Comment on a proposed method for finding barrier height distributions

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(Received 6 December 1994; accepted 11 April 1995)

Straub and Thirumalai[1] and Straub *et al.*,[2] have proposed a method for finding the distribution $g(E)$ of the heights E of potential energy barriers in many-body systems. Keyes[3] and Straub and Choi,[4] gave further discussion and elaboration. The method uses an integral equation:

$$f_u(T)=\int_0^\infty dE\ \bar{f}_u(T,E)g(E) \tag{1}$$

to relate the barrier height distribution $g(E)$ to the fraction of time $f_u(T)$ that a system at temperature T will be found in the "unstable" part of configuration space. The integral equation contains a kernel $\bar{f}_u(T,E)$; a simple and intuitively plausible guess for the kernel was proposed in Refs. 1 and 2:

$$\bar{f}_u(T,E)=\frac{e^{-2\xi^2}\int_0^\xi dx\ e^{x^2}}{\int_0^\xi dx\ e^{-x^2}+e^{-2\xi^2}\int_0^\xi dx\ e^{x^2}}, \tag{2}$$

where $\xi=(E/2kT)^{1/2}$. Given the unstable fraction $f_u(T)$ (found, e.g., by computer simulation), one solves the integral equation for $g(E)$. The method was applied to a model polypeptide in Refs. 1 and 2, and to a model liquid in Ref. 3. It led to surprisingly similar barrier height distributions in these two quite dissimilar systems.

Unforunately there seems to be no way of directly checking the reliability of the proposed method in the many-body systems to which it is being applied. This comment presents a highly simplified one-dimensional potential energy function for which the method actually can be tested. In this test, the method does not work.

As illustrated in Fig. 1, a one-dimensional potential $U(x)$ is broken up into cells of alternating minima and maxima. In a "min" cell, centered on $x=4j$, the potential is harmonic upwards,

$$U_{\min}(x)=a_j^2[-1+(x-4j)^2],\quad 4j-1<x<4j+1. \tag{3}$$

The minimum value of the potential in this cell is $-a_j^2$. Note that the potential vanishes at its endpoints in the cell. In a "max" cell, centered on $x=4j+2$, the potential is harmonic downwards,

$$U_{\max}(x)=b_j^2[1-(x-4j-2)^2],\quad 4j+1<x<4j+3. \tag{4}$$

The maximum value of the potential in this cell is $+b_j^2$. Again the potential vanishes at its endpoints. Overall, the potential is continuous in x, but its first derivative is discontinuous at $x=4j+1$ and $4j+3$.

The coefficients a_j and b_j determine the curvatures, or frequencies, of the potential. In the present example, a and b are chosen independently from the same uniform distribution $\rho(a)$ or $\rho(b)$,

$$\rho(a)=1,\quad 0<a<1,$$
$$=0,\quad 1<a. \tag{5}$$

To get from one potential minimum to another, one must go over a barrier. Because this is a one-dimensional potential, any individual barrier height E is either $a_j^2+b_j^2$ or $b_j^2+a_{j+1}^2$. The distribution of barrier heights $g(E)$ can be found by averaging the delta function $\delta(E-a^2-b^2)$ over a and b,

$$g(E)=\int_0^\infty da\int_0^\infty db\ \rho(a)\rho(b)\delta(E-a^2-b^2). \tag{6}$$

In the present example, using Eq. (5), the barrier height distribution is

$$g(E)=\pi/4,\quad 0<E<1,$$
$$=\pi/4-\arctan(\sqrt{(E-1)}),\quad 1<E<2, \tag{7}$$
$$=0,\quad 2<E.$$

Now we find $f_u(T)$, the fraction of occupancy of the unstable configurations, or those configurations for which the curvature of the potential is negative. This fraction is the total partition function of the unstable region divided by the total partition function of both stable and unstable regions,

$$f_u(T)=\frac{Q_u(T)}{Q_s(T)+Q_u(T)}. \tag{8}$$

If there are N (min,max) pairs, then

$$Q_u(T)=\sum_j\ \int_{-1}^1 dx\ \exp[-\beta b_j^2(1-x^2)], \tag{9}$$

$$Q_s(T)=\sum_j\ \int_{-1}^1 dx\ \exp[-\beta a_j^2(-1+x^2)]. \tag{10}$$

Each individual term in these sums is determined by a specific a or b that is chosen randomly from the distribution ρ,

