work with finitely discontinuous potentials such as square wells.

Nevertheless, the value of any nonperturbative approach to semiclassical statistical mechanics will be evidenced mainly by its potential applicability to many body problems. Certainly the formalism developed in this paper is no exception. Thus, considered from this point of view, this formalism is automatically a reasonable candidate because of its classical, phase space integral, appearance.

Perhaps just as importantly though, is the possibility of furthering our understanding of semiclassical approximations involving poorly behaved systems. In particular it would be interesting to find out if the WKB basis for this work implies that it will run into difficulties in multidimensional non-separable cases.

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References

1. L. Verlet, Physics Rev. 165, 201 (1968).
2. E. Wigner, Phys. Rev. 40, 749 (1932).
3. J. G. Kirkwood, Phys. Rev. 44, 31 (1933).
4. P. C. Hemmer, Physics Letters 27A, 377 (1968).
5. B. Jancovici, Phys. Rev. 178, 295 (1969).
6. B. Kahn and G. E. Uhlenbeck, Physica 5, 399 (1938).
7. Y. Singh, Molecular Physics 27, 1687 (1974).
8. J. Ram and Y. Singh, Molecular Physics 30, 629 (1975).
9. S. K. Sinha and Y. Singh, Phys. Rev. A 15, 2505 (1977).
10. B. P. Singh and S. K. Sinha, J. Chem. Phys. 67, 3645 (1977).
11. E. J. Derderian and W. A. Steele, J. Chem. Phys. 55, 9795 (1971); J. Chem. Phys. 59, 992 (1973).
12. R. M. Stratt and W. H. Miller, J. Chem. Phys. 67, 5894 (1977).
13. S. M. Hornstein and W. H. Miller, Chem. Phys. Lett. 13, 298 (1972).
14. M. Berrondo and S. Y. Larsen, J. Chem. Phys. 68, 5302 (1978).
15. J. E. Adams and W. H. Miller, J. Chem. Phys. 67, 5775 (1977).
16. R. E. Langer, Phys. Rev. 51, 669 (1937).
17. The details of the numerical calculations were identical to those described in reference 12, Section IV.
18. Equivalently, it may be thought of as the quantum mechanical Slater sum.

Figure Captions

Figure 1. Actual potentials, V, (solid line) and their semiclassical replacements, $V + \Delta V$, (dashed line) for a) hard sphere and b) particle in a box systems.

Figure 2. Partition function for a particle in a box. $\theta = (a/\hbar)(2m/\beta)^{1/2}$.

Figure 3. Ensemble average energy for a particle in a box relative to the classical value.

Figure 4. One dimensional hard sphere radial distribution function. $\xi = (x-a)(4m/\hbar^2\beta)^{1/2}$.

