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Note on Miller's method to compute partition functions for the case of hard spheres

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sitions to the stable $X_2^+(\frac{1}{2}u^2P_{3/2})$ state.[12] The rate determining steps for the overall rate of conversion of $X^+(^2P_{1/2})$ into this ion are the rate coefficient for the Reaction (3) and the mean lifetime of $X_2^+(\frac{1}{2}u^2P_{1/2})$ against collisional breakup [reverse of Reaction (3)] as compared to the radiative lifetime of this complex. The rate coefficients for Reaction (3) and the reverse of Reaction (3) are naturally sensitive to the ratio of the mean translational ion–neutral energy to the binding energy of the complex ion in (3).

Applied to the present problem this means that in xenon the reaction rate for (3) is appreciable due to the high binding energy of the Xe_2^+ complex. In argon, which is supposed to have a lower binding energy for the complex in (3), this reaction is not appreciable at room temperature. If, however, the mean ion–neutral energy is lowered by a factor of 4, Reaction (3) proceeds with high probability. Krypton at room temperature takes an intermediate position: In neon the reaction rate for (3) is small even at 77 K because of the smallness of the binding energy of the $Ne_2^+(\frac{1}{2}u^2P_{1/2})$ complex.

From this model it is also conceivable that in the limit of small ratios of ion energy to binding energy the rate of conversion of both atomic ion species into molecular ions is about equal; This is because collisional breakup of the molecular ion $X_2^+(\frac{1}{2}u^2P_{1/2})$ is unlikely then and the rate determining factor for (1) as for (3) is the long range polarization attraction which is naturally the same for both atomic ion species.

Molecular ions produced via Reaction (3) and an optical transition must initially be in highly excited vibrational states. This vibrational excitation may however be easily removed in further collisions with the parent gas.[13]

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[1] R. S. Mulliken, J. Chem. Phys. **52**, 5170 (1970).

[2] W. F. Liu and D. C. Conway, J. Chem. Phys. **60**, 784 (1974).

[3] W. F. Liu and D. C. Conway, J. Chem. Phys. **62**, 3070 (1975).

[4] H. Helm, Chem. Phys. Lett. **36**, 97 (1975); J. Phys. B **9**, 2931 (1976).

[5] H. Helm and M. T. Elford, J. Phys. B **10**, 983 (1977); and 3rd Int. Symp. Plasmachem., Limoges (1977), Contributed Papers Vol. III.

[6] H. Helm, Phys. Rev. A **14**, 680 (1976).

[7] H. Helm and M. T. Elford, XIIIth Int. Conf. Phen. Ionized Gases, Berlin (1977), Contributed Papers, p. 63.

[8] The lifetime of the $X^+(^2P_{1/2})$ state against radiative decay into the $^2P_{3/2}$ state is 116 sec for neon decreasing to 48 msec for xenon [R. H. Garstang, J. Res. Natl. Bur. Std. Sect. A **68**, 61 (1964)].

[9] D. C. Lorents, R. E. Olson, and G. M. Conklin, Chem. Phys. Lett. **20**, 589 (1973).

[10] P M. Dehmer and J. L. Dehmer, J. Chem. Phys. **67**, 1774 (1977).

[11] J. S. Cohen and B. Schneider, J. Chem. Phys. **61**, 3230 (1974).

[12] Based on the results of Dehmer and Dehmer (Ref. 10) the photon energies would in xenon be around 1.1 eV ($\frac{1}{2}u^2P_{1/2} \rightarrow \frac{1}{2}g^2P_{3/2}$) and 0.3 eV ($\frac{1}{2}g^2P_{3/2} \rightarrow \frac{1}{2}u^2P_{3/2}$), respectively, for a transition around 4.5 Å nuclear separation.

[13] T. M. Miller, J. H. Ling, R. P. Saxon, and J. T. Moseley, Phys. Rev. A **13**, 2171 (1976).

Note on Miller's method to compute partition functions for the case of hard spheres[a)]

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A classical path approximation has been obtained by Miller[1] to compute the diagonal part of the density matrix. The idea of the method, as described in Ref. 1, is to use the exact integral expression for the density

$$\rho(\mathbf{r}) = \int d\mathbf{r}_2\, d\mathbf{r}_3 \cdots d\mathbf{r}_N\, \langle \mathbf{r} | e^{-\beta H/N} | \mathbf{r}_2 \rangle \cdots \langle \mathbf{r}_N | e^{-\beta H/N} | \mathbf{r} \rangle, \quad (1)$$

for $N = 2$; (note that this, by itself, is *not* an approximation) and evaluate the matrix element $\langle \mathbf{r} | e^{-\beta H/2} | \mathbf{r}_2 \rangle$ by the method of steepest descent. The resulting partition function is hence given by

$$Z \simeq \frac{1}{(2\pi)^n} \int d\mathbf{p} \int d\mathbf{r} \exp\left[-2 \int_0^{\beta/2} H(t)\, dt \right], \quad (2)$$

for n degrees of freedom, and using natural units $\hbar = 1$ and the particle's mass $m = 1$. Here the actionlike integral is to be integrated over a "classical trajectory" but with an upside down potential, which makes the

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Hamiltonian time dependent $H(t)$. The results obtained by Miller[1] for a smooth potential are indeed very good, yielding corrections, to all orders in $\hbar$, to the classical result. When compared to the Wigner–Kirkwood asymptotic expansion, discrepancies arise in order $\hbar^4$, in terms involving the fourth derivative of the potential.

