Beware of Singularities When Calculating Clathrate Hydrate Cell Potentials!

Ronald M. Pratt
Dept. of Mathematics, Fresno Pacific University, Fresno, CA 93702

Adam L. Ballard and E. D. Sloan, Jr.
Center for Hydrate Research, Chemical Engineering and Petroleum Refining Dept., Colorado School of Mines,
Golden CO 80401

A thermodynamic model for calculating the chemical potential of water in clathrate hydrates was presented by van der Waals and Platteeuw (1959). Parrish and Prausnitz (1972) introduced a computer algorithm using this model to predict the formation pressures of clathrate hydrates. Additional details of the model and the algorithm are discussed by Sloan (1998). Coding the algorithm, however, poses a problem: the calculations diverge if care is not taken. Although we do not imply that most hydrate researchers are incorrectly calculating Langmuir constants, there is certainly an inconsistency in the literature, and anyone getting started in hydrate formation modeling is sure to encounter these problems. We will discuss where the problems occur and why they have gone unnoticed for over forty years.

The difficulty arises in the numerical integration to calculate the Langmuir constant

$$C_{im} = \frac{4\pi}{k_B T} \int_0^{R_m - a_i} \exp\left[-\frac{\omega_{im}(r)}{k_B T} \right] r^2 dr \qquad (1)$$

where k_B is Boltzmann's constant, T is the temperature, R_m is the hydrate cavity radius, a_i is the hard sphere core diameter of guest molecule i, and C_{im} is the Langmuir constant of guest molecule i in hydrate cavity m. Note that, by setting the upper limit of the integral in Eq. 1 to $R_m - a_i$, it is assumed that interactions between the guest molecule and the hydrate cavity are confined to the cavity. That is, there are no interactions beyond $r = R_m - a_i$. The function $\omega_{im}(r)$ is the overall cell potential derived by McKoy and Sinanoglu (1963)

$$\omega_{im}(r) = 2\epsilon_i z_m \left[\frac{\sigma_i^{12}}{R_m^{11} r} \left(\delta_{im}^{10} + \frac{a_i}{R_m} \delta_{im}^{11} \right) - \frac{\sigma_i^6}{R_m^5 r} \left(\delta_{im}^4 + \frac{a_i}{R_m} \delta_{im}^5 \right) \right] \qquad (2)$$

where

$$\delta_{im}^N = \frac{1}{N} \left[\left(1 - \frac{r}{R_m} - \frac{a_i}{R_m} \right)^{-N} - \left(1 + \frac{r}{R_m} - \frac{a_i}{R_m} \right)^{-N} \right] \qquad (3)$$

and z_m is the coordination number. The Kihara potential parameters a_i, σ_i, and ϵ_i serve as adjustable parameters for the model. The problems now seem obvious. They lie in the division by r term in Eq. 2 and the first parenthetical term in Eq. 3, that is when $r = 0$ and $r = R_m - a_i$. Since the integral in the Langmuir constant expression, Eq. 1, contains both of these values at its limits, the cell potential will always contain singularities.

Note that the upper limit for the integral in Eq. 1 is often presented in the literature as R_m rather than $R_m - a_i$ (Sloan, 1998). For the Kihara potential $r = R_m - a_i$ physically corresponds to the guest molecule's spherical core radius touching the edge of the cage. Therefore, it does not physically make sense to evaluate Eq. 1 for values of $r > R_m - a_i$.

It should also be noted that, although the Kihara parameters are treated as adjustable parameters and therefore empirically determined, the spherical core radius a_i of any guest molecule will always be bounded by the expression $0 < a_i < R_m$. Otherwise, the guest molecule will not fit into the hydrate cavity. Because of this, the second parenthetical term in Eq. 3 will never have division by zero. We will show that upon closer inspection, however, that the singularities at $r = 0$ and $r = R_m - a_i$ are very well defined. If the limit of Eq. 1 is taken as r approaches zero (using L'Hôpital's rule), it reduces to

$$\lim_{r \to 0} \omega_{im}(r)$$
$$= 2\epsilon_i z_m \left[\frac{\sigma_i^{12}}{R_m^{11}} \left(\delta_{im}'^{10} + \frac{a_i}{R_m} \delta_{im}'^{11} \right) - \frac{\sigma_i^6}{R_m^5} \left(\delta_{im}'^4 + \frac{a_i}{R_m} \delta_{im}'^5 \right) \right] \qquad (4)$$

Correspondence concerning this article should be addressed to E. D. Sloan, Jr.

where

$$\delta^N = \frac{2}{R_m}\left(1 - \frac{a_i}{R_m}\right)^{-(N+1)}. \tag{5}$$

Evaluation of Eq. 4 leads to a finite value for $\omega_{im}(r)$ at $r = 0$, indicating that the singularity is removable. In other words, there is no singularity if care is taken in evaluating the cell potential. Similar reasoning can be used to find that

$$\lim_{r \to R_m - a_i} \omega_{im}(r) = +\infty. \tag{6}$$

As discussed above, this means that the guest molecule's spherical core radius is touching the edge of the cage, leading to infinite repulsion.

Using the above results at $r = 0$, the exponential term in the Langmuir constant expression will be a finite number and the integrand will become zero (due to the r^2 term). At $r = R_m - a_i$, the potential, $\omega_{im}(r)$, will tend to positive infinity reducing the exponential term to zero, again making the integrand zero. The integrand in Eq. 1 will therefore contain no singularities.

Although the Langmuir constant expression is theoretically stable, implementation of this calculation on a computer can be unstable due to the behavior of the integrand at its limits. If the user is not cautious when evaluating the potential function at $r = R_m - a_i$ and $r = 0$, the calculation will produce an overflow error. A simple fix to the problem would be to evaluate the integral from 0 to $R_m - a_i - \xi$, where ξ is a small number (say 0.0001 Å). The evaluation at $r = 0$ can be performed using Eqs. 4 and 5. We therefore modify Eq. 1 to read

$$C_{im} = \frac{4\pi}{k_B T}\int_0^{R_m - a_i - \xi} \exp\left[-\frac{\omega_{im}(r)}{k_B T}\right] r^2 dr \tag{7}$$

where the value of the integrand at $r = 0$ is zero. This minor modification eliminated all occurrences of divergence in the calculations. Though the problems we encountered arose in modeling Structure H formation, it should be pointed out that the modifications discussed above should be made for all cavity evaluations for all clathrate structures.

These equations have been used in hydrate modeling for over forty years, and the singularities have been always there. However, depending on which numerical integration method is used to evaluate the Langmuir constant expression, the singularities may never be encountered. The Adaptive Simpson's Algorithm for numerical integration is a very efficient method for the type of integral in Eq. 1 and is one of the most common methods used. Using this approach will never require that the integrand be evaluated at the upper limit of $R_m - a_i$, therefore avoiding the singularity.

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Manuscript received Feb. 15, 2000, and revision received Feb. 2, 2001.