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# The band gap in silicon nanocrystallites

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## Abstract

The gap in semiconductor nanocrystallites has been extensively studied both theoretically and experimentally over the last two decades. We have compared a recent ‘state-of-the-art’ theoretical calculation with a recent ‘state-of-the-art’ experimental observation of the gap in Si nanocrystallite. We find that the two are in substantial disagreement, with the disagreement being more pronounced at smaller sizes. Theoretical calculations appear to overestimate the gap. To reconcile the two we present two scenarios. (i) Recognizing that the experimental observations are for a distribution of crystallite sizes, we proffer a phenomenological model to reconcile the theory with the experiment. We suggest that similar considerations must dictate comparisons between the theory and experiment *vis-à-vis* other properties such as radiative rate, decay constant, and absorption coefficient. (ii) Either surface passivation or surface orientation may also resolve the conflict between the theory and the experiment. We have carried out tight-binding calculations on silicon clusters to study the role of surface passivation and surface orientation.

## 1. Introduction

Semiconductor nanocrystallites, more popularly known as quantum dots (QDs), have been extensively studied over the past decade and a half. The system is interesting from the point of view of basic physics, with the carriers being confined to an essentially ‘zero-dimensional’ structure. The efficient luminescence observed in some of these crystallites makes them promising candidates for use in opto-electronic devices [1]. Further, the inexorable drive towards device miniaturization makes them technologically significant.

The earliest theoretical works in this field were reported in the early 1980s [2, 3]. For over a decade after, most of the theoretical works reported were based on effective mass theory (EMT) and tight-binding (TB) semi-empirical approaches. These works predicted the

experimentally observed trends for quantum confinement (QC), i.e. the inverse dependence of the enhanced band gap on the nanocrystallite size [4]. These calculations were, however, performed for a single nanocrystallite, whereas experiments are performed on an ensemble of QDs of varying sizes. We pointed out earlier that the existence of an ensemble of QDs of varying sizes must be taken into account in any theoretical formulation [5–7]. Though improved theoretical calculations were pursued later, this aspect has largely been ignored.

In a recent work Ogut *et al* [8] reported ‘state-of-the-art’ theoretical calculations based on first principles. This work is claimed to be in excellent agreement with an early experimental work [9] and is claimed to be superior to semi-empirical calculations. We compared their calculations to later ‘state-of-the-art’ experimental results of van Buuren *et al* [10]. We found that there was a large disagreement between the two. This comparison is presented in section 2. In section 3, we proffer a phenomenological scheme for this underestimation of the band gap and suggest a possible reconciliation between the theory and experiment. In section 4, we present a calculation for silicon nanocrystallites based on a TB scheme. In this section we analyse two more possibilities, namely surface passivation and surface orientation, for resolving such discrepancies between theory and experiment. Surface orientations have generally not been considered in theoretical calculations. We find that the results of our calculations for partially hydrogen-passivated bond-centred (BC) clusters are in good agreement with the experimental work. These results in no way provide a unique resolution of the disagreement between the theory and the experiment. The aim here is to analyse some of the possible mechanisms and highlight the importance of phenomenological studies, ignored in earlier debates on these papers [8]. Conclusions are presented in section 5.

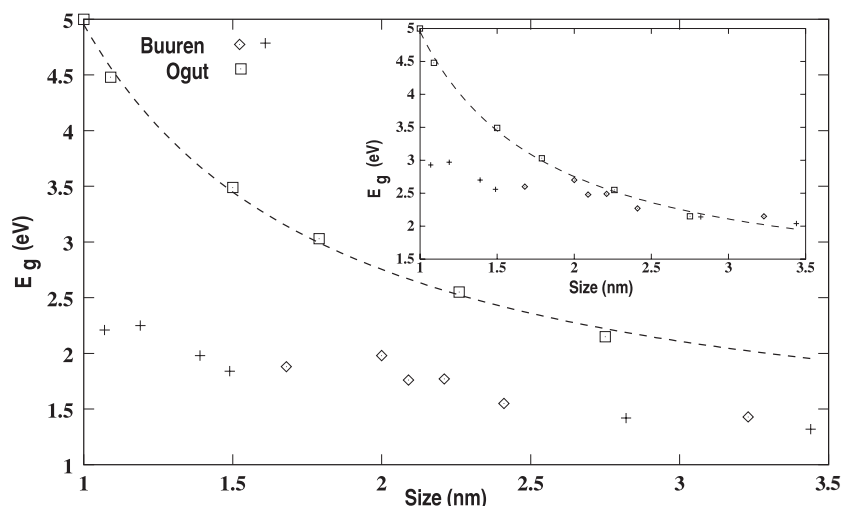
## 2. Comparison: theory versus experiment