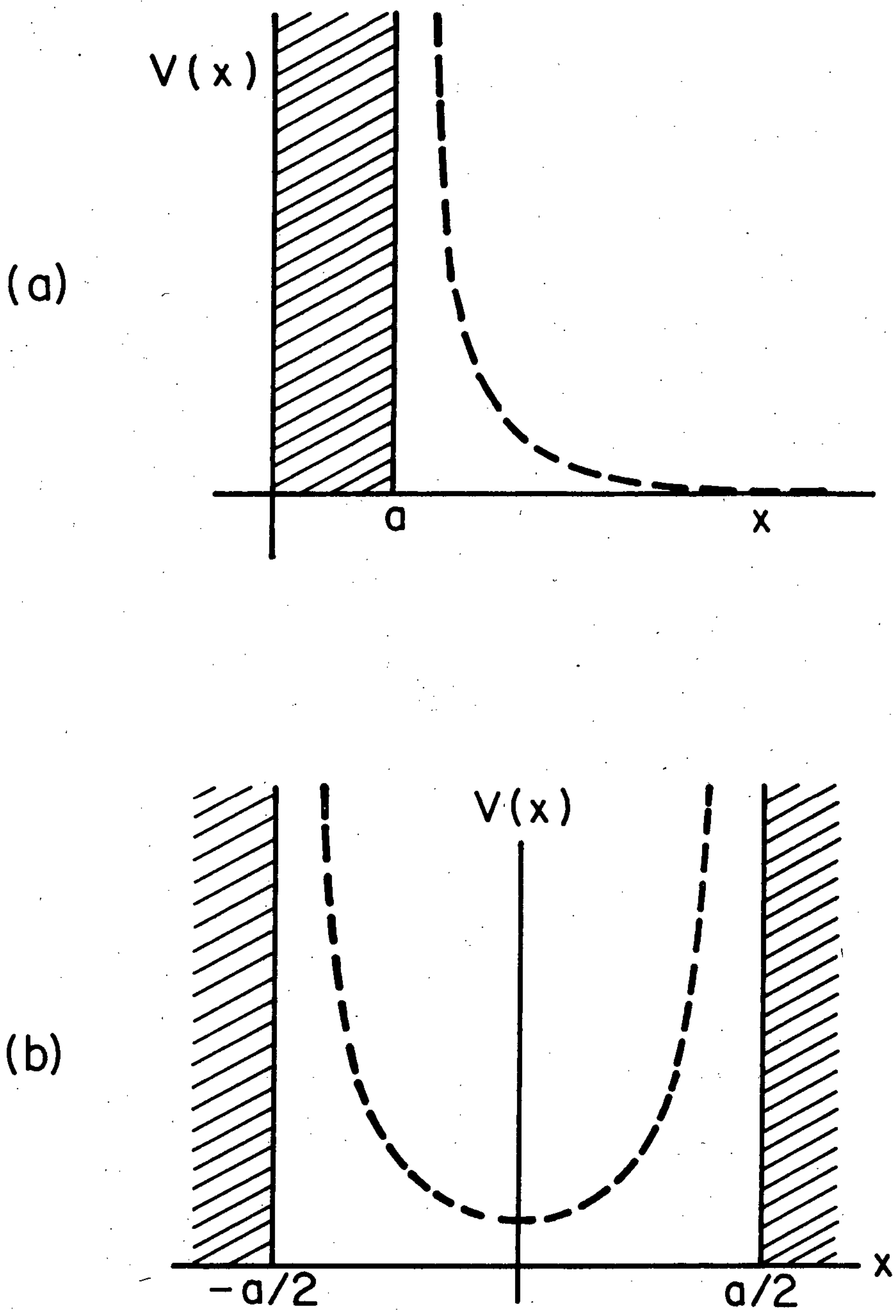

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Figure 1

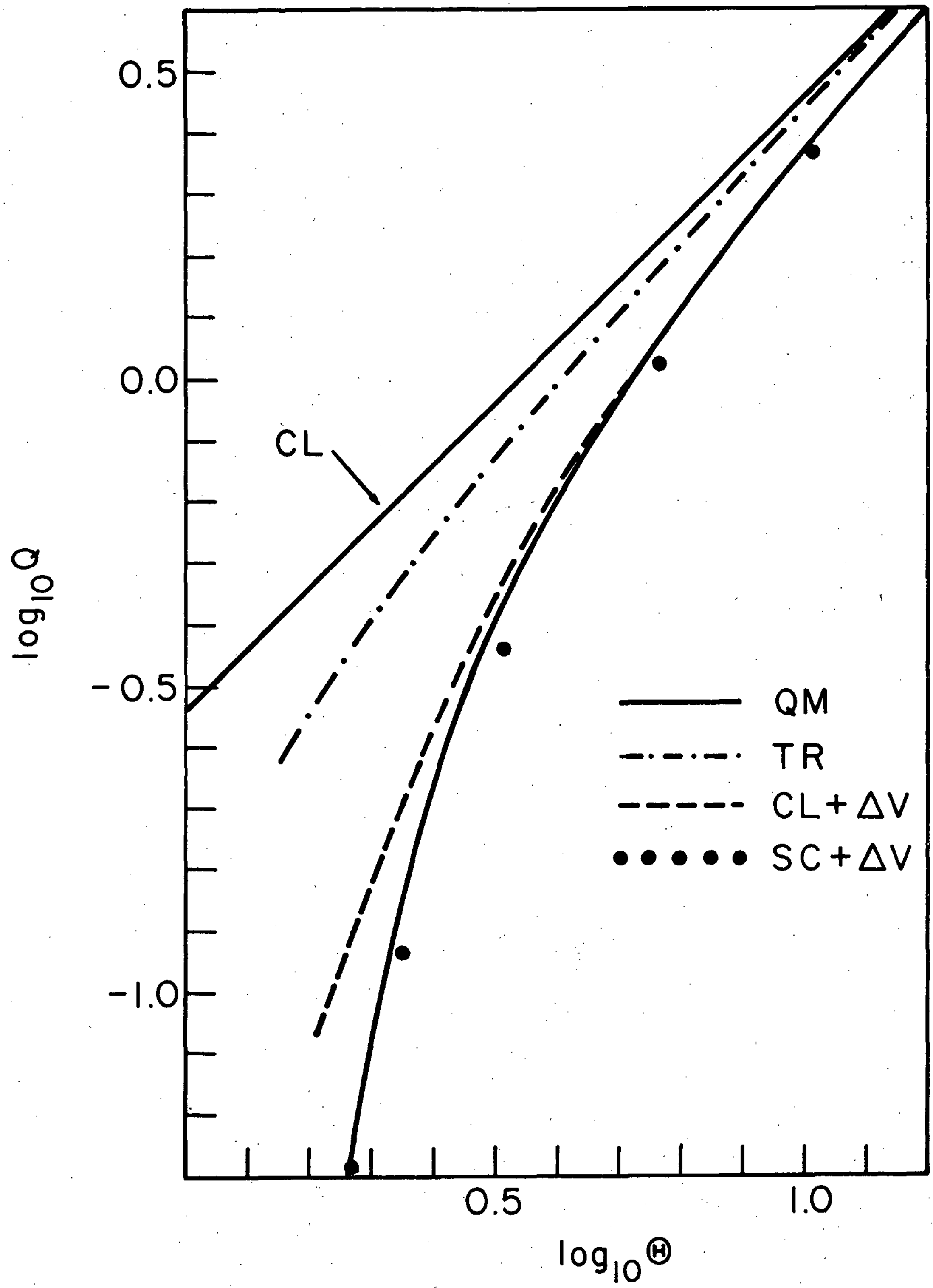

