Universal Scaling Laws of Diffusion in a Binary Fluid Mixture

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A new universal scaling law relating the self-diffusivities of a binary fluid mixture and the excess entropies of its components is derived using mode coupling theory, reproducing the empirical scaling laws of Dzugutov [Nature (London) **381**, 137 (1996)] and Hoyt *et al.* [Phys. Rev. Lett. **85**, 594 (2000)] as special cases. The derived scaling laws are tested through numerical calculations for binary Lennard-Jones fluid mixtures for a wide range of physical parameters, and a very good correlation is observed. We have also arrived at a new universal scaling relationship between the cross-diffusivity and entropy for the first time.

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Diffusion phenomena in fluids and fluid mixtures [1] are of immense importance in various disciplines and have been investigated from time to time using the latest probes or tools available at each stage. The earlier theoretical approaches that were developed mainly along the lines of kinetic theory [2,3] have been shown to predict results that compare reasonably well with the experimental results [3] for hard spherelike colloidal suspensions. For a general fluid, however, a more successful and recent theoretical tool is the mode coupling theory (MCT) [4,5] which provides expressions for diffusivity in terms of various static pair correlation functions as well as collective dynamical quantities, which may be often difficult to calculate for complex fluids in general. Thus, it is worthwhile to investigate if these expressions can be further simplified or approximated so that the properties entering into the final scheme can be obtained not only through theoretical routes but are accessible from experimental results as well. The simplest such quantity is the static structure factor $s(\mathbf{k})$ or the radial distribution function (RDF) $g(\mathbf{r})$. The objective of this paper is to investigate the possibility of expressing the self- and cross-diffusivities of a binary fluid mixture in terms of these static quantities alone.

This paper is motivated by two recent important investigations [6,7] in this direction. Thus, Dzugutov [6] proposed a universal scaling law relating the dimensionless scaled diffusion constant D^* of a pure (one-component) fluid to its excess entropy S as $D^* = A\exp(S)$, where A is a parameter equal to 0.049 and the excess entropy S is defined as $S = -(1/2)\rho \int d\mathbf{r}\,\{g(\mathbf{r})\ln g(\mathbf{r}) - [g(\mathbf{r}) - 1]\}$ with ρ representing the bulk fluid density. Here $D^* = D/(\Gamma\sigma^2)$, where σ is the hard core diameter, D is the self-diffusion constant, and Γ is the collisional frequency which is defined in Enskog theory as $\Gamma = 4\sigma^2 g(\sigma)\rho(\pi k_B T/m)^{1/2}$ with $g(\sigma)$ denoting the RDF evaluated at the contact point σ, m is the mass of a fluid particle, and k_B and T represent the Boltzmann constant and absolute temperature, respectively.

An important aspect of this scaling law is that it connects the dynamical quantity D^* with an equilibrium property $g(\mathbf{r})$ and it is universal in nature irrespective of the type of interparticle interaction. It is thus quite important to extend it to the case of binary mixtures, the first attempt at which was made by Dzugutov [6] by replacing the various quantities appearing in the relation by those of the individual components in the mixture with no inclusion of any cross-RDF. Recently Hoyt *et al.* [7] proposed, for a binary mixture of two components α and β, a new scaling law given by

$$D^* \equiv \left(\frac{D_\alpha}{\chi_\alpha}\right)^{x_\alpha}\left(\frac{D_\beta}{\chi_\beta}\right)^{x_\beta} = A\exp(S), \tag{1}$$

where D_α and D_β represent the self-diffusion constants of the respective components with mole fractions x_α and x_β, and the component scaling factor χ_μ is defined as

$$\chi_\mu = 4(\pi k_B T)^{1/2} \sum_\nu \sigma_{\mu\nu}^4 \rho_\nu g_{\mu\nu}(\sigma_{\mu\nu}) \left(\frac{m_\mu + m_\nu}{2m_\mu m_\nu}\right)^{1/2} \tag{2}$$

for $\mu = \alpha$ or β. Here ρ_α and ρ_β denote the individual components of the total density $\rho(= \rho_\alpha + \rho_\beta)$, m_α and m_β are the respective particle masses, $\sigma_{\alpha\alpha}$ and $\sigma_{\beta\beta}$ are the hard core diameters (or positions of the first peaks in RDF for continuous potentials) with $\sigma_{\mu\nu} = (\sigma_{\mu\mu} + \sigma_{\nu\nu})/2$, and the total excess entropy is given by $S = x_\alpha S_\alpha + x_\beta S_\beta$, where S_μ is the partial molar entropy for the μth component as given by

$$S_\mu = -\frac{1}{2}\sum_\nu \rho_\nu \int d\mathbf{r} \times \{g_{\mu\nu}(\mathbf{r})\ln g_{\mu\nu}(\mathbf{r}) - [g_{\mu\nu}(\mathbf{r}) - 1]\}. \tag{3}$$