In a letter, Ogut *et al* [8] employed a carefully argued *ab initio* methodology to obtain the size-dependent optical gap of Si QDs with sizes ranging from 1 to 3 nm. These authors chose to compare their calculations with the experimental observations of Furukawa and Miyasato [9]. A little later, van Buuren *et al* [10] reported state-of-the-art measurements of the band edges of Si QDs with average diameters ranging from 1 to 5 nm. By adding the measured conduction band (CB) and valence band (VB) shifts to the band gap of bulk Si they obtained the band gap of the Si QDs.

Recent PL and extended x-ray absorption data for oxygen-terminated silicon nanocrystallites of size <4 nm, were found to match these observations [11]. These band gaps are smaller than most reported theoretical calculations. This fact was noted by van Buuren *et al* who chose to compare their observations with older calculations by Wang and Zunger [12]. We also note that several first-principles and local density approximation (LDA) calculations on nanocrystalline forms of Si have been reported in the past [13]. It appears that theoretical calculations overestimate the gap.

A comparison of the ‘state-of-the-art’ theoretical calculations [8] with the ‘state-of-the-art’ experimental observations [10] reveals that the two are in substantial disagreement with each other. This comparison is presented in figure 1. In fact the Ogut *et al* calculation does worse than Wang and Zunger’s (not shown in figure 1) and other semi-empirical theoretical calculations. Perhaps the only commonality between the theory and experiment depicted in the figure may be stated in terms of a bland QC dictum: ‘the band gap increases as the size decreases’.

The disagreement between theory and experiment is enhanced at smaller dot sizes. When we impose a constant upward shift of 0.72 eV on the data of van Buuren *et al* such that they match with the theoretical calculation at 3.5 nm, the increasing divergence at smaller



**Figure 1.** The figure compares the ‘state-of-the-art’ experimental band gap obtained by van Buuren *et al* [10] with the ‘state-of-the-art’ theoretical one obtained by Ogut *et al* [8]. The two are in considerable disagreement. In the inset we have shifted the data from [8] up by 0.72 eV to ensure an agreement with [6] at 3.5 nm size. The discrepancy between the theory and the experiment appears pronounced at smaller sizes. The dashed curve is our fit to the calculations of [6] ( $E_g(d) = 1.1 + c/d^{1.22}$ ). The ‘+’ symbols show data arrived at by using a relationship between CB and VB edges by van Buuren *et al* (see [10]).

sizes is clearly manifested. This is depicted in the inset of figure 1. On the other hand, we may translate the experimental data horizontally by 1.75 nm and force an agreement with the (extrapolated) theoretical calculations. This would imply that the QD sizes have been seriously underestimated by van Buuren *et al*. While the latter does not exclude the possibility of some underestimation, a 1.75 nm error is unlikely.

*Ab initio* calculations are computationally demanding at large QD sizes. As we have pointed out, the disagreement between theory and experiment is pronounced at smaller dot sizes. It should be possible to re-examine or repeat the *ab initio* calculation in this computationally feasible intermediate regime.

### 3. Phenomenology

The observation of visible photoluminescence (PL) in a variety of semiconductor nanocrystallites has fuelled a large body of research work in the past decade [5, 8, 9, 14–16]. PL has acquired the role of the central characterizing tool in this field. The PL spectra from such systems are broad, and often asymmetric about the peak energy. The growth of the QDs is a stochastic process. In an earlier work we argued that one needs to consider the distribution of crystallite sizes to compare with the experimental spectral lineshape [5, 6]. A Gaussian size distribution was used in those works. For semiconductor nanostructures, the log-normal size distribution has considerable experimental [10, 17, 18] and theoretical [7, 15, 16] support. Specifically, Yorikawa and Muramatsu [15] presented an explanation of PL spectra based on the log-normal distribution of porous silicon QD size. The experimental work reported by van Buuren *et al* also shows a log-normal distribution.

