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A Monte Carlo evaluation of thermal desorption rates[a)]

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In a paper which appeared recently,[1] we described a transition state method for calculating thermal desorption rate constants that incorporates a Monte Carlo evaluation of the relevant averages which appear in the formalism. Particular emphasis was placed on the fact that this technique is uniquely versatile in that it permits the inclusion of a great variety of effects, e.g., finite adatom concentrations and interaction anharmonicity, to which the rates are potentially quite sensitive. Subsequently, we have also shown[2] that these rate constants calculated within the transition state theory (TST) framework may be corrected dynamically via a procedure first suggested by Chandler[3] so as to produce an essentially exact description of desorption kinetics. By implementing this two-step process, one should be able to investigate quite realistic systems with an accuracy which compares favorably with that obtainable in the best of the recent experiments.

The present note is submitted in order to point out an especially advantageous consequence of using a Monte Carlo evaluation of the TST desorption rate constants. This advantage lies in the availability of importance sampling techniques[4] as a means of generating averages over a distribution characterized by a particular temperature while sampling from a distribution which describes the system at yet a different temperature. For the case of thermal desorption, one finds that the rate may be expressed as

$$\begin{aligned} L(q,T) &= \tfrac{1}{2}\langle |\dot{x}|\,\delta(x-q)\rangle \\ &= (2\beta\pi m)^{-1}\langle\delta(x-q)\rangle_\beta \\ &= (2\beta\pi m)^{-1}\frac{\int dx\,\delta(x-q)\,e^{-\beta V}}{\int dx\,e^{-\beta V}} \\ &= (2\beta\pi m)^{-1}\frac{\int dx\,\delta(x-q)\,e^{-\beta V}e^{\beta_0 V}e^{-\beta_0 V}}{\int dx\,e^{-\beta V}e^{\beta_0 V}e^{-\beta_0 V}} \\ &= (2\beta\pi m)^{-1}\frac{\langle\delta(x-q)\exp[-V(\beta-\beta_0)]\rangle_{\beta_0}}{\langle\exp[-V(\beta-\beta_0)]\rangle_{\beta_0}}, \end{aligned} \tag{1}$$

where the notation is the same as that used previously,[1] namely, that x is the adatom coordinate normal to the surface, q is the critical distance beyond which the adatom is assumed to be desorbed, m is the adatom mass, V is the total system potential, and $\beta \equiv (k_B T)^{-1}$, with k_B being Boltzmann's constant. Thus, a single Monte Carlo calculation performed at a conveniently chosen temperature T_0 is all that is needed in order for one to obtain the complete temperature dependence of the rate. A certain amount of discretion must be exercised, of course, in using Eq. (1) inasmuch as it will not yield correct results when extended to temperatures at which there appear dramatically different physical characteristics such as highly structural overlayers or reconstructed crystal surfaces. However, since even a meager amount of experimental information will probably be sufficient in determining at what points such processes occur, one is likely to be able to avoid overreaching the region within which importance sampling will be useful.

One may also easily show that direct Monte Carlo–TST determinations of Arrhenius activation energies are possible. Specifically, the activation energy E_a may be written as

$$E_a = \frac{k_B T^2}{k}\frac{\partial k}{\partial T}, \tag{2}$$

where k is the rate constant. By substituting the transition state expression for k into the above equation, one then obtains the general TST relation

$$E_a^{\mathrm{TST}} = \frac{\langle H\,|\dot{x}|\,\delta(x-q)\rangle}{\langle |\dot{x}|\,\delta(x-q)\rangle} - \langle H\rangle, \tag{3}$$

with H being the classical Hamiltonian for the system, which for a thermal process reduces to

$$E_a^{\mathrm{TST}} = \tfrac{1}{2}k_B T + \frac{\langle V\delta(x-q)\rangle}{\langle\delta(x-q)\rangle} - \langle V\rangle .$$

Equation (3) is, of course, essentially just Tolman's[5] definition of the activation energy, namely, the average energy of desorbing ("activated") particles minus the average energy of all those which are adsorbed, although one should note that the TST average over the energies of those particles which are energetic enough to desorb is a velocity-weighted one. The same Monte Carlo calculation which yields the individual rate constants thus also provides "local" activation energies.

