PHYSICAL REVIEW A VOLUME 44, NUMBER 2 15 JULY 1991

Semiclassical propagators and Wigner-Kirkwood expansions for hard-core potentials

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(Received 28 December 1990)

We illustrate the perturbative nature of Wigner-Kirkwood expansions showing that for strongly repulsive potentials quantum corrections are not properly taken into account. We then present an alternative calculation of quantum corrections for such cases based on well-known semiclassical methods. We begin with a simple example and then go on to consider a semiclassical expansion for the propagator of a particle in the vicinity of the boundary of a sphere and show that by treating the classical physics nonperturbatively an extra term, corresponding to reflection, appears in addition to the Wigner-Kirkwood term. We calculate quantum corrections to all orders and sum the semiclassical series, recovering the results of previous authors for both the propagator and the direct second virial coefficient. We conclude with a discussion of the implications of our analysis for more general potentials.

I. INTRODUCTION

The study of quantum-mechanical corrections to classical statistical mechanics has been of interest since soon after the beginnings of quantum mechanics.[1] Since the original contributions there have been a number of rederivations and applications of Wigner-Kirkwood expansions.[2,3] In recent years there has been some renewed interest in this area with the contributions of Fujiwara, Osborn, and Wilk[4] and, independently, Makri and Miller.[5] These authors derive expansions of the form

$$\langle \mathbf{r}|e^{-\beta H}|\mathbf{r}_i\rangle=\frac{1}{\lambda^3}\exp\left[-\frac{\pi}{\lambda^2}(\mathbf{r}-\mathbf{r}_i)^2-\beta\int_0^1 V(\mathbf{r}_i+\xi(\mathbf{r}-\mathbf{r}_i))d\xi\right]\exp\left[\sum_{n=2}^{\infty}\frac{(-\beta)^n}{n!}W_n(\mathbf{r},\mathbf{r}_i)\right], \tag{1.1}$$

where $\lambda^2=(2\pi\hbar^2/m)\beta$, $\beta=1/kT$, and the W_n are polynomials in the potential and its derivatives. We shall refer to these expansions and their variants as generalized Wigner-Kirkwood expansions. Expansions of this form have also, to various extents, been examined by a number of other authors.[6-9] Expanding out the second exponential and taking $\mathbf{r}_i\rightarrow\mathbf{r}$ recovers the usual Wigner-Kirkwood expansion. These series can be seen to be manifestly inadequate with regard to two applications. For strongly repulsive potentials, generically represented by the Lennard-Jones form, the Wigner-Kirkwood expansions have been extensively used to calculate quantum corrections to direct second virial coefficients.[2,10] We shall have more to say about these later. These series, however, do not yield the corrections for the corresponding exchange coefficients. This can be readily seen with reference to the exchange second virial coefficient b_2^{exch}. Here one requires the antipodal matrix element,

$$\langle \mathbf{r}|e^{-\beta H}|-\mathbf{r}\rangle\ . \tag{1.2}$$

The generalized Wigner-Kirkwood expansions (1.1) for these matrix elements require the average of the potential from $-\mathbf{r}$ to $\mathbf{r}$. This requires an integration through the origin. For strongly repulsive potentials the answer is divergent. In this circumstance the generalized Wigner-Kirkwood expansions are clearly inadequate. Other methods allow b_2^{exch} to be calculated for the Lennard-Jones potential.[9,11] The result is exponentially suppressed compared to the direct contribution in the high-temperature limit.

In the case of hard-core potentials,

$$V(r)=\begin{cases}0, & |\mathbf{r}|>a\\ \infty, & |\mathbf{r}|<a\end{cases} \tag{1.3}$$

(where $\mathbf{r}\in\mathbb{R}^3$), the Wigner-Kirkwood expansions are inadequate for both the direct and exchange second virial coefficients. This is well known and has been commented upon in the literature.[3] This inadequacy is commonly attributed to the nonanalyticity of this potential. Despite this, through other methods, we know the variation of the second virial coefficients through a wide temperature range from extensive numerical calculations.[12] These numerical calculations produce various predictions concerning the high-temperature behavior, all of which were subsequently confirmed analytically using various methods.[11,13-16]

In this paper we wish to present arguments that attempt to clarify the circumstances under which generalized Wigner-Kirkwood expansions can be used. In cases such as the hard-core potential, where the generalized Wigner-Kirkwood expansions cannot be used, we shall present an alternative formulation. Within this formulation we shall calculate the matrix elements $\langle \mathbf{r}|e^{-\beta H}|\mathbf{r}_i\rangle$ for $\mathbf{r}\cong\mathbf{r}_i$ for a single particle in the external hard-core potential (1.3). We shall not consider the antipodal matrix elements for reasons which we will outline in Sec. VI. Unlike the generalized Wigner-Kirkwood expansion we shall not be able to explicitly consider the N-particle case. The generalization of our formulation to this case will be conceptually clear but calculationally forbidding.

The techniques we shall be using are in fact an elaboration of the following well-known[17–19] result in the semiclassical limit of time-dependent quantum mechanics,

$$\langle \mathbf{r}|e^{-iHt/\hbar}|\mathbf{r}_i\rangle \cong \left[\frac{i}{2\pi\hbar}\right]^{3/2} \sum_{\alpha} \left[\det\left[\frac{\partial^2 S_{\rm cl}(\mathbf{r},t|\mathbf{r}_i)}{\partial x_i \partial y_j}\right]\right]^{1/2} \exp\left[\frac{i}{\hbar}S_{\rm cl}(\mathbf{r},t|\mathbf{r}_i)\right](1+\cdots)\ , \tag{1.4}$$

where $S_{\rm cl}$ is the classical action of a particle which is at $\mathbf{r}_i=(y_1,y_2,y_3)$ at time 0 and $\mathbf{r}=(x_1,x_2,x_3)$ at time t and the sum is over all classical paths that satisfy these conditions. Caustics have been neglected. We shall use a semiclassical ansatz presented in the appendixes of a paper by McLaughlin.[20] This *Ansatz* represents an application of Keller's geometric theory of diffraction to the Schrödinger equation and is an extension of (1.4). We shall work with Schrödinger propagators, using the substitution $t=-i\beta\hbar$ to recover Boltzmann factors. Our reasons for not working directly with Boltzmann factors are outlined in Sec. VI.

There are two other main techniques of treating quantum mechanics in the semiclassical approximation. These are the WKB approximation[19] and the path-integral method.[18,21] The WKB approximation normally refers to time-independent quantum mechanics. It can be applied to the problem at hand if one uses the Watson[22] representation,

$$e^{-\beta H}=\frac{1}{2\pi i}\int_c dz\, e^{-\beta z}G(z)\ . \tag{1.5}$$

This, however, requires the time-independent Green's function at complex energies. We shall use this formulation in a simple context in Sec. IV. In general, however, we find this technique to be less transparent and more difficult to calculate with than those based on (1.4). This comment also applies to the direct use of path integrals. It is convenient at times, however, to use the path integral for purposes of visualization of the calculation.

In Sec. II we shall use the above-mentioned *Ansatz* and a variation of it to recover the generalized Wigner-Kirkwood expansion. In particular, we illustrate that this expansion arises from treating the classical problem underlying the quantum problem in a perturbative manner. In Sec. III we consider the use of the generalized Wigner-Kirkwood expansions with strongly repulsive potentials. We also consider the possibility of recovering results for the hard-core potential by using a limiting procedure. We illustrate the inadequacy of the generalized Wigner-Kirkwood expansions in these cases. We then go on to present an alternative treatment for calculating semiclassical propagators when the generalized Wigner-Kirkwood expansions fail. As a preliminary exercise we consider in Sec. IV quantum propagation on the half line. In Sec. V we consider semiclassical propagation in the potential (1.3) for $|\mathbf{r}|$, $|\mathbf{r}_i|\cong a$. We expand the semiclassical propagator in powers of a^{-1}, calculating to order a^{-2} quantum corrections to all orders in $\hbar$. We then formally sum these (asymptotic) series to obtain the full quantum propagator to order a^{-2}. We use our expression for the propagator to evaluate the high-temperature series for the direct second virial coefficient, finding that we obtain a series in agreement with previous results. We also find that our expression for the propagator agrees with the (integral) expression of previous authors.[14,15] In Sec. VI we discuss the possible generalization of our method and also consider its limitations.

II. THE PERTURBATIVE NATURE OF THE WIGNER-KIRKWOOD EXPANSION

In examining the classical limit of one-body Boltzmann factors we shall work with the following Ansätze[20]

$$\langle \mathbf{r}|e^{-iHt/\hbar}|\mathbf{r}_i\rangle=\frac{1}{(2\pi i\hbar)^{d/2}}\exp\left[\frac{i}{\hbar}S(\mathbf{r},t|\mathbf{r}_i)\right] \times\sum_{j=0}^{\infty}(i\hbar)^j b_j(\mathbf{r},t|\mathbf{r}_i)\ , \tag{2.1}$$

$$\langle \mathbf{r}|e^{-iHt/\hbar}|\mathbf{r}_i\rangle=\frac{1}{(2\pi i\hbar)^{d/2}}\exp\left[\frac{i}{\hbar}S(\mathbf{r},t|\mathbf{r}_i)\right] \times\exp\left[\frac{i}{\hbar}\sum_{j=1}^{\infty}\hbar^j R_j(\mathbf{r},t|\mathbf{r}_i)\right]\ , \tag{2.2}$$

where d is the dimensionality of the configuration space being considered. One can consider these to be generalizations of Morette's expression (1.4). Substituting these into the Schrödinger equation and equating powers of $\hbar$ one obtains a hierarchy of equations for each set of unknown coefficients. From (2.1) one obtains the hierarchy

$$\frac{1}{2m}(\nabla S)^2+V(\mathbf{x})+\frac{\partial S}{\partial t}=0\ , \tag{2.3}$$

$$-\frac{1}{2m}\nabla^2 b_{j-2}+\frac{\nabla S\cdot\nabla b_{j-1}}{m}+\frac{\nabla^2 S}{2m}b_{j-1}+\frac{\partial b_{j-1}}{\partial t}=0\ , \tag{2.4}$$

where $b_{-1}=0$. [Note the sign error in McLaughlin's (A4).] From (2.2) one obtains

$$\frac{1}{2m}(\nabla S)^2+V(\mathbf{x})+\frac{\partial S}{\partial t}=0\ , \tag{2.5}$$

$$-\frac{i}{2m}\nabla^2 R_{j-1}+\frac{1}{m}\nabla S\cdot\nabla R_j+\frac{1}{2m}\sum_{k=1}^{j-1}\nabla R_k\cdot\nabla R_{j-k}+\frac{\partial R_j}{\partial t}=0\ . \quad (2.6)$$

The first equation in both hierarchies, (2.3) and (2.5), is just the Hamilton-Jacobi equation. Solving this is equivalent to solving the classical equations of motion. The connection between the Hamilton-Jacobi equation and the Schrödinger equation is of course well known.[23]

As we want the solution of the Schrödinger equation corresponding to the propagator, we need to solve for the unknown functions in (2.3)–(2.6) subject to the initial condition:

$$\lim_{t\to 0}\langle \mathbf{r}|e^{-iHt/\hbar}|\mathbf{r}_i\rangle=\delta(\mathbf{r}-\mathbf{r}_i)\ . \quad (2.7)$$

As a mathematical problem the most difficult aspect of this procedure is to solve the Hamilton-Jacobi equation since it is nonlinear. Once this is done the remaining equations of each hierarchy are linear and can be solved via the method of characteristics. The characteristics are simply the classical paths. Thus, in principle, determining the classical paths is the most difficult aspect of the solution of each hierarchy. This, of course, is in general a nontrivial task. In order to make progress one must either consider cases where the classical mechanics is simple, use perturbation theory, or do numerical calculations. We shall limit ourselves to the first two options. (McLaughlin gives an explicit formula for the b_j in terms of b_{j-1}. As b_0 is readily written in terms of S [see (1.4)] this allows one to obtain all the b_j recursively from S. We shall not follow this procedure for two reasons. First, we shall be able to readily solve the partial differential equations that shall appear. Second, McLaughlin's use of a "canonical problem" to determine initial conditions on the unknown functions is not appropriate here. We shall derive the required initial conditions by other means.)