We consider the log-normal size distribution,  $P(d)$ , of diameter  $d$  centred around a mean diameter  $d_0$ :

$$P(d) = \frac{1}{\sqrt{2\pi}\sigma d} \exp\left[-\frac{(\ln d - \mu)^2}{2\sigma^2}\right] \quad (1)$$

$$d_m = \exp(\mu - \sigma^2) \quad (2)$$

$$d_0 = \exp\left(\frac{\sigma^2}{2} + \mu\right) \quad (3)$$

where  $d_m$  is the dot size for which the maximum occurs in the log-normal distribution and  $\{\mu, \sigma\}$  are some characteristic constants.

The number of electrons in a dot of diameter  $d$  participating in a PL process is proportional to  $d^3$ . Thus, for an ensemble of QDs, the probability distribution of electrons participating in the PL process is

$$P_e(d) = \frac{1}{\sqrt{2\pi}\sigma d} b d^3 \exp\left[-\frac{(\ln d - \mu)^2}{2\sigma^2}\right] \quad (4)$$

where  $b$  is a suitable normalization constant.

In general, the optical band gap is attributed to the energy upshift of the electron and yields

$$E = E_\infty + \frac{C}{d^n} \quad (5)$$

where  $E$  is the enhanced gap,  $E_\infty$  is the bulk silicon gap (1.12 eV),  $C$  is an appropriately dimensioned (energy  $\times$  (length) <sup>$n$</sup> ) constant and  $n$  is the exponent [5, 6] with  $n \in [1, 2]$ .

Hence the energy upshift,  $\Delta E$ , due to confinement in QDs is

$$\Delta E = \frac{C}{d^n} \quad (6)$$

$$\Delta E_0 = \frac{C}{d_0^n} \quad (7)$$

where  $\Delta E_0$  is a mean upshift, which is related to the mean diameter  $d_0$  of the QDs.

Now, convoluting the upshift (equation (6)) with the log-normal size distribution (equation (4)),

$$P(\Delta E) = \int_0^\infty \delta\left(\Delta E - \frac{C}{d^n}\right) \frac{d^2}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(\ln d - \mu)^2}{2\sigma^2}\right] d(d). \quad (8)$$

The above integral can be easily solved using the properties of the Dirac delta function, which yields

$$P(\Delta E) = \frac{b}{\sqrt{2\pi}\sigma n C} \left(\frac{C}{\Delta E}\right)^{(3+n)/n} \exp\left[-\frac{\{(1/n)\log(C/\Delta E) - \mu\}^2}{2\sigma^2}\right]. \quad (9)$$

For the PL peak, we equate the derivative of equation (9) to zero. The shift in the PL peak position,  $\Delta E_p$ , is given by

$$\Delta E_p = C \exp[-\{(3+n)\sigma^2 + \mu\}n] \quad (10)$$

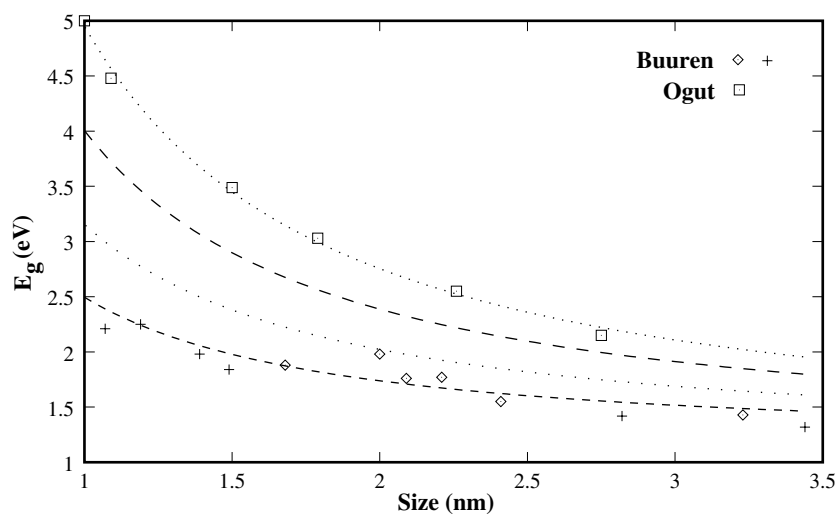
$$= \frac{C}{d_0^n} \left(\frac{d_m}{d_0}\right)^{n[2n+5]/3}. \quad (11)$$