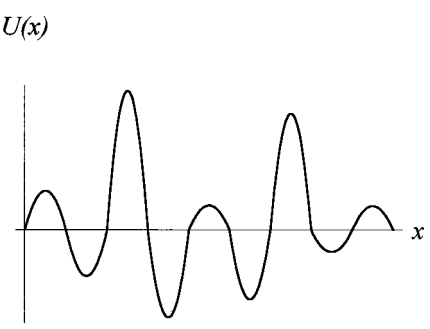

FIG. 1. A realization of a random one-dimensional potential.

and so the total Q_u and Q_s are sums of a very large number of independent random variables. The mean and the variance of any individual term are both finite and independent of N. Then, according to the Law of large numbers, the sum for any specific sequence of a's and b's is very close to its average. Of course there are fluctuations about the average, but they have a negligible order of magnitude when N is very large. Consequently, for any particular realization of the one-dimensional potential, we can estimate the stable and unstable partition functions by

$$Q_u(T)=N\int_0^\infty db\ \rho(b)\int_{-1}^{1}dx\ \exp[-\beta b^2(1-x^2)] + O(N^{1/2}), \tag{11}$$

$$Q_s(T)=N\int_0^\infty da\ \rho(a)\int_{-1}^{1}dx\ \exp[-\beta a^2(-1+x^2)] + O(N^{1/2}). \tag{12}$$

By changing variables, the integrals can be related to error functions and Dawson's integral (where $\beta=1/kT$, for convenience $k=1$, and the fluctuations are dropped),

$$Q_u=N\,\frac{2}{\beta^{1/2}}\int_0^{\beta^{1/2}}ds\ \frac{1}{s}\,e^{-s^2}\int_0^s dt\ e^{t^2}, \tag{13}$$

$$Q_s=N\,\frac{2}{\beta^{1/2}}\int_0^{\beta^{1/2}}ds\ \frac{1}{s}\,e^{s^2}\int_0^s dt\ e^{-t^2}. \tag{14}$$

Figure 2 shows the resulting $f_u(T)$ as a function of T. At low temperatures, Q_s is proportional to $T^{3/2}e^{1/T}$ and this dominates the fraction of unstable configurations because Q_u is proportional to $T^{1/2}$. Then the unstable fraction $f_u(T)$ is proportional to $T^{-1}e^{-1/T}$ for small T.

Now we use these results to test the Straub–Thirumalai integral equation. On changing variables to $x=E/T$, Eq. (1) becomes

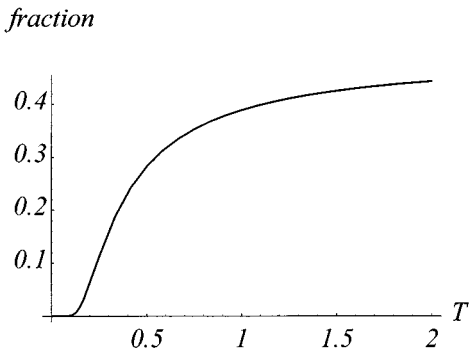

FIG. 2. Fraction $f_u(T)$ of unstable configurations at temperature T.

$$f_u(T)=T\int_0^\infty dx\ \bar{f}_u(x)g(Tx) \tag{15}$$

which reduces in the limit of small T to

$$f_u(T)\to Tg(0)\int_0^\infty dx\ \bar{f}_u(x). \tag{16}$$

The remaining integral over x is approximately 1.06. If $g(0)$ does not vanish, then the unstable fraction must be linear in T. [The converse of this argument was used in Refs. 1–3 to conclude that, in a polypeptide and in a liquid, $g(E)$ does not vanish at low E.] In the one-dimensional example studied here, $g(0)$ does not vanish, and $f_u(T)$ is *not* linear in T for small T; it varies as $T^{-1}e^{-1/T}$. The integral equation, with the proposed kernel $f_u(T,E)$, is not consistent with the exact behavior of this one-dimensional model potential.

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