Let us first treat the potential $V(\mathbf{x})$ as a perturbation on the free system. We shall do this by writing the potential as $\epsilon V(\mathbf{x})$ and treating ϵ as an expansion parameter. We shall solve the equations in each hierarchy as a perturbation series in ϵ. This procedure will recover the generalized Wigner-Kirkwood expansion.

We first consider the hierarchy given by (2.3) and (2.4). We assume that S and b_j can be expanded as power series in ϵ, i.e.,

$$S=\sum_{i=0}^{\infty}\epsilon^i S^i,\quad b_j=\sum_{i=0}^{\infty}\epsilon^i b_j^i\ . \quad (2.8)$$

Substituting these into (2.3) and (2.4) we obtain

$$\frac{1}{2m}(\nabla S^0)^2+\frac{\partial S^0}{\partial t}=0\ , \quad (2.9)$$

$$\frac{\partial S_1}{\partial t}+\frac{\nabla S^0\cdot\nabla S^1}{m}+V(x)=0\ , \quad (2.10)$$

$$\frac{\partial S^i}{\partial t}+\frac{1}{m}\nabla S^0\cdot\nabla S^i+\frac{1}{2m}\sum_{k=1}^{i-1}\nabla S^k\cdot\nabla S^{i-k}=0,\quad i\geq 1 \quad (2.11)$$

$$\frac{\partial b_0^0}{\partial t}+\frac{\nabla S^0\cdot\nabla b_0^0}{m}+\frac{\nabla^2 S^0}{2m}b_0^0=0\ , \quad (2.12)$$

$$\frac{\partial b_0^i}{\partial t}+\frac{\nabla S^0\cdot\nabla b_0^i}{m}+\frac{\nabla^2 S^0}{2m}b_0^i+\sum_{k=1}^{i}\frac{\nabla S^k\cdot\nabla b_0^{i-k}}{m}+\sum_{k=1}^{i}\frac{\nabla^2 S^k}{m}b_0^{i-k}=0,\quad i\geq 1 \quad (2.13)$$

$$\frac{\partial b_j^i}{\partial t}+\frac{\nabla S^0\cdot\nabla b_j^i}{m}+\frac{\nabla^2 S^0}{2m}b_j^i+\sum_{k=1}^{i}\frac{\nabla S^k\cdot\nabla b_j^{i-k}}{m}+\sum_{k=1}^{i}\frac{\nabla^2 S^k}{2m}b_j^{i-k}-\frac{1}{2m}\nabla^2 b_{j-1}^i=0,\quad i\geq 1,\quad j\geq 1\ . \quad (2.14)$$

We now have a double power series for the full propagator representing a perturbation series in both $\hbar$ and the strength parameter ϵ:

$$\langle \mathbf{r}|e^{-iHt/\hbar}|\mathbf{r}_i\rangle=\frac{1}{(2\pi i\hbar)^{d/2}}\exp\left[\frac{i}{\hbar}\sum_{i=0}^{\infty}\epsilon^i S^i(\mathbf{r},t|\mathbf{r}_i)\right]\times\sum_{j=0}^{\infty}\sum_{i=0}^{\infty}(i\hbar)^j\epsilon^i b_j^i(\mathbf{r},t|\mathbf{r}_i)\ . \quad (2.15)$$

The initial condition, (2.7), is independent of ϵ. This implies that

$$S^i(\mathbf{r},0|\mathbf{r}_i)=b_j^i(\mathbf{r},0|\mathbf{r}_i)=0\quad \text{for } i\geq 1 \text{ and all } j\ . \quad (2.16)$$

The initial conditions thus determine S^i and b_j^i for all $i\geq 1$ on a hyperplane in space-time. [We are solving first-order partial differential equations in four variables $(\mathbf{r},t)$ on the domain $\mathbb{R}^3\otimes\mathbb{R}^+$. We shall designate this domain as space-time for obvious reasons. It is amusing that the space time concept finds a natural setting in a nonrelativistic situation.] These conditions, together with the partial differential equations are sufficient to determine all the S^i and b_j^i over all space-time for $i\geq 1$. Now as $\epsilon\to 0$ the potential term vanishes and (2.15) must reduce to the free propagator. This identification determines the $i=0$ terms. They are

$$S^0(\mathbf{r},t|\mathbf{r}_i)=\frac{m(\mathbf{r}-\mathbf{r}_i)^2}{2t},\quad b_0^0=\frac{m}{t^{d/2}},\quad b_j^0=0\ . \quad (2.17)$$

One can readily verify that these functions satisfy the relevant equations in the hierarchy. Furthermore, it is clear that the initial condition (2.7) is satisfied. Now we are left with the task of solving for S^i and b_j^i for $i\geq 1$ subject to the initial conditions (2.16).

The S^i, $i \geq 1$ all satisfy a partial differential equation of the following form:

$$\frac{\partial F(\mathbf{r},t|\mathbf{r}_i)}{\partial t}+\frac{\mathbf{r}-\mathbf{r}_i}{t}\cdot\nabla F(\mathbf{r},t|\mathbf{r}_i)=G(\mathbf{r},t|\mathbf{r}_i)\ , \quad (2.18)$$

where $G(\mathbf{r},t|\mathbf{r}_i)$ is a known function and the explicit form for S^0 has been substituted. This equation can readily be solved via standard techniques (see the Appendix) to obtain

$$F(\mathbf{r},t|\mathbf{r}_i)=\int_0^t G\left[\mathbf{r}_i+\frac{\mathbf{r}-\mathbf{r}_i}{t}\tau,\tau\middle|\mathbf{r}_i\right]d\tau+C\left[\frac{\mathbf{r}-\mathbf{r}_i}{t}\right]\ , \quad (2.19)$$

where C is an arbitrary function that is determined via the initial conditions. Equation (2.19) is readily verified by direct substitution into (2.18). Using this formula one can establish the explicit form of the S^i. The first few of these are

$$S^1(\mathbf{r},t|\mathbf{r}_i)=-t\int_0^1 V(\mathbf{r}_i+\xi(\mathbf{r}-\mathbf{r}_i))d\xi\ , \quad (2.20)$$

$$S^2(\mathbf{r},t|\mathbf{r}_i)=-\frac{t^3}{m}\int_0^1(1-\xi)d\xi\int_0^\xi \xi_1 d\xi_1 \nabla V(\mathbf{r}_i+\xi(\mathbf{r}-\mathbf{r}_i))\cdot\nabla V(\mathbf{r}_i+\xi_1(\mathbf{r}-\mathbf{r}_i))\ . \quad (2.21)$$

The b_j^i, $i \geq 1$, all satisfy a partial differential equation of the form

$$\frac{\partial F(\mathbf{r},t|\mathbf{r}_i)}{\partial t}+\frac{\mathbf{r}-\mathbf{r}_i}{t}\cdot\nabla F(\mathbf{r},t|\mathbf{r}_i)+\frac{d}{2t}F(\mathbf{r},t|\mathbf{r}_i)=G(\mathbf{r},t|\mathbf{r}_i)\ . \quad (2.22)$$

The general solution to this equation is

$$F(\mathbf{r},t|\mathbf{r}_i)=\int_0^t\left[\frac{\tau}{t}\right]^{d/2}G\left[\mathbf{r}_i+\frac{\mathbf{r}-\mathbf{r}_i}{t}\tau,\tau\middle|\mathbf{r}_i\right]d\tau+\frac{1}{t^{d/2}}C\left[\frac{\mathbf{r}-\mathbf{r}_i}{t}\right] \quad (2.23)$$

(see the Appendix). Using this general solution one readily verifies that the first few b_j^i are

$$b_0^1(\mathbf{r},t|\mathbf{r}_i)=\frac{m}{t^{d/2}}\frac{t^2}{2m}\int_0^1\xi(1-\xi)\nabla^2 V(\mathbf{r}_i+\xi(\mathbf{r}-\mathbf{r}_i))d\xi\ , \quad (2.24)$$

$$b_1^1(\mathbf{r},t|\mathbf{r}_i)=\frac{m}{t^{d/2}}\frac{t^3}{8m^2}\int_0^1\xi^2(1-\xi)^2\nabla^4 V(\mathbf{r}_i+\xi(\mathbf{r}-\mathbf{r}_i))d\xi\ . \quad (2.25)$$

The calculation of higher-order terms can be done, but this becomes tedious. As we only wish to illustrate the perturbative nature of Wigner-Kirkwood expansions we shall content ourselves with the first few terms (see Ref. 4 for higher-order terms).