We employ equation (11) in (5) to get

$$E = E_\infty + \Delta E_p \quad (12)$$

$$= E_\infty + \frac{C}{d_0^n} \left(\frac{d_m}{d_0}\right)^{n[2n+5]/3}. \quad (13)$$

Equation (13) represents the final form for estimating a more realistic size dependence of the optical gap. The exponent  $n = 1.22$  and  $C = 3.9$  in appropriate units, for the results of



**Figure 2.** The figure depicts the theoretical data of [8] and the experimental data of [10]. It also shows the band gap of crystallites if a log-normal size distribution is incorporated in the Ogut *et al* calculation. Of the four lines depicted in the figure, the lowest one (dashed curve) and the next two (dotted and dashed curves) correspond to log-normal distributions with  $d_m/d_0 = 0.7, 0.8,$  and  $0.9$  respectively. The topmost dotted curve is the fit to the data of [6] as mentioned in the caption to figure 1 and the text. We notice that the downshift of the band gap is larger for smaller crystallite sizes. We also notice that  $d_m/d_0 = 0.7$  shows excellent agreement with the experimental results of van Buuren *et al* [10].

Ogut *et al* shown in figure 1. Kanemitsu *et al* [17] obtained the size distribution of oxidized Si nanocrystallites produced by laser breakdown of silane gas. The optimum log-normal fit to these experimental data yields  $d_m/d_0 \in [0.7, 0.95]$ . We have used three values 0.7, 0.8, and 0.9 of the ratio  $d_m/d_0$  in equation (13) and depicted them alongside the data from Ogut *et al* and van Buuren *et al* in figure 2. We see that our calculation with the value 0.7 brings the Ogut *et al* result into complete agreement with the van Buuren *et al* result. Further, our phenomenological model produces more pronounced downshifts at smaller sizes. This is once again in agreement with the experimental trend. The asymmetric distribution of the dot size with stretched tailing towards larger QDs is responsible for the lower  $d_m/d_0$  ratio, though the skewness may not be as pronounced as  $d_m/d_0 = 0.7$ . Thus, for a more asymmetric log-normal distribution one obtains a more prominent downshift at smaller sizes.

#### 4. Passivation and surface orientation effects

As mentioned earlier, there may be no unique resolution to the disagreement between theory and experiment. We explore in this section the role of surface passivation and surface orientation in modifying the band gap. These effects are studied by taking recourse to detailed TB calculations. We employ non-orthogonal TB calculations keeping track of matrix elements up to six neighbours. This is in the spirit of quantum chemical calculations in which, unlike in TB work in condensed matter, the interaction between atoms and neighbours is maintained down to negligibly small values. Our methodology is similar to those of Proot *et al* [19] and Delerue *et al* [20], who however consider matrix elements up to three neighbours ( $Z = 3$ ). We have employed four orbitals per site. Our work is also similar in spirit to the work of Menon and Subbaswamy [21]. Our empirical parameters are chosen to match the bulk band structure, and

the Si–Si and Si–H vibrational frequencies. We remind the reader that there exists an earlier history of cluster calculations in which a similar TB methodology was employed [22, 23].

Since our crystallites are of small sizes they have a large surface-to-volume ratio. Hence we expect that surface orientation to play an important role in determining the electronic structure and consequent opto-electronic properties. We have carried out electronic structure calculations on cluster sizes as large as 4 nm. The surface orientation is varied by suitably selecting the central site. We consider four possible cluster orientations with the central site being:

- (i) bond-centred (BC),
- (ii) hexagon-centred (HC),
- (iii) substitutional-centred (SC),
- (iv) tetrahedron-centred (TC).

For a QD, the surface-to-volume ratio  $S/V \sim 1/d$ . The number of atoms in the cluster  $N \sim d^3$ . Thus the number of dangling bonds  $N_d \sim d^2$ . For the four cluster types that we have considered in this work, we find that

$$N_d = ad^b. \quad (14)$$

The exponent  $b = 2.05$  for the BC cluster. For the other cluster types, too,  $b \approx 2$ . Thus our clusters obey the expected scaling law. The  $N_d$  surface dangling bonds are usually passivated by hydrogen atoms. In our cluster we find that the content of monohydride species dominates over the dihydride and trihydride species. We shall report calculations for both the fully passivated and the partially passivated clusters.