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Figure 2

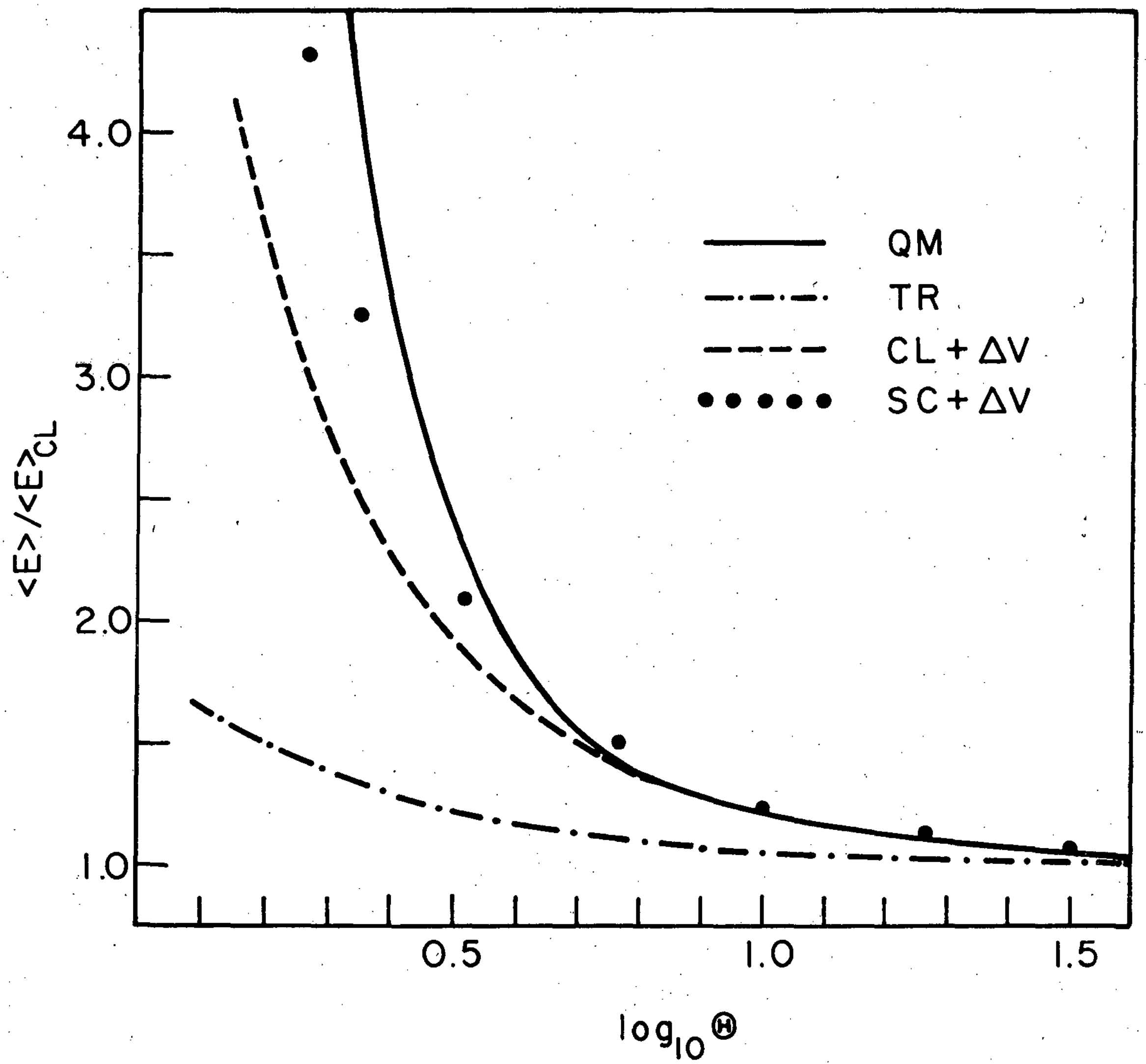

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