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Finally, we indicate a particularly interesting feature of the TST activation energy described above, that it represents an upper bound to the exact value. Note first that the exact rate constant is given by the equation

$$k = \kappa k_{\mathrm{TST}} ,$$

where κ is the adatom sticking probability. Substitution of k into Eq. (2) therefore yields an expression for the exact activation energy

$$\begin{aligned} E_a &= \frac{k_B T^2}{\kappa k_{\mathrm{TST}}} \frac{\partial}{\partial T}(\kappa k_{\mathrm{TST}}) \\ &= \frac{k_B T^2}{k_{\mathrm{TST}}} \frac{\partial k_{\mathrm{TST}}}{\partial T} + \frac{k_B T^2}{\kappa} \frac{\partial \kappa}{\partial T} \\ &= E_a^{\mathrm{TST}} + \frac{k_B T^2}{\kappa} \frac{\partial \kappa}{\partial T} . \end{aligned}$$

However, since for a simple desorptive event the sticking probability is likely to be a nonincreasing function of the temperature, one may conclude that for such simple processes

$$E_a \leq E_a^{\mathrm{TST}} .$$

(Since $k \leq k_{\mathrm{TST}}$, the above condition means that the desorption frequency factor calculated within the TST formalism must also provide an upper bound.) Of course, such a bounding argument would be of little value if it were not for the fact that the activation energy can be computed to arbitrarily good accuracy via the Monte Carlo method.

Although in our earlier paper[1] we suggested that the synthesis of transition state theory and pseudodynamical Monte Carlo techniques would prove to be a singularly useful means of obtaining desorption rate data, it now appears clear that the inclusion of importance sampling makes this approach even more powerful. The method does, for example, overcome the usual problems associated with the simulation of intrinsically rare events,[6] while at the same time permitting the study of the adatom concentration effects which are practically inaccessible by other methods. It is, in fact, this rather unique versatility of the Monte Carlo–TST formalism which most strongly commends itself to those interested in investigating adsorption/desorption phenomena.

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ERRATA

Erratum: Bispectral analysis as a probe of quasielastic light scattering intensity fluctuations [J. Chem. Phys. 72, 6123 (1980)]

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In a recent paper, this author suggested that the measurement of the homodyne bispectrum $\langle I(0)I(t)I(\tau)\rangle$ might be of use in interpreting light scattering spectra of solutions containing several noninteracting diffusing species, in that the second time cumulants of the bispectrum were

$$K_{02} = K_{20} = \sum_{i,j} \bar{a}_i^2 \bar{a}_j^2 (\Gamma_i - \Gamma_j)^2 \Big/ \Big(\sum_m \bar{a}_m^2\Big)^2 , \tag{1a}$$

$$K_{11} = \Big[-\sum_{i,j} \bar{a}_i^4 \bar{a}_j^2 (\Gamma_i - \Gamma_j)^2 \times \sum_{i\neq j\neq k\neq i} \bar{a}_i^2 \bar{a}_j^2 \bar{a}_k^2 (\Gamma_j - \Gamma_i)(\Gamma_j + \Gamma_k) \Big] \Big/ \Big(\sum_m \bar{a}_m^2\Big)^3 , \tag{1b}$$

where $\bar{a}_i$ and Γ_i are the root-mean-square scattering amplitudes and the decay rate, respectively, for species i. For a system containing two diffusing species, $K_{11} = \frac{1}{2} K_{02}$; for a system containing more than two species, K_{11} and K_{02} do not appear to be related by a simple constant.

Contrary to the appearance remarked upon in Ref. 1, it is possible to manipulate Eq. (1b) into a form which is simply related to Eq. (1a), namely,

$$K_{11} = \Big[-\frac{1}{2} \sum_{i,j} \bar{a}_i^2 \bar{a}_j^2 (\Gamma_i - \Gamma_j)^2 (\bar{a}_i^2 + \bar{a}_j^2) - \frac{1}{2} \sum_{i\neq j\neq k\neq i} \bar{a}_j^2 \bar{a}_i^2 (2\Gamma_j^2 - 2\Gamma_j \Gamma_i) \bar{a}_k^2 \Big] \Big/ \Big(\sum_i \bar{a}_i^2\Big)^3 ; \tag{2}$$

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