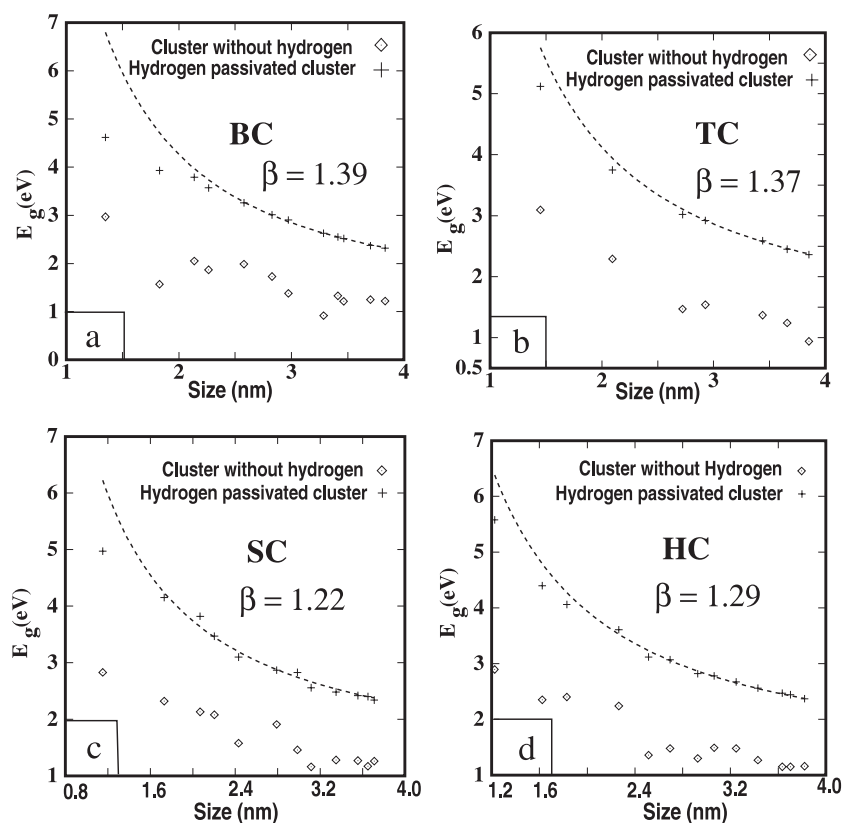
In figure 3 we plot band-gap variation with size for all the four geometries mentioned above. We find that for the passivated clusters

$$E_g(d) = E_{g0} + \frac{\alpha}{d^\beta}. \quad (15)$$

The exponent  $\beta = 1.39$  and  $\alpha = 188.37$  in appropriate units ( $\text{eV nm}^{1.39}$ ) for the BC cluster, as shown in figure 3(a). In the above equation,  $E_{g0}$  is the band gap of bulk silicon (1.12 eV). It is clear from the figure that the band gap asymptotically approaches the bulk value as the cluster size is increased. We note that the fully passivated clusters have larger band gaps. Because the dangling bonds introduce extra states in the gap, this leads to lower gaps for unpassivated clusters. The exponents  $\beta$  for the passivated TC (figure 3(b)), SC (figure 3(c)), and HC clusters (figure 3(d)) are 1.37, 1.22, and 1.29 respectively.

Examination of the above figures reveals that a partially passivated silicon cluster is in agreement with the experimental finding of van Buuren *et al*. Once again we hasten to add that this is by no means a unique explanation. We also point out that the exponent values are in approximate agreement with the TB calculations of Delerue *et al* [20] who find the exponent 1.39 for the SC cluster.

There exists also the issue of surface orientation. The four types of cluster on which we have reported calculations in figure 3 do yield somewhat different gaps and a dependence on size. We find that the partially passivated BC cluster which consists mainly of monohydrides would match the data of van Buuren *et al*. This is depicted in figure 4. We also note that the partially passivated BC cluster with an oxide coverage also yields reasonable results. The role of oxygen passivation has been investigated by Wolkin *et al* [24] in the context of porous silicon QDs. We are not able to account for the observation of Wolkin *et al* that there is no red-shift when the sample is placed in pure hydrogen.