We can follow a similar procedure to the above in solving the second hierarchy, (2.5) and (2.6). If

$$S=\sum_{i=0}^{\infty}\epsilon^i S^i,\quad R_j=\sum_{i=0}^{\infty}\epsilon^i R_j^i\ , \quad (2.26)$$

then S^0, S^1, and S^2 are the same as for the first hierarchy

$$R_1^0=\frac{id}{2}\ln\frac{t}{m},\quad R_j^0=0\quad \text{for } j\geq 1 \quad (2.27)$$

because of the initial condition and

$$R_1^1(\mathbf{r},t|\mathbf{r}_i)=-\frac{it^2}{2m}\int_0^1\xi(1-\xi)\nabla^2 V(\mathbf{r}_i+\xi(\mathbf{r}-\mathbf{r}_i))d\xi\ , \quad (2.28)$$

$$R_2^1(\mathbf{r},t|\mathbf{r}_i)=\frac{t^3}{8m^2}\int_0^1\xi^2(1-\xi)^2\nabla^4 V(\mathbf{r}_i+\xi(\mathbf{r}-\mathbf{r}_i))d\xi\ . \quad (2.29)$$

If we substitute these expressions into (2.2) and expand the second exponential (after separating out the R_1^0 term) we obtain agreement, as we must, with (2.1), using the b_j^i (2.24) and (2.25). Furthermore, we also agree with the results of previous authors.[4,5] Using the language of Ref. 4 we can consider (2.2) to be, in a sense, the result of using a linked-graph method to exponentiate the first *Ansatz.* Using the terminology of diagrammatic perturbation theory we can consider the b_j^i coefficients in (2.1) to correspond, when we perturb in the potential, to reducible diagrams, whereas the R_j^i of (2.2) correspond to irreducible diagrams.

We have thus recovered the generalized Wigner-Kirkwood expansions from (2.1) and (2.2). Our approach differs from those of previous authors[4,5] in that they perturb about the free propagator. Because of this they automatically have a perturbation expansion in the potential. Our approach is more general, as it allows the potential to be treated nonperturbatively within the semiclassical approximation. In later sections we will find situations where the classical problem must, of necessity, be treated nonperturbatively.

There are a number of approaches in the literature which are similar to what we have done above.[7,8,24,25] Fujiwara[8] and Choquard[7] both use Morette's expression and treat the classical path perturbatively to obtain a Wigner-Kirkwood expansion of the propagator. Our work differs from theirs in that they expand in powers of the time, obtaining a short-time expansion. Our expansions coincide with these short-time expansions for dimensional reasons. The work of Osborn and Molzahn[24] is much closer in spirit to our analysis. They begin with an *Ansatz* which differs from (2.2) by a factor of $t^{-d/2}$. They consider a large-mass expansion of the classical paths rather that a small-potential expansion. In terms of classical paths, however, the two approaches are equivalent, because a large mass increases the inertia of the particle and thus decreases the effectiveness of the potential in deviating the particle from straight-line motion. Their procedure also recovers the Wigner-Kirkwood expansion. Even closer to the spirit of our work is that of Makri and Miller.[25] Here the action is expanded in powers of the potential but only in one dimension. The analogous multidimensional form is written down. Furthermore, (1.4) is the basis of the calculation and thus higher-order terms cannot be obtained. Much of this previous work is concerned with the evaluation of short-time propagators for use in the Feynman path integral.

Our treatment of the generalized Wigner-Kirkwood expansion not only reproduces previous results, it is also able to go beyond them. It is clear from our discussion that the Wigner-Kirkwood expansion assumes that the action scale in the problem is large compared to $\hbar$ and the potential energy is small compared to the kinetic energy. We now address the relaxation of the latter assumption.

III. WIGNER-KIRKWOOD EXPANSIONS AND STRONGLY REPULSIVE POTENTIALS

We now examine a case where the Wigner-Kirkwood expansion is not satisfactory. Let us calculate quantum corrections to the direct second virial coefficient for the hard-core potential (1.3). We do this by considering the case of a power-law potential

$$V(\mathbf{r})=V_0\left[\frac{a}{r}\right]^n . \tag{3.1}$$

It is plausible that we should be able to obtain results for the hard-core potential by calculating with this potential and taking $n\to\infty$ at an appropriate point in the calculation. This approach to the hard-core case is due to DeWitt.[26]

Substituting (3.1) into the generalized Wigner-Kirkwood expansion gives the following semiclassical expansion for the Boltzmann factor:

$$\langle\mathbf{r}|e^{-\beta H}|\mathbf{r}\rangle=\frac{1}{2^{3/2}\lambda^3}\exp\left[-\beta V_0\left[\frac{a}{r}\right]^n-\frac{\beta V_0}{12\pi}\left[\frac{\lambda}{a}\right]^2 n(n-1)\left[\frac{a}{r}\right]^{n+2} -\frac{\beta V_0}{240\pi^2}\left[\frac{\lambda}{a}\right]^4(n+2)(n+1)n(n-1)\left[\frac{a}{r}\right]^{n+4}+\frac{(\beta V_0)^2}{24\pi}\left[\frac{\lambda}{a}\right]^2 n^2\left[\frac{a}{r}\right]^{2n+2}\cdots\right] . \tag{3.2}$$

If one factorizes this into four exponentials and expands all of them except for the first, then one obtains the Wigner-Kirkwood expansion for (3.1). This form of the semiclassical Boltzmann factor was considered by DeWitt.[26] By substituting this Boltzmann factor into the expression for the direct second virial coefficient,

$$b_2=\frac{1}{2!}\frac{2^{3/2}}{\lambda^3}\int d\mathbf{r}\langle\mathbf{r}|e^{-\beta H}-e^{-\beta H_0}|\mathbf{r}\rangle , \tag{3.3}$$

and integrating, DeWitt obtains in the limit $n\to\infty$,

$$b_2=-\frac{2\pi a^3}{3\lambda^6}\left[1+\frac{n}{16\pi}\left[\frac{\lambda}{a}\right]^2-\frac{n^3}{960\pi^2}\left[\frac{\lambda}{a}\right]^4+\cdots\right] . \tag{3.4}$$

The Wigner-Kirkwood series that DeWitt uses is slightly different from ours, but this is a result of the use of integration by parts. Equation (3.4) does not have a limit as $n\to\infty$ and this is indicative of a failure of the Wigner-Kirkwood expansion [DeWitt does suggest that (3.4) is part of a series, which when summed, does have a limit as $n\to\infty$. The analysis in Sec. V shows that this view can be taken but is not the full story.] As a result of this difficulty, quantum corrections to the hard-core direct virial coefficient have been calculated using other methods.[11–16] Through naive manipulations, however, one can obtain alternative answers for the hard-core limit. For instance, if, in DeWitt's calculation the hard-core limit is taken before the integration over $\mathbf{r}$ is carried out, then only the first term in (3.4), i.e., the classical answer, is obtained. One can uncover further ambiguity by working directly with the generalized Wigner-Kirkwood expansion (3.2). If one takes the hard-core limit in this form of the propagator, then one obtains, for $\mathbf{r}<a$, a divergent answer, even before integrating. This is because the fourth term appears with a positive sign. The ambiguity of the hard-core limit is further evidence of the failure of the Wigner-Kirkwood expansion. However, this is not the only evidence. Even in the power-law case there are problems. As $r\to\lambda$ in (3.2) the first and second quantum "corrections" become of the same order of magnitude as the classical term. Worse still, the positive sign in the fourth term causes the propagator to diverge as $r\to 0$. These problems indicate that as r becomes small, quantum corrections become large. One can see then that while the Wigner-Kirkwood expansions are integrable for strongly repulsive potentials, the generalized Wigner-Kirkwood expansions are not.

In light of the derivation of the generalized Wigner-Kirkwood expansions in Sec. II, these problems are not surprising. They are simply a reflection of the fact that the effects of a strongly repulsive potential cannot be obtained by perturbing about the free solution. However, problems arise only when the potential is strong. For $|\mathbf{r}|,|\mathbf{r}_i|\gg a$, typical potentials are weak. As such, one expects that the generalized Wigner-Kirkwood expansion gives, in some sense, a correct expression for the propagator in this limit. The problem with using generalized Wigner-Kirkwood expansions to calculate virial coefficients is that one needs an expression for the propagator that is uniformly valid for all $\mathbf{r}$. These expansions clearly do not provide such an expression for strongly repulsive potentials.

IV. NONPERTURBATIVE CLASSICAL INPUT INTO SEMICLASSICAL EXPANSIONS— A SIMPLE EXAMPLE

In Sec. II we demonstrated that the Wigner-Kirkwood expansion is more than a semiclassical expansion of the propagator. It also assumes that the interactions in the underlying classical problem are small enough to be treated perturbatively. For strongly repulsive potentials this latter assumption is not valid and needs to be removed in some sense. We shall spend the rest of this paper considering some simple contexts in which this can be done. The procedure for calculating the semiclassical propagator was outlined in the first part of Sec. II. In applying this procedure to the case of strongly repulsive potentials let us first consider the problem qualitatively. The first step is to obtain the classical action. This is most readily obtained by first calculating the classical path $\mathbf{r}_c(t)$. Substituting this into the Lagrangian yields an explicit function of time. Integrating this function over time from some initial time to some final time yields the classical action. As is well known[17–19] the classical path $\mathbf{r}_c(t)$ required for this evaluation is a solution of Newton's equations of motion subject to the boundary conditions $\mathbf{r}_c(0)=\mathbf{r}_i$, $\mathbf{r}_c(t)=\mathbf{r}$. Unlike the initial-value problem this boundary-value problem can have more than one solution (in fact, it may not have a solution at all). This is the case for strongly repulsive potentials. Let us consider, as a specific example, the case where $\mathbf{r}_i \cong \mathbf{r}$. We shall be considering this case quantitatively for a hard-core potential in Sec. V. For a single particle propagating from $\mathbf{r}_i$ to $\mathbf{r}\cong\mathbf{r}_i$ in time t in the field of a strongly repulsive potential, there are in fact two classical paths satisfying the boundary-value problem. One, the direct path, goes directly from $\mathbf{r}_i$ to $\mathbf{r}$. For this path, if $|\mathbf{r}|,|\mathbf{r}_i| \gg a$ one can write the classical path as a perturbation series in powers of the potential strength. The second classical path, the reflected path, begins at $\mathbf{r}_i$ moving toward the origin, reflects off the potential barrier, and returns to $\mathbf{r}$ in time t. This path cannot be obtained via a perturbation expansion in the potential strength. This is because at the turning point the potential energy dominates the kinetic energy.

The presence of reflections has been noted in the path-integral formulation of the semiclassical limit, and some calculations have been done.[27,28] These reflections are, of course, related to turning points in the WKB theory. There is, of course, an enormous literature on this.[19] However, as we noted in the Introduction, the application of the time-independent theory to the problem at hand is less transparent than the time-dependent approach we are taking.

How does the semiclassical calculation proceed when there are multiple solutions to the classical problem? For each of these solutions one can construct a classical action and the subsequent quantum corrections. One then has a number of semiclassical solutions to the Schrödinger equation. Because of the linearity of the Schrödinger equation the most general semiclassical solution is a linear superposition of these. In general, there will be a number of underdetermined parameters in this superposition, which will be determined via initial and boundary conditions.