We have carried out the calculation of the second virial coefficient for hard spheres of diameter σ within the classical path approximation.[2] The results that we obtain in this case are not as pleasing. We *do* find a correction to the classical result which is proportional to the thermal wavelength λ (and thus to $\hbar$), in agreement with the behavior of the leading term of the high temperature asymptotic expansion. As will be seen, however, the coefficient of λ/σ does not agree with the known result.[3]

For our case it is enough to compute the contribution I from the relative motion of two hard spheres with reduced mass $\mu = 1/2$

$$I = Z - Z^{(0)} , \tag{3}$$

where $n = 3$.

Let us now evaluate the integrals appearing in (2) to obtain Miller's approximation. Dividing the integration over $\mathbf{r}$ into two volumes, a sphere Ω_1 of radius σ and the remainder of space Ω_2, we obtain

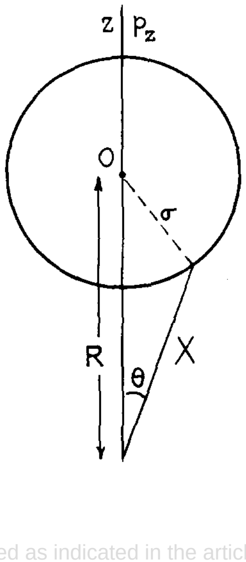
$$I = I_{c1} + \frac{1}{8\pi^3}\int d\mathbf{p} \times \int_{\Omega_2}\left\{\exp\left[-2\int_0^{\beta/2} H(t)\,dt\right] - \exp(-\beta p^2)\right\} d\mathbf{r} , \tag{4}$$

where the part from Ω_1 is the classical result

$$I_{c1} = -\frac{1}{2\pi^2}\int_0^\infty dp\, p^2 e^{-\beta p^2}\frac{4\pi}{3}\sigma^3 = -\frac{\sqrt{2}}{3}\pi\left(\frac{\sigma}{\lambda}\right)^3 , \tag{5}$$

and λ is the thermal wavelength $\lambda = \sqrt{2\pi\beta}$.

Outside the sphere, the only trajectories giving a finite contribution to I are those which reach the sphere Ω_1 within a time $\beta/2$. In this event the "action integral" diverges, while $Z^{(0)}$ does not vanish. Otherwise we are faced with a free particle problem, yielding no contribution to the virial coefficient. For a fixed momentum p, the relevant paths must intercept the sphere Ω_1 so they must start off from a distance $x \le p\beta$. Referring to where we have fixed the z and p_z axes, we can write the integral as



$$I^1 = -\frac{1}{8\pi^3}\int_0^\infty 2\pi p^2\,dp \int \sin\theta\, d\theta \int 4\pi r^2 e^{-\beta p^2} dr , \tag{6}$$

where, for a given x, only a cone of angles contributes, from $\theta = 0$ which corresponds to a head-on collision to $\theta = \Theta$ when the collision is a grazing one.

Associated with these angles would be two values of r: $r_1 = x + \sigma$ and $r_0 = \sqrt{x^2 + \sigma^2}$. Changing an integration variable to x, we find

$$I^1 = -\frac{1}{\pi}\int_0^\infty dp\, p^2 e^{-\beta p^2}\int_0^{p\beta} dx \int_{\sqrt{x^2+\sigma^2}}^{x+\sigma}\frac{r^2 - x^2 - \sigma^2}{2rx^2}\, r^2\, dr . \tag{8}$$

In this form the integral can be readily evaluated, with the end result

$$I^1 = -\tfrac{1}{2}(\sigma/\lambda)^2 . \tag{9}$$

The normalized quantum correction in this approximation is obtained as the quotient between Eqs. (9) and (5), i.e.,

$$B^*_{\mathrm{corr}} = 3/(2\sqrt{2}\pi)(\lambda/\sigma) . \tag{10}$$

If we now compare this result with the correction[3] to first order in λ

$$B^* = 1 + 3/(2\sqrt{2})(\lambda/\sigma) + O(\lambda^2) , \tag{11}$$

we notice that Eq. (10) is wrong by a factor of π.

We would like to conclude that in this particular case, the fact of using exact classical dynamics for each piece in the trajectory represents no real advantage, since the paths which do contribute are always straight lines with constant velocity. On the other hand, to include only *one* intermediate point in the closed path is not a good approximation for the case of hard spheres.

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[b] Consultant at the Instituto Mexicano del Petroleo, Mexico.

[1] W. H. Miller, J. Chem. Phys. 58, 1664 (1973).

[2] See S. M. Stratt and W. H. Miller, J. Chem. Phys. 67, 5894 (1977). This paper contains results very similar to ours. We are grateful to the authors for making a proof copy available to us at the time of review.

[3] M. E. Boyd, S. Y. Larsen and J. E. Kilpatrick, J. Chem. Phys. 45, 499 (1966); J. J. D'Arruda and R. N. Hill, Phys. Rev. A 1, 1791 (1970).