**Figure 3.** Energy dependences of (a) the BC, (b) the TC, (c) the SC, and (d) the HC cluster on the cluster size ( $d = 2r$ ). The details are described in section 4.

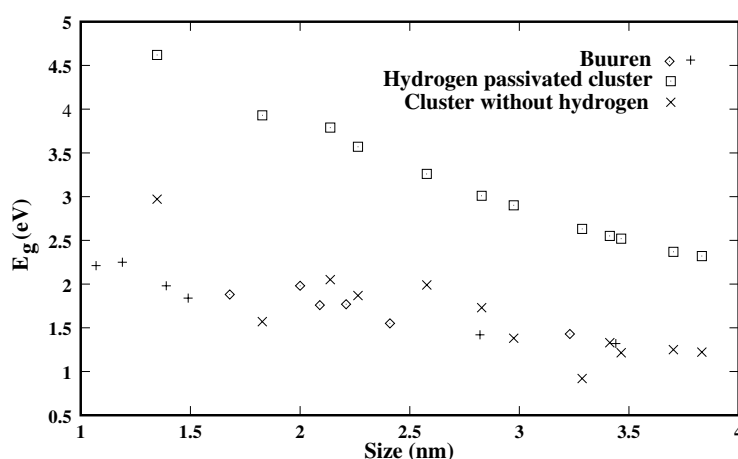
## 5. Conclusions

We find that a recent ‘state-of-the-art’ theoretical calculation [8] for the optical gap is in substantial disagreement with a closely following ‘state-of-the-art’ experimental work [10]. The comparison is even worse for smaller crystallite sizes. The experimental work reported a log-normal size distribution for nanocrystallite samples, whereas the theoretical work was performed on a single crystallite. This theoretical calculation showed a very good agreement with decade-old experimental work, whereas other semi-empirical works were shown to be in poor agreement. In contrast, we find that the semi-empirical works were in better agreement with the van Buuren *et al* experimental work.

*Ab initio* calculations are computationally demanding at large QD sizes. As we have pointed out, the disagreement between theory and experiment is pronounced at smaller dot sizes. It should be possible to re-examine or repeat the *ab initio* calculation in this computationally feasible intermediate regime.

We have used the methodology discussed in earlier works [5–7] with a log-normal distribution. We have shown that the Ogut *et al* results can be in better agreement with experimental work if the size distribution is explicitly taken into account. In our formulation the downshift of the optical gap is larger for smaller crystallite sizes, making this exercise even more relevant to the present case.





**Figure 4.** The band gap of silicon nanocrystallites as a function of cluster size. The diamonds and the plus signs represent the data from van Buuren *et al*. The crosses and the square boxes are the results of our TB calculations for the partially hydrogen-passivated and fully passivated BC silicon crystallites. We can see that there is a very good agreement between the experimental data of van Buuren *et al* [10] and our calculation with partially passivated clusters.

We caution however that the disagreement between the theory and the experiment may not be solely related to a distribution of crystallite sizes. Other factors could be crucial. These are:

- (i) partial passivation,
- (ii) passivation with species other than hydrogen,
- (iii) surface reconstruction,
- (iv) surface orientation,
- (v) flattening of the dot, and
- (vi) size underestimation by the microscopic techniques.

Some of these factors have been mentioned by van Buuren *et al* [10].

We have analysed two of the above-mentioned possibilities, namely surface passivation and surface orientation, in section 4. In that section we presented a calculation for silicon nanocrystallites based on the TB scheme. Surface orientations have generally not been considered in theoretical calculations. The band gap is found to be strongly dependent on the cluster geometry and surface passivation. We find that the results of our calculations for partially hydrogen-passivated BC clusters are in good agreement with the experimental work.

There has been a growing realization that the existence of an ensemble of QDs of varying sizes must be taken into account in order to explain experimental observations [5–7, 14–16, 25, 26]. Tentative attempts have been made to understand the radiative rate, decay constant, absorption data, etc, based on these considerations. Perhaps any theoretical calculation on a single nanocrystallite should be supplemented with effective size averaging before a comparison with experiment is made.

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