Let us now consider quantitatively a simple case in which multiple classical paths appear. We consider the quantum propagator of a particle on a half line, i.e.,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}=i\hbar\frac{\partial\Psi}{\partial t} \quad \text{for } x>0\ , \tag{4.1}$$

$$\Psi(x,0)=\delta(x-x_i)\ , \tag{4.2}$$

$$\frac{\partial\Psi}{\partial x}(0,t)=\alpha\Psi(0,t), \quad t>0\ . \tag{4.3}$$

We begin with this example, as the solution is well known via other techniques.[29,30] The boundary condition at $x=0$ can be thought of as a treatment of a typical potential, which has a strongly repulsive core to prevent the particle from entering the $x<0$ region, via the zero-range approximation. For $\alpha<0$ a bound state appears.

For this problem there is both a direct and a reflected path. The classical actions for these paths are

$$\frac{m(x\pm x_i)^2}{2t}\ , \tag{4.4}$$

where the plus sign is for the reflected path and the minus sign for the direct path. Using these two solutions to the Hamilton-Jacobi equation, we can generate two semiclassical solutions. As stated earlier, the most general solution is a linear superposition. We shall, in fact, assume the following form for the semiclassical solution:

$$\Psi(x,t)=\frac{1}{(2\pi i\hbar)^{1/2}}\left[\left[\frac{m}{t}\right]^{1/2}\exp\left[\frac{im(x-x_i)^2}{2\hbar t}\right] +\exp\left[\frac{im(x+x_i)^2}{2\hbar t}\right] \times\sum_{j=0}^{\infty}(i\hbar)^j b_j(x,t)\right]\ . \tag{4.5}$$

[We shall only use the semiclassical *Ansatz* (2.1) in this section and in Sec V. Problems arise in the use of the other *Ansatz*. We shall outline these in Sec. VI.] In (4.5) we assume that the semiclassical solution for the direct part is the free propagator. One can justify this assumption by appealing to the path-integral formalism. In the path-integral formalism the semiclassical limit will involve two families of paths, one family concentrated about the reflected path and one concentrated about the direct path. The evaluation of the path integral over the paths concentrated about the direct path will yield the free propagator because these paths are not affected by the presence of the potential. The same, of course, cannot be said of the reflected path and thus we retain the full *Ansatz* for this case. One can also justify (4.5) by viewing it as the standard trick for finding the Green's function satisfying the boundary-value problem (4.1)–(4.3). Here one adds a solution of the homogeneous problem to the free-space Green's function and then chooses the solution to the homogeneous problem to satisfy the boundary conditions. The ultimate justification is that this *Ansatz* is general enough to yield the solution of (4.1)–(4.3).

We obtain the $b_j(x,t)$ in (4.5) by solving the hierarchy of equations (2.4), subject to the boundary conditions

$$b_0(0,t)=\left[\frac{m}{t}\right]^{1/2}, \tag{4.6}$$

$$b_1(0,t)=\frac{t}{mx_i}\left[\frac{\partial b_0}{\partial x}(0,t)-\alpha b_0(0,t)-\alpha\left[\frac{m}{t}\right]^{1/2}\right], \tag{4.7}$$

$$b_{j+1}(0,t)=\frac{t}{mx_i}\left[\frac{\partial b_j}{\partial x}(0,t)-\alpha b_j(0,t)\right],\quad j\geq 1\ . \tag{4.8}$$

These are readily derived by substituting (4.5) into the boundary condition (4.3) and equating powers $\hbar$. Let us now solve the hierarchy.

$b_0(x,t)$ satisfies

$$\frac{\partial b_0}{\partial t}+\frac{x+x_i}{t}\frac{\partial b_0}{\partial x}+\frac{1}{2t}b_0=0 \tag{4.9}$$

subject to (4.6). This partial differential equation is a special case of Eq. (2.22) with $d=1$ and $\mathbf{r}_i=-x_i$. The general solution is

$$b_0(x,t)=\frac{1}{t^{1/2}}C\left[\frac{x+x_i}{t}\right]. \tag{4.10}$$

Imposing the boundary condition (4.6) determines the arbitrary function C to be $m^{1/2}$. Because the Laplacian of b_0 is zero b_1 also satisfies Eq. (4.9). The arbitrary function in this case is easily determined using the boundary condition (4.7). One obtains

$$b_1(x,t)=-\left[\frac{m}{t}\right]^{1/2}\frac{2\alpha}{m}\frac{t}{x+x_i}\ . \tag{4.11}$$

The partial differential equation for b_2 has a nonzero inhomogeneous term. Using (2.22) the general solution becomes

$$b_2(x,t)=\left[\frac{m}{t}\right]^{1/2}\left[\left[\frac{t}{m}\right]^2\frac{2\alpha}{(x+x_i)^3}+\frac{1}{m^{1/2}}C\left[\frac{x+x_i}{t}\right]\right]. \tag{4.12}$$

Imposing (4.8) for $j=1$ yields

$$b_2(x,t)=\left[\frac{m}{t}\right]^{1/2}\left[\frac{t}{m}\right]^2\left[\frac{2\alpha}{(x+x_i)^3}+\frac{2\alpha^2}{(x+x_i)^2}\right]. \tag{4.13}$$

The nice thing about this calculation is that the existence of an exact solution[29,30] suggests that one can solve the hierarchy to infinite order. After the calculation of a few more terms (we went to b_5) a pattern emerges. The general term is

$$b_j(x,t)=(-1)^j\left[\frac{m}{t}\right]^{1/2}\left[\frac{t}{m}\right]^j\left[\sum_{k=1}^{j-1}\frac{2\alpha^k k(k+1)\times\cdots\times(2j-k-1)}{2^{j-k}(1)(2)\times\cdots\times(j-k)}\frac{1}{(x+x_i)^{2j-k}}+\frac{2\alpha^j}{(x+x_i)^j}\right],\quad j\geq 2\ . \tag{4.14}$$

This can be established by induction. Recovering the full propagator from this series is clearly not a straightforward task. It can of course be done, but the clearest way to do this is by first examining the exact propagator. For convenience we do the comparison via the Boltzmann factor (Euclidean propagator).

Rather than simply quoting the exact propagator we shall instead outline its derivation. We do this as there is a subtlety in the problem, which is best treated explicitly. The boundary-value problem for the Boltzmann factor is

$$\frac{\partial\Psi}{\partial\beta}=\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}\quad\text{for } x>0\ , \tag{4.15}$$

$$\Psi(x,0)=\delta(x-x_i)\ , \tag{4.16}$$

$$\frac{\partial\Psi}{\partial x}(0,\beta)=\alpha\Psi(0,\beta),\quad \beta>0\ . \tag{4.17}$$

We solve (4.15)–(4.17) via Laplace transform techniques using the Watson form, (1.5) of the inverse Laplace transform. In this representation the Laplace transform is

$$G(x,z)=\int_0^\infty e^{\beta z}\Psi(x,\beta)d\beta\ . \tag{4.18}$$

One readily deduces that this Laplace transform satisfies

$$\frac{\partial^2 G(x,z)}{\partial x^2}+\frac{2mz}{\hbar^2}G(x,z)=-\frac{2m}{\hbar^2}\delta(x-x_i)\ . \tag{4.19}$$

Solving this in the standard way[31] one obtains

$$G(x,z)=i\left[\frac{m}{2\hbar^2 z}\right]^{1/2}\left\{\exp\left[i\left[\frac{2mz}{\hbar^2}\right]^{1/2}|x-x_i|\right]+\exp\left[i\left[\frac{2mz}{\hbar^2}\right]^{1/2}|x+x_i|\right]\right.$$
$$\left.+\frac{2}{(i/\alpha)\left[\frac{2mz}{\hbar^2}\right]^{1/2}-1}\exp\left[i\left[\frac{2mz}{\hbar^2}\right]^{1/2}|x+x_i|\right]\right\}, \tag{4.20}$$

where one chooses the branch of the square root such that $\mathrm{Im}(\sqrt{z})>0$. At this point one could obtain the inverse Laplace transform of (4.20) by consulting a table of Laplace transform pairs. In doing this, however, the above-mentioned subtlety may be overlooked. In order to avoid this, and because it is much more instructive, we shall evaluate the inverse Laplace transform explicitly.

In order to compare our semiclassical series to the exact answer, we need an asymptotic (large-temperature) evaluation of the inverse Laplace transform. This can be done by the method of steepest descent. A steepest-descent evaluation of contour integrals similar to that which appears in the inverse Laplace transform is in fact, done in the book of Carrier, Krook, and Pearson[32] and we shall follow this. It turns out, in fact, that this method allows the integral to be done exactly. One divides the inverse Laplace transform into three separate integrals corresponding to the three terms of (4.20). Then one rescales the complex variable z,

$$s=\beta z\frac{\lambda^2}{4\pi(x\pm x_i)^2}\ . \tag{4.21}$$

The minus sign is used in the first integral and the plus sign in other two. The steepest-descent contour is then given by

$$s=\left[y+\frac{i}{2}\right]^2,\quad -\infty<y<\infty\ . \tag{4.22}$$

The contour integral then becomes

$$\Psi(x,\beta)=\frac{2(x-x_i)}{\lambda^2}\int_{-\infty}^{\infty}dy\,\exp\left[-4\pi\frac{(x-x_i)^2}{\lambda^2}(y^2+\tfrac{1}{4})\right]+\frac{2(x+x_i)}{\lambda^2}\int_{-\infty}^{\infty}dy\,\exp\left[-4\pi\frac{(x+x_i)^2}{\lambda^2}(y^2+\tfrac{1}{4})\right]$$
$$-\alpha\frac{2}{\pi}\exp\left[\frac{-\pi(x+x_i)^2}{\lambda^2}\right]\int_0^{\infty}dy\frac{1}{y^2+1}\exp\left[-\frac{\pi}{\lambda^2}\left[x+x_i+\frac{\lambda^2\alpha}{2\pi}\right]^2y^2\right]$$
$$-\Theta\left[\lambda^2-\frac{2\pi(x+x_i)}{|\alpha|}\right]\Theta(-\alpha)2\alpha\exp\left[\frac{\lambda^2\alpha^2}{4\pi}+\alpha(x+x_i)\right], \tag{4.23}$$

where

$$\Theta(x)=\begin{cases}0, & x<0\\ 1, & x>0\end{cases}$$

is the Heaviside step function. The final term is a pole contribution, which is only present for $\alpha<0$ and $\lambda^2>2\pi(x+x_i)/|\alpha|$. Under these conditions the deformation of the original contour to the steepest-descent contour picks up a pole corresponding to a bound state. Note that, for fixed x,x_i, this pole contribution does not appear when one takes the high-temperature limit. The first two integrals are trivial. The third one is easily integrated by writing it as

$$I(\beta)=e^{\beta}\int_0^{\infty}dy\frac{1}{y^2+1}\exp[-\beta(y^2+1)] \tag{4.24}$$

differentiating under the integral sign with respect to β, to obtain a differential equation for $I(\beta)$, and then integrating this to yield an error function. Alternatively one can simply change variables to $x=\sqrt{y}$ to obtain one of the integral representations of the confluent hypergeometric function (which is a more convenient form for analytic continuation in the temperature variable to obtain the Schrödinger propagator). The net result is

$$\langle x|e^{-\beta H}|x_i\rangle=\frac{1}{\lambda}\left[\exp\left[\frac{-\pi(x-x_i)^2}{\lambda^2}\right]+\exp\left[\frac{-\pi(x+x_i)^2}{\lambda^2}\right]\right]$$
$$-\alpha\exp\left[\frac{\lambda^2\alpha^2}{4\pi}+\alpha(x+x_i)\right]\mathrm{erfc}\left[\frac{\sqrt{\pi}}{\lambda}\left[x+x_i+\frac{\lambda^2\alpha}{2\pi}\right]\right]$$
$$-\Theta\left[\lambda^2-\frac{2\pi(x+x_i)}{|\alpha|}\right]\Theta(-\alpha)2\alpha\exp\left[\frac{\lambda^2\alpha^2}{4\pi}+\alpha(x+x_i)\right]. \tag{4.25}$$