Figure 3

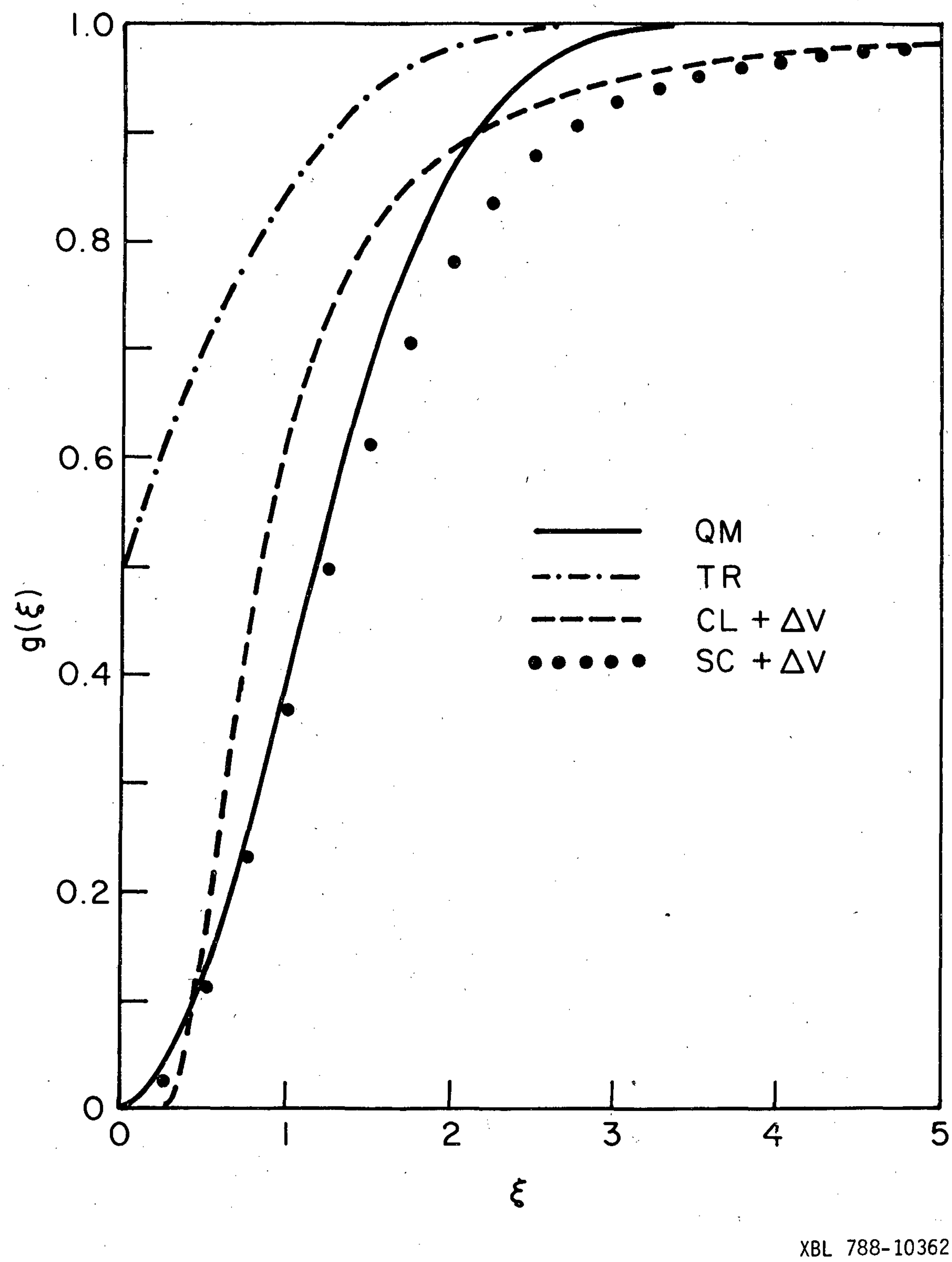

Figure 4

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