(Note that the Wigner-Kirkwood expansion, as outlined in Sec. II, would only yield the first term, i.e., the free propagator.) Note that the use of a table of Laplace-transform pairs would not have yielded the bound-state term. The reason for this, we suspect, is that the inverse Laplace transform of the third term of (4.20) was originally used in heat-conduction problems, where the boundary condition at the origin in (4.17) corresponds to convection at $x=0$ into the air at $x<0$. Here negative α is unphysical. Hence the negative-α case was not examined.

We can now compare the result with our series. To do this we want a small λ expansion of (4.25). We therefore need the large argument expansion of the error function

$$\int_x^\infty \exp(-u^2)du=\frac{\exp(-x^2)}{2x}\left[1+\sum_{n=1}^{\infty}(-1)^n\frac{(1)(3)(5)\times\cdots\times(2n-1)}{(2x^2)^n}\right], \tag{4.26}$$

where $x^2=(\pi/\lambda^2)(x+x_i+\lambda^2\alpha/2\pi)^2$. Using the binomial theorem to write $1/x^{2n}$ as a power series in λ, rearranging the resulting double series, and grouping with the rest of (4.25), we find agreement with our semiclassical calculation, except for the bound-state term. This means that if we were to carry out the reverse procedure, formally summing the asymptotic series in (4.5), we would recover all of the exact propagator, except for the bound-state term. This cautions us in attempting a formal summation of an asymptotic series. The fact that the bound-state term is not obtained in the semiclassical calculation is understandable, as this is a high-temperature asymptotic series and the bound-state contribution is exponentially small (i.e., it is subdominant with respect to all the terms of the asymptotic series and will hence never appear, even at infinite order in such a series). Alternatively, in the high-temperature limit, for fixed x and x_i, the bound-state pole moves inside the steepest-descent contour and thus does not contribute [as indicated by the Θ functions in (4.25)]. Having considered a simple example of our procedure we now move onto a somewhat more difficult example.

V. PROPAGATION IN THE VICINITY OF A 3D HARD-CORE POTENTIAL

We now turn to the case of the semiclassical propagator for the hard-core potential (1.3). As we outlined in the Introduction and as we elaborated in Secs. III the Wigner-Kirkwood expansion is inadequate for this case. It should by now be clear that this inadequacy is due to the fact that classical mechanics in a hard-core potential is nonperturbative. The classical mechanics in this case, however, is more complicated than the simple one-dimensional example of Sec. IV. As one can see from Fig. 1, propagation from $\mathbf{r}_i$ to $\mathbf{r}$ is via two paths. However, if $\mathbf{r}$ lies in the shaded region there are no classical paths at all. This is, of course, sensible as the shaded region is the geometrical optics shadow. As propagation into this region is purely by diffraction and the geometric optics approximation must break down, we cannot treat this case with our methods. We shall limit our consideration to the complement of the shadow region.

The procedure to follow is straightforward, in principle. We simply solve the semiclassical hierarchy in much the same manner as was done for the simple example of Sec. IV. However, in this case the action for the reflected path is not readily expressed as an explicit function of $\mathbf{r}$, $\mathbf{r}_i$, and t. We thus consider the simpler case

$$\theta(\mathbf{r},\mathbf{r}_i),\ \frac{|\mathbf{r}|-a}{a},\frac{|\mathbf{r}_i|-a}{a}\ll 1\ , \tag{5.1}$$

i.e., both the source and the field points are near the hard-core surface and each other. $\theta(\mathbf{r},\mathbf{r}_i)$ denotes the angle between $\mathbf{r}$ and $\mathbf{r}_i$. Under these conditions the geometry is "close" to that of a half space, for which the propagator is easily written via the method of images. The classical mechanics is also much simpler. In considering this case we are following previous authors.[14,15] These authors also consider the hard-core propagator. They do not, however, consider the semiclassical limit, nor do they obtain an explicit expression for the propagator. Their aim is to evaluate the high-temperature series for the direct second virial coefficient. Their procedure involves expanding the (Euclidean) propagator in inverse powers of a, i.e.,

$$\langle\mathbf{r}|e^{-\beta H}|\mathbf{r}_i\rangle=G_0(\mathbf{r})+\frac{1}{a}G_1(\mathbf{r})+\frac{1}{a^2}G_2(\mathbf{r})+\cdots\ . \tag{5.2}$$

By expanding the boundary condition in powers of a^{-1} and substituting (5.2) into the subsequent expansion and into the Schrödinger equation, they obtain inhomogeneous boundary-value problems on the half space for each of the $G_i(\mathbf{r})$. Solving these, the previous authors obtain

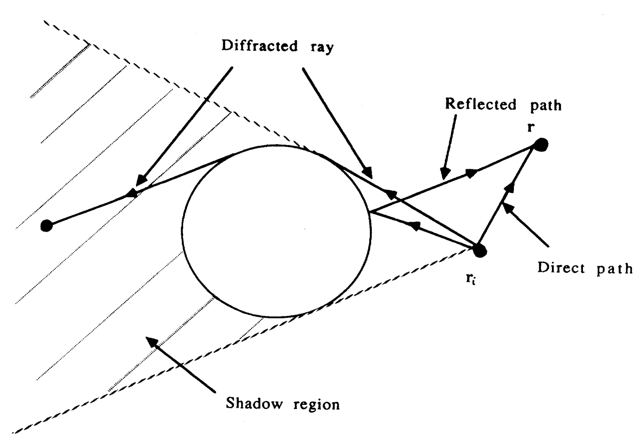

FIG. 1. Semiclassical propagation in a hard-core potential.

integral forms of $G_1(\mathbf{r})$ and $G_2(\mathbf{r})$. Our semiclassical approach will yield the explicit expression for $G_1(\mathbf{r})$ and $G_2(\mathbf{r})$. This will allow us to evaluate the integral forms presented by previous authors.

We thus wish to solve semiclassically the following boundary-value problem for the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi=i\hbar\frac{\partial\Psi}{\partial t}\ , \tag{5.3}$$

$$\Psi(\mathbf{r},0)=\delta(\mathbf{r}-\mathbf{r}_i)\ , \tag{5.4}$$

$$\Psi(\mathbf{P},t)=0 \quad \text{for } \mathbf{P}\in\{\mathbf{r}:|\mathbf{r}|=a\} \quad \text{for all } t>0\ , \tag{5.5}$$

where, for simplicity, we only consider the case of homogeneous Dirichlet boundary conditions. For much the same reasons as in Sec. IV we shall work with the following *Ansatz:*

$$\Psi(x,\rho,t|x_i)=\frac{1}{(2\pi i\hbar)^{3/2}}\left[\left[\frac{m}{t}\right]^{3/2}\exp\left[\frac{im[(x-x_i)^2+\rho^2]}{2\hbar t}\right]+\exp\left[\frac{iS(x,\rho,t|x_i)}{\hbar}\right]\sum_{j=0}^{\infty}(i\hbar)^j b_j(x,\rho,t|x_i)\right]\ . \tag{5.6}$$

Like previous authors, because of the cylindrical symmetry, we have used a cylindrical coordinate system whose origin is on the surface of the sphere of radius a and whose axis goes through the source point $\mathbf{r}_i$ and the center of the sphere. The boundary surface, in these coordinates, is

$$x=-a+(a^2-\rho^2)^{1/2}$$
$$=-\frac{\rho^2}{2a}-\frac{\rho^4}{8a^3}-\frac{\rho^6}{16a^5}+\cdots\ . \tag{5.7}$$

In order to make the nature of the approximation (5.1) clear, we shall take a slightly different approach to that of previous authors. Let us perform the following rescalings:

$$x=\gamma x_{\text{new}},\quad \rho=\gamma\rho_{\text{new}},\quad S=\gamma^2 S_{\text{new}},\quad b_j=\gamma^{-2j}b_{j\,\text{new}}\ . \tag{5.8}$$

Let us henceforth drop the "new" subscript and use the rescaled variables until otherwise stated (this procedure should not lead to confusion). The boundary surface, expressed in terms of the rescaled variables becomes

$$x=-\tfrac{1}{2}\epsilon\rho^2-\tfrac{1}{8}\epsilon^3\rho^4+\cdots\ , \tag{5.9}$$

where $\epsilon=\gamma/a$. Thus by having x and ρ of order unity and $\epsilon\ll 1$ we impose (5.1), and under such conditions the boundary is clearly a perturbation of a plane. The hard-core problem for the case (5.1) thus becomes a perturbation of the half-plane problem. To calculate (5.6) under conditions (5.1) we now expand the unknown functions in a power series in ϵ:

$$S(x,\rho,t|x_i)=\left[\frac{m[(x+x_i)^2+\rho^2]}{2t}\right]+\epsilon S_1(x,\rho,t|x_i)$$
$$+\epsilon^2 S_2(x,\rho,t|x_i)+\cdots\ , \tag{5.10}$$

$$b_0(x,\rho,t|x_i)=-\left[\frac{m}{t}\right]^{3/2}+\epsilon b_0^1(x,\rho,t|x_i)$$
$$+\epsilon^2 b_0^2(x,\rho,t|x_i)+\cdots\ , \tag{5.11}$$

$$b_j(x,\rho,t|x_i)=\epsilon b_j^1(x,\rho,t|x_i)+\epsilon^2 b_j^2(x,\rho,t|x_i)$$
$$+\cdots,\quad j>0 \tag{5.12}$$

where, as in Sec. II, we have used our knowledge of the $\epsilon\to 0$ solution. [Knowledge of the half-space solution for the boundary conditions (5.5) saves us from explicitly considering the half-space classical mechanics, although this is of course straightforward.] We can satisfy the boundary condition (5.5) by imposing

$$S(\mathbf{P},t|x_i)=\frac{m(\mathbf{P}-\mathbf{r}_i)^2}{2t}\ ,$$
$$b_0(\mathbf{P},t|x_i)=-\left[\frac{m}{t}\right]^{3/2}\ , \tag{5.13}$$
$$b_j(\mathbf{P},t|x_i)=0\ ,$$

where $j>0$ and $\mathbf{P}$ is on the surface of the sphere.

Substituting (5.10)–(5.12) into (5.13) and using (5.7) one determines the following boundary conditions on the unknown functions:

$$S_1(0,\rho,t|x_i)=\frac{mx_i}{t}\rho^2\ , \tag{5.14}$$

$$S_2(0,\rho,t|x_i)=\tfrac{1}{2}\rho^2\frac{\partial S_1}{\partial x}(0,\rho,t|x_i)\ , \tag{5.15}$$

$$b_j^1(0,\rho,t|x_i)=0\ , \tag{5.16}$$

$$b_j^2(0,\rho,t|x_i)=\tfrac{1}{2}\rho^2\frac{\partial b_j^1}{\partial x}(0,\rho,t|x_i)\ . \tag{5.17}$$

Substituting (5.10)–(5.12) into (2.3) and (2.4) one obtains the hierarchy of partial differential equations given in (2.9)–(2.14) for the unknown functions, except that $V(\mathbf{x})=0$ and the interpretation of the perturbation expansion is different. In Sec. II the perturbation series was one in powers of the potential, whereas here the perturbation parameter indicates deviations from the limit (5.1). Solving the partial differential equations using methods which should by now be familiar, one determines, after a considerable amount of algebra,

$$S_1(x,\rho,t|x_i)=\frac{m}{t}\frac{x_i^2\rho^2}{x+x_i}\ , \tag{5.18}$$

$$S_2(x,\rho,t|x_i)=\frac{m}{2t}\left[\frac{x_i^4\rho^4}{(x+x_i)^4}+\frac{4x_i^4\rho^2}{(x+x_i)^2}-\frac{2x_i^3\rho^4}{(x+x_i)^3}-\frac{4x_i^3\rho^2}{x+x_i}\right], \tag{5.19}$$

$$b_j^1(x,\rho,t|x_i)=\left[\frac{m}{t}\right]^{3/2}\left[\frac{-t}{m}\right]^j\left[\frac{[3]_j x_i x\rho^2}{(x+x_i)^{2j+3}}+\frac{[1]_j 2x_i x}{(x+x_i)^{2j+1}}\right], \tag{5.20}$$

where

$$[a]_j=\begin{cases}1, & j=0\\ a(a+2)(a+4)\cdots(a+2j-2), & j>0\end{cases}$$

$$b_j^2(x,\rho,t|x_i)=\left[\frac{m}{t}\right]^{3/2}\left[\frac{-t}{m}\right]^j\frac{1}{(x+x_i)^{2j}}\times(A_j+B_j\rho^2+C_j\rho^4), \tag{5.21}$$

where

$$A_j=\delta_{j,0}\tfrac{2}{3}x_i x-[1]_j 2x_i x+\tfrac{4}{3}[3]_j\frac{x_i x(x^2-x_i x+x_i^2)}{(x+x_i)^2}, \tag{5.22}$$

$$B_j=[1]_j\frac{x_i}{x+x_i}-[3]_j\frac{x_i x(5x^2+6x_i x+3x_i^2)}{(x+x_i)^4}+[5]_j\frac{4x_i x(x^2-x_i x+x_i^2)}{(x+x_i)^4}, \tag{5.23}$$

$$C_j=\tfrac{1}{2}[3]_j\frac{x_i}{(x+x_i)^3}-[5]_j\frac{3x_i x(x^2+x_i x+x_i^2)}{(x+x_i)^6}+\tfrac{5}{2}[7]_j\frac{x_i x(x^2-x_i x+x_i^2)}{(x+x_i)^6}. \tag{5.24}$$

We evaluated b_j^1 and b_j^2 to about $j=4$. This was sufficient to establish the pattern for general j as shown above. The general j case was then established by induction. We need to calculate quantum corrections to all orders in order to facilitate comparison with previous results.

We now formally sum the (divergent) semiclassical series in $\hbar$ using the identity

$$\sum_{j=0}^{\infty}\frac{[n]_j}{(-2z)^j}=z^{n/2}e^z\Gamma\left[-\frac{n}{2}+1,z\right], \tag{5.25}$$

where $\Gamma(a,z)$ is the incomplete gamma function. Our experience in Sec. IV indicates that the formal summation will give the correct answer, as there are no bound states. We shall be able to verify this by comparing our answer to that of previous authors. In order to facilitate comparison with previous work we now replace m by $m/2$ (previous workers used the reduced mass, as their propagator was that for the relative coordinate in an equal-mass two-body problem) and convert to the Boltzmann factor. Also our scaling procedure has served its purpose, quantifying the perturbation series about the limit (5.1). We thus revert back to the original (unscaled) variables with the understanding that the unscaled variables are all much less than a. We obtain for the full propagator

$$\langle \mathbf{r}|e^{-\beta H}|\mathbf{r}_i\rangle=\frac{1}{2^{3/2}\lambda^3}\exp\left[-\frac{\pi[(x-x_i)^2+\rho^2]}{2\lambda^2}\right]+\frac{1}{2^{3/2}\lambda^3}\exp\left[-\frac{\pi}{2\lambda^2}\left[(x+x_i)^2+\rho^2+\frac{1}{a}Q_1+\frac{1}{a^2}Q_2+\cdots\right]\right]\left[-1+\frac{\lambda}{a}M+\left[\frac{\lambda}{a}\right]^2N+\cdots\right], \tag{5.26}$$

where

$$Q_1(x,\rho,t|x_i)=\frac{2x_i^2\rho^2}{x+x_i}, \tag{5.27}$$

$$Q_2(x,\rho,t|x_i)=\left[\frac{x_i^4\rho^4}{(x+x_i)^4}+\frac{4x_i^4\rho^2}{(x+x_i)^2}-\frac{2x_i^3\rho^4}{(x+x_i)^3}-\frac{4x_i^3\rho^2}{x+x_i}\right], \tag{5.28}$$

$$M=\frac{x_i x\rho^2}{\lambda^4}e^z\left[\frac{\pi}{2}\right]^{3/2}\Gamma(-\tfrac{1}{2},z)+\frac{2x_i x}{\lambda^2}e^z\left[\frac{\pi}{2}\right]^{1/2}\Gamma(\tfrac{1}{2},z), \tag{5.29}$$

$$N=D+E\left[\frac{\rho}{\lambda}\right]^2+F\left[\frac{\rho}{\lambda}\right]^4, \tag{5.30}$$

$$D=\frac{2}{3}\frac{x_i x}{\lambda^2}-\frac{2x_i x(x+x_i)}{\lambda^3}e^z\left[\frac{\pi}{2}\right]^{1/2}\Gamma(\tfrac{1}{2},z)+\frac{4}{3}\frac{x_i x(x+x_i)(x^2-x_i x+x_i^2)}{\lambda^5}e^z\left[\frac{\pi}{2}\right]^{3/2}\Gamma(-\tfrac{1}{2},z), \tag{5.31}$$

$$E=\frac{x_i}{\lambda}e^z\left[\frac{\pi}{2}\right]^{1/2}\Gamma(\tfrac{1}{2},z)-\frac{x_i x(5x^2+6x_i x+3x_i^2)}{(x+x_i)\lambda^3}e^z\left[\frac{\pi}{2}\right]^{3/2}\Gamma(-\tfrac{1}{2},z)$$

$$+\frac{4x_i x(x+x_i)(x^2-x_i x+x_i^2)}{\lambda^5}e^z\left[\frac{\pi}{2}\right]^{5/2}\Gamma(-\tfrac{3}{2},z)\;, \tag{5.32}$$

$$F=\frac{1}{2}\frac{x_i}{\lambda}e^z\left[\frac{\pi}{2}\right]^{3/2}\Gamma(-\tfrac{1}{2},z)-\frac{3x_i x(x^2+x_i x+x_i^2)e^z}{(x+x_i)\lambda^3}\left[\frac{\pi}{2}\right]^{5/2}\Gamma(-\tfrac{3}{2},z)$$

$$+\frac{5}{2}\frac{x_i x(x+x_i)(x^2-x_i x+x_i^2)}{\lambda^5}e^z\left[\frac{\pi}{2}\right]^{7/2}\Gamma(-\tfrac{5}{2},z)\;, \tag{5.33}$$

where $z=\pi(x+x_i)^2/2\lambda^2$. We now compare this result with previous work. Previous work obtained an expression for the propagator of the form

$$\langle \mathbf{r}|e^{-\beta H}|\mathbf{r}_i\rangle=G_0(\mathbf{r})+\frac{1}{a}G_1(\mathbf{r})+\frac{1}{a^2}G_2(\mathbf{r})+\cdots\;, \tag{5.34}$$

where the $G_i(\mathbf{r})$ are

$$G_0(\mathbf{r})=\frac{1}{8(\pi D\beta)^{3/2}}\left[\exp\left[-\frac{(x-x_i)^2+\rho^2}{4D\beta}\right]-\exp\left[-\frac{(x+x_i)^2+\rho^2}{4D\beta}\right]\right]\;, \tag{5.35}$$

$$G_1(\mathbf{r})=\frac{xx_i}{8(\pi D\beta)^2}\exp\left[-\frac{\rho^2}{4D\beta}\right]\int_0^\beta d\tau\frac{1}{\tau^{1/2}(\beta-\tau)^{1/2}}\exp\left[-\frac{x_i^2}{4D\tau}-\frac{x^2}{4D(\beta-\tau)}\right]\left[1+\frac{\tau\rho^2}{4D\beta(\beta-\tau)}\right]\;, \tag{5.36}$$

$$G_2(\mathbf{r})=\frac{xx_i}{32\beta^2(\pi D)^{5/2}}\exp\left[-\frac{\rho^2}{4D\beta}\right]$$

$$\times\int_0^\beta d\tau\frac{1}{(\beta-\tau)^{3/2}}\exp\left[-\frac{x^2}{4D(\beta-\tau)}\right]\int_0^\tau d\eta\frac{1}{\eta^{1/2}(\tau-\eta)^{1/2}}\exp\left[-\frac{x_i^2}{4D\eta}\right]$$

$$\times\left[4D(\beta-\tau)+\frac{\tau\rho^2}{\beta}-\left[1+\frac{x_i^2}{2D\eta}\right]\left[\frac{4\tau\rho^2(\beta-\tau)}{\beta^2}+\frac{8D(\beta-\tau)^2}{\beta}+\frac{\tau^2\rho^2}{4D\beta^3}\right]\right]\;, \tag{5.37}$$

where $D=\hbar^2/m$. Note that the sign in front of $\tau\rho^2/\beta$ is misprinted in Eq. (15) of the paper by Hemmer and Mork.[15] One can readily recast our result in the form of (5.34). In order to compare our propagator with previous results we evaluate the above integrals. In the previous work this evaluation is not attempted. As far as we know this has not been done since. We illustrate this evaluation by outlining the calculation of the ρ^2 term in $a^{-2}G_2(\mathbf{r})$. The term in the large parentheses with coefficient ρ^2 can be written

$$\rho^2\left[1+\frac{4(\beta-\tau)^2}{\beta^2}-\frac{5(\beta-\tau)}{\beta}+\frac{2x_i^2(\beta-\tau)^2}{D\eta\beta^2}-\frac{2x_i^2(\beta-\tau)}{D\eta\beta}\right]\;, \tag{5.38}$$

where the variables τ,η have been arranged so that only the combinations $\beta-\tau$, $\tau-\eta$, and η appear. The reason for this will become apparent presently. The integral in question can thus be written

$$I_T=\frac{\rho^2 xx_i}{32a^2\beta^2(\pi D)^{5/2}}\exp\left[-\frac{\rho^2}{4D\beta}\right]\left[I_1+\frac{4}{\beta^2}I_2-\frac{5}{\beta}I_3+\frac{2x_i^2}{D\beta^2}I_4-\frac{2x_i^2}{D\beta}I_5\right]\;, \tag{5.39}$$

where $I_i, i=1,\ldots,5$ are all convolution integrals. We can thus use Laplace transforms to evaluate these integrals. We again use the Watson form of the Laplace transform and inversion formula. We shall need the following Laplace transform pairs:

$$J_m(z,\Delta)=\int_0^\infty d\beta\, e^{\beta z}\beta^{m/2}\exp\left[-\frac{\Delta^2}{4D\beta}\right]$$
$$=-\sqrt{\pi}\frac{i^{m+1}}{z^{(m+1)/4}}\frac{1}{2^{(m+1)/2}}\left[\frac{\Delta}{D^{1/2}}\right]^{(m+3)/2}\times h^{(1)}_{(m+1)/2}(z^{1/2}D^{-1/2}\Delta)\ , \quad (5.40)$$

$$J_m(z,0)=\int_0^\infty d\beta\, e^{\beta z}\beta^{m/2}=-\frac{i^m}{z^{(m/2)+1}}\Gamma\left[\frac{m}{2}+1\right]\ , \quad (5.41)$$

$$K_n=\int_0^\infty d\beta\, e^{\beta z}(4\beta)^{n/2}i^n\mathrm{erfc}\left[\frac{\Delta}{2D^{1/2}\beta^{1/2}}\right]=i^{n+2}\frac{\exp(iz^{1/2}D^{-1/2}\Delta)}{z^{(n/2)+1}}\ , \quad (5.42)$$

where $h_m^{(1)}$ are the spherical Hankel functions of the first kind[33] and $i^n\mathrm{erfc}z$ are the iterated error functions.[33] Note that (5.42) is quoted for the usual Laplace transform in the Laplace transform tables of Refs. 29 and 33. It is readily established by writing $e^{\beta z}=(d/d\beta)[(1/z)e^{\beta z}]$, integrating by parts, and then using the identity

$$i^n\mathrm{erfc}z=-\frac{z}{n}i^{n-1}\mathrm{erfc}z+\frac{1}{2n}i^{n-2}\mathrm{erfc}z,\quad n=1,2,3\ldots \quad (5.43)$$

(see Eq. (7.2.5, Ref. 33) to establish a recursion relation between K_n and K_{n-2}. K_{-1} is related to J_{-1} and K_0 can be related to J_{-3} via an integration by parts.

We illustrate the evaluation of the $I_i(\beta)$ with the case $i=2$:

$$I_2(\beta)=\int_0^\beta d\tau(\beta-\tau)^{1/2}\exp\left[-\frac{x^2}{4D(\beta-\tau)}\right]\times\int_0^\tau d\eta\frac{1}{\eta^{1/2}(\tau-\eta)^{1/2}}\exp\left[-\frac{x_i^2}{4D\eta}\right]. \quad (5.44)$$

By the convolution theorem

$$L\{I_2(\beta)\}=J_1(z,x)J_{-1}(z,0)J_{-1}(z,x_i)\ , \quad (5.45)$$

where $L\{\ \}$ denotes the Laplace transform operation. Using the explicit forms of the spherical Hankel functions[33] one obtains

$$L\{I_2(\beta)\}=\frac{\pi^{3/2}x}{2D^{1/2}}i^4\frac{\exp[iz^{1/2}D^{-1/2}(x+x_i)]}{z^2}+\frac{\pi^{3/2}}{2}i^5\frac{\exp[iz^{1/2}D^{-1/2}(x+x_i)]}{z^{5/2}}\ . \quad (5.46)$$

Using (5.42) one then obtains

$$I_2(\beta)=\frac{\pi^{3/2}x}{D^{1/2}}2\beta i^2\mathrm{erfc}\left[\frac{x+x_i}{2D^{1/2}\beta^{1/2}}\right]+4\pi^{3/2}\beta^{3/2}i^3\mathrm{erfc}\left[\frac{x+x_i}{2D^{1/2}\beta^{1/2}}\right]. \quad (5.47)$$

In a similar fashion one establishes that

$$I_1(\beta)=\frac{2\pi^{3/2}}{xD^{-1/2}}\mathrm{erfc}\left[\frac{x+x_i}{2D^{1/2}\beta^{1/2}}\right]\ , \quad (5.48)$$

$$I_3(\beta)=2\pi^{3/2}\beta^{1/2}i\ \mathrm{erfc}\left[\frac{x+x_i}{2D^{1/2}\beta^{1/2}}\right]\ , \quad (5.49)$$

$$I_4(\beta)=\frac{2\pi^{3/2}x}{x_i}\beta^{1/2}i\ \mathrm{erfc}\left[\frac{x+x_i}{2D^{1/2}\beta^{1/2}}\right]+\frac{4\pi^{3/2}D^{1/2}}{x_i}\beta i^2\mathrm{erfc}\left[\frac{x+x_i}{2D^{1/2}\beta^{1/2}}\right]\ , \quad (5.50)$$

$$I_5(\beta)=\frac{2\pi^{3/2}D^{1/2}}{x_i}\mathrm{erfc}\left[\frac{x+x_i}{2D^{1/2}\beta^{1/2}}\right]. \quad (5.51)$$

Using (5.43) and

$$\Gamma(\tfrac{1}{2},x^2)=\sqrt{\pi}\,\mathrm{erfc}x\ , \quad (5.52)$$

$$\Gamma(\alpha,x)=x^{\alpha-1}e^{-x}+(\alpha-1)\Gamma(\alpha-1,x) \quad (5.53)$$

repeatedly, one obtains, after a tedious calculation

$$I_T=\frac{1}{2^{3/2}\lambda^3}\left[\frac{\lambda}{a}\right]^2\exp\left[\frac{-\pi\rho^2}{2\lambda^2}\right]\left[\frac{\rho^2x_i}{\lambda^3}\left[\frac{\pi}{2}\right]^{1/2}\Gamma(\tfrac{1}{2},z)-\frac{\rho^2x_ix(x_i+5x)}{\lambda^5}\left[\frac{\pi}{2}\right]^{3/2}\Gamma(-\tfrac{1}{2},z)+\frac{4\rho^2x_ix(x+x_i)(x^2-x_ix+x_i^2)}{\lambda^7}\left[\frac{\pi}{2}\right]^{5/2}\Gamma(-\tfrac{3}{2},z)-\frac{4\pi\rho^2x_i^3x}{(x_i+x)^2\lambda^4}e^{-z}\right] \quad (5.54)$$

where $z=\pi(x+x_i)^2/2\lambda^2$. The evaluation of the other integrals in (5.36) and (5.37) proceed similarly. After casting our result, (5.26)–(5.33) into the form (5.34) we find, after a little algebra, that our result and the result of previous authors agree. The high-temperature series for the direct second virial coefficient

$$b_2=\frac{2^{3/2}}{2!\lambda^3}\int d\mathbf{r}\langle\mathbf{r}|e^{-\beta H}-e^{-\beta H_0}|\mathbf{r}\rangle$$
$$=-\frac{2\pi a^3}{3\lambda^6}\left[1+\frac{3}{2\sqrt{2}}\frac{\lambda}{a}+\frac{1}{\pi}\left[\frac{\lambda}{a}\right]^2+\frac{1}{16\sqrt{2}\pi}\left[\frac{\lambda}{a}\right]^3+\cdots\right] \tag{5.55}$$

is readily established from the expression for the propagator and is in agreement with the results of previous authors.[11,12,14–16]

VI. DISCUSSION

The underlying motivation of this work has been the evaluation of (5.55) via semiclassical means. Experience with Wigner-Kirkwood expansions indicated that the high-temperature series could be obtained via semiclassical methods. Our initial thoughts were that a semiclassical evaluation that included the reflected path would yield (5.55). This procedure, however, only yields the first two terms. If one tries to calculate the third term using the semiclassical series, then one encounters divergent integrals. The presence of such divergent integrals is due to the asymptotic nature of the semiclassical series. As a result the calculation of the third- and higher-order terms requires the full quantum-mechanical behavior, which we obtained in our case via a formal summation of the asymptotic series. The realization that (5.55) relies on more than just the semiclassical form of the propagator is, we feel, one of the main lessons of this work.

In Secs. IV and V we only evaluated the quantum corrections for one of the two semiclassical *Ansätze* that we presented in Sec. II. We have done this because, in reproducing the virial coefficient results we needed to calculate the quantum corrections to all orders. In the first hierarchy b_j only depends on b_{j-1} and this has allowed us to calculate to all orders. In the second hierarchy, however, R_j depends on all lower-order times. This makes it difficult to calculate to all orders. As such we did not attempt to work with the second *Ansatz*. In fact, it appears from our simple model of Sec. IV that the second *Ansatz* may be inappropriate for hard-core propagators, as it is not clear that the known answer for the propagator can be expressed in this form.

As we mentioned in the Introduction the reader may wonder why, since our interest is primarily in Boltzmann factors, we have considered the Schrödinger propagator at all. Why were not the Boltzmann factors directly calculated? The similarity between the two objects on a formal level, being related by a simple formal substitution ($t\rightarrow i\hbar\beta$), means that the more general point of view requires little extra effort. As the more general point of view is desirable, we take advantage of its ready availability. There are, however, problems, with the direct treatment of the Boltzmann factor. If one tries to develop a semiclassical *Ansatz* for the Bloch equation

$$\frac{\partial\Psi}{\partial\beta}+H\Psi=0\ , \tag{6.1}$$

say, of the form

$$\langle\mathbf{r}|e^{-\beta H}|\mathbf{r}_i\rangle=\frac{1}{(2\pi\hbar)^{d/2}}\exp\left[-\frac{1}{\hbar}S(\mathbf{r},\beta|\mathbf{r}_i)\right]\times\sum_{j=0}^{\infty}\hbar^j b_j(\mathbf{r},\beta|\mathbf{r}_i)\ , \tag{6.2}$$

then one does not recover the Hamilton-Jacobi equation as the first term in the hierarchy. This leads us to wonder to what sort of "classical limit" such an *Ansatz* corresponds. Because $\hbar$ appears in the $t\rightarrow -i\hbar\beta$ substitution, one might then be inclined to consider the following equation:

$$\hbar\frac{\partial\Psi}{\partial t}+H\Psi=0 \tag{6.3}$$

for $\langle\mathbf{r}|e^{-tH/\hbar}|\mathbf{r}_i\rangle$, substituting $t=\hbar\beta$ at the end of the calculation. A semiclassical *Ansatz* of the form (6.2) (with $\beta=t$ in the right-hand side) above then yields

$$\frac{1}{2m}(\nabla S)^2-V(\mathbf{x})+\frac{\partial S}{\partial t}=0\ , \tag{6.4}$$

i.e., the Hamilton-Jacobi equation with a potential whose sign is reversed. This reversal of the sign of the potential in going from the Schrödinger propagator to the Boltzmann factor also appears in the path-integral formulation and is not surprising. For the Wigner-Kirkwood expansion, where the potential is treated as a perturbation, this change of sign does not cause difficulty. Also, if the hard-core case is treated as a boundary-value problem, then the potential does not appear and so the sign problem is not relevant. If, however, one considers a strongly repulsive potential, e.g., (3.1), then there is a problem. This potential has well-behaved classical paths and our procedure for deriving the semiclassical series for the Schrödinger propagator is well defined. For the Boltzmann factor, though (6.4) dictates that one must consider the classical paths of the sign-reversed potential. The classical paths in such a potential have a dramatically different behavior, as they tend to collapse into the origin. This difficulty is more disconcerting when one recalls that the $n\rightarrow\infty$ limit of the power-law potential should recover the hard-core case. However, as we have stated, the hard-core case can plausibly be handled as a boundary-value problem. Because of these difficulties with the direct treatment of the Boltzmann factor, we have elected to take a naive view and work with the Schrödinger propagator, where collapse problems do not arise, recovering the Boltzmann factor via the naive $t\rightarrow -i\hbar\beta$ substitution. As we have recovered a number of previous results with this naive method we are confident that it is in some sense a valid procedure. However, it is clear that there are subtleties in the relationship between the Schrödinger propagator and the Boltzmann factor that are not understood and deserve further investigation. It is amusing to note that in our case we can handle the Schrödinger propagator, but difficulties arise with Boltzmann factors, whereas in the mathematical treatment of the path-integral method, the situation is the opposite.

Our treatment of the hard-core potential raises questions regarding the treatment of strongly repulsive potentials, in general. As we noted in Sec. III the Wigner-Kirkwood expansion is well behaved mathematically and yields finite virial coefficients for power-law potentials. This is also clearly the case for typical (interatomic or internuclear) potentials, in general. As a result the Wigner-Kirkwood expansions have been widely used to calculate quantum corrections.[2] However, the difficulties in the generalized Wigner-Kirkwood expansions, which we discussed in Sec. III, will also be present for typical potentials. This is because typical potentials have a strongly repulsive core, which cannot be treated in the perturbative manner that appears intrinsic to the Wigner-Kirkwood expansions. It appears that in such cases the Wigner-Kirkwood expansion only gives the asymptotic form of the propagator as $|\mathbf{r}|\to\infty$, as only the weakly attractive tail can be treated perturbatively (note that for the Boltzmann factor the contribution of any reflection is exponentially suppressed with respect to the direct path). This asymptotic behavior is insufficient to indicate the high-temperature properties. As is apparent from the evaluation of the hard-core virial coefficients, the major part of the integrand is the region $a<r<a+\lambda$, i.e., within λ of the turning point. Here the reflected and direct actions are of similar magnitude. The proper treatment of semiclassical propagators for strongly repulsive potentials is indicated by our treatment of the hard-core case. One needs to determine the classical paths and evaluate the corresponding classical action. For each path one needs to solve a hierarchy of partial differential equations for the quantum corrections. One then takes a linear superposition of each resulting semiclassical series. In this calculation there will be unknown functions, which can be determined via the imposition of boundary conditions on the propagator (for example, the vanishing of the propagator as $|\mathbf{r}|\to 0$). Propagation in the vicinity of turning points require a full quantum-mechanical treatment. The carrying out of this procedure is indeed difficult. However, for the purposes of calculating virial coefficients, our hard-core calculation indicates, as we outlined above, that these can be determined by knowing the behavior of the propagator near the turning points. The classical mechanics for a general strongly repulsive potential in the vicinity of the turning points may be amenable to calculation, as it was in the hard-core case. Note also that our considerations indicate that previous high-temperature expansions of b_2 for, say, the Lennard-Jones potential[2,10,11] are incomplete. Observing the structure of the high-temperature series of b_2 for the hard-core case, we note that the first term is the classical term and that the higher-order terms all come from reflections. These terms are corrections in powers of λ. Thus we expect reflection corrections for the Lennard-Jones case that are of powers of λ and thus are of similar order of magnitude to the terms that are derived from the Wigner-Kirkwood expansion.

Our semiclassical treatment, while an improvement on the Wigner-Kirkwood expansion, does have limitations, the most severe of which is that it relies on the presence of classical paths. For propagation into the shadow region in the hard-core problem (see Fig. 1) there are clearly no classical paths so that we cannot apply our formalism. This is not surprising, as propagation into the shadow region is a purely diffraction phenomenon and our *Ansatz* is of the form of a perturbation about the geometric (matter) optics limit. Evaluation of the antipodal matrix element (1.2) requires a means of treating propagation into the shadow region. There is some prospect of a modification of our treatment to handle such cases. The action in the hard-core case is essentially the path length squared. While there are no classical paths into the shadow region there are paths that skirt the hard core and are of minimum length and therefore of minimum action. Indeed, such paths (see Fig. 1), referred to as diffracting paths or enveloping rays, have been considered by previous authors.[13,27,28,34] From a path-integral point of view these paths will dominate the path integral in the semiclassical limit, despite the fact that they are not classical paths. In particular, Lieb's evaluation[13] of the exchange second virial coefficient via that path-integral method shows that in the high-temperature limit such minimum-length (though nonclassical) paths dominate the path integral. In actual fact there is some hope that propagation into the shadow region can be handled via our *Ansatz*, as the minimum action paths, while not being classical paths, still satisfy Hamilton's variational principle of mechanics so that the action constructed from them should nevertheless be solutions of the Hamilton-Jacobi equation. The issue of propagation into the shadow region is one which we hope to examine further.

ACKNOWLEDGMENT

One of us (C.P.) acknowledges the financial assistance of the Australian government.

APPENDIX

In this Appendix we describe the solution of the linear inhomogeneous partial differential equation

$$\frac{\partial F(\mathbf{r},t|\mathbf{r}_i)}{\partial t}+\frac{\mathbf{r}-\mathbf{r}_i}{t}\cdot\nabla F(\mathbf{r},t|\mathbf{r}_i)+\frac{d}{2t}F(\mathbf{r},t|\mathbf{r}_i)=G(\mathbf{r},t|\mathbf{r}_i)\ . \quad \text{(A1)}$$

The methods of solving such equations can be found in almost any standard textbook on partial differential equations.[35,36] Here we merely outline the solution of this particular case for the purpose of completeness.

One solves this equation via the method of characteristics. This method is motivated by the fact that the combination of partial derivatives in (A1) reduces to an ordinary derivative along curves in space time that are called characteristic curves. If a region of space time can be filled with such curves and if the function F is specified on a hypersurface in this region, which intersects each characteristic curve only once, then one can solve for F in this region. The characteristic curves are functions $\mathbf{r}_c(\sigma)$ and $t_c(\sigma)$, which satisfy

$$\frac{d\mathbf{r}_c}{d\sigma}=\frac{\mathbf{r}_c-\mathbf{r}_i}{t}, \quad \frac{dt_c}{d\sigma}=1 , \tag{A2}$$

the solutions of which are $t_c=\sigma$ and $\mathbf{r}_c=\mathbf{r}_i+\mathbf{v}\sigma$, where $\mathbf{v}$ is arbitrary constant vector (these are the classical paths corresponding to the action S_0).

Consider now the function

$$H(\mathbf{v},\sigma|\mathbf{r}_i)=F(\mathbf{r}_i+\mathbf{v}\sigma,\sigma|\mathbf{r}_i) , \tag{A3}$$

then

$$\frac{\partial H}{\partial\sigma}(\mathbf{v},\sigma|\mathbf{r}_i)=\frac{\partial F}{\partial t}(\mathbf{r}_i+\mathbf{v}\sigma,\sigma|\mathbf{r}_i)+\mathbf{v}\cdot\nabla F(\mathbf{r}_i+\mathbf{v}\sigma,\sigma|\mathbf{r}_i) . \tag{A4}$$

By letting $t=\sigma$ and $\mathbf{r}=\mathbf{r}_i+\mathbf{v}\sigma$ in (A1) and using (A4), one obtains

$$\frac{\partial H}{\partial\sigma}(\mathbf{v},\sigma|\mathbf{r}_i)+\frac{d}{2\sigma}H(\mathbf{v},\sigma|\mathbf{r}_i)=G(\mathbf{r}_i+\mathbf{v}\sigma,\sigma|\mathbf{r}_i) , \tag{A5}$$

which is readily integrated to give

$$H(\mathbf{v},\sigma|\mathbf{r}_i)=\int_0^\sigma\left[\frac{\tau}{\sigma}\right]^{d/2}G(\mathbf{r}_i+\mathbf{v}\tau,\tau|\mathbf{r}_i)d\tau+\frac{1}{\sigma^{d/2}}C(\mathbf{v}) , \tag{A6}$$

where C is an arbitrary function. Using (A3) one readily establishes (2.23). Equation (2.18) is simply the $d=0$ case of (2.22).

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