The scaling law of Hoyt *et al.* [7] clearly involves the cross-RDF $g_{\alpha\beta}(\mathbf{r})$ in addition to the self-RDF's $g_{\alpha\alpha}(\mathbf{r})$ and $g_{\beta\beta}(\mathbf{r})$ in the scale factors χ_α and χ_β as well as in the excess partial molar entropies S_α and S_β. The universal scaling laws proposed by Dzugutov [6] as well as Hoyt *et al.* [7] are rather simple and are found to work well for most of the one- and two-component systems, respectively. However, one of the major drawbacks is that

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both of the scaling laws are only empirical and, moreover, for a binary mixture, the scaling law relates only D^* which is a particular combination of the individual diffusivities D_α and D_β as given in Eq. (1) and does not provide any relation or prescription for the individual diffusivities. For mixtures, there is also a cross-diffusivity which has so far remained outside the scope of these scaling laws. In this paper, we provide a satisfactory derivation of the scaling laws in a binary mixture for the individual component self-diffusivities as well as the cross-diffusivity.

For this purpose, we start with the expressions for diffusivity within the framework of MCT which we recently proposed [8] for a binary mixture and assume that the diffusion is controlled by the structural relaxation of the fluid particles, and hence the total friction acting on a tagged particle of the μth component can be split into the binary part ξ_μ^B and the density fluctuation contribution $\xi_\mu^{\rho\rho}$, thereby leading to the expression of the corresponding diffusion constant as $D_\mu = k_BT/(\xi_\mu^B + \xi_\mu^{\rho\rho})$. In order to obtain an explicit expression for $\xi_\mu^{\rho\rho}$, we adopt the concepts of MCT and assume that only the collective density mode couples to the motion of the tagged particle and hence the relevant decay channels are provided by the bilinear modes of the form $n_\mu^*(\mathbf{k})n(\mathbf{k})$, where $n_\mu(\mathbf{k})$ and $n(\mathbf{k})$, respectively, represent the tagged particle density and the collective density in Fourier space. The standard MCT procedure [8] then leads to the expression

$$\xi_\mu^{\rho\rho} = \left(\frac{k_BT}{24\pi^3\rho}\right)\int_0^\infty dt \int d\mathbf{k} \times k^2 \frac{[\rho_\alpha h_{\mu\alpha}(\mathbf{k}) + \rho_\beta h_{\mu\beta}(\mathbf{k})]^2}{[s(\mathbf{k})]^2} G_\mu(\mathbf{k},t)G(\mathbf{k},t), \tag{4}$$

where $h_{\mu\nu}(\mathbf{k})$ is the total correlation in Fourier space and $s(\mathbf{k}) = s_{\alpha\alpha}(\mathbf{k}) + s_{\beta\beta}(\mathbf{k}) + 2s_{\alpha\beta}(\mathbf{k})$ with $s_{\mu\nu}(\mathbf{k})$ denoting the partial static structure factors, whereas $G(\mathbf{k},t)$ and $G_\mu(\mathbf{k},t)$ represent, respectively, the collective- and self-dynamic structure factors.

Because of the slow dynamics of the diffusive process of the tagged particle, one can assume [4] in Eq. (4) the result $G_\mu(\mathbf{k},t) \approx G_\mu(\mathbf{k},0) = 1$. Although a formal expression for $G(\mathbf{k},t)$ can be obtained by using the projection operator formalism developed by Zwanzig [9], it is difficult to express it in simple analytical form. Therefore, we employ the hydrodynamic limit and Markovian approximation and express it as $G(\mathbf{k},t) = s(\mathbf{k})\exp[-D_\mu k^2 t/s(\mathbf{k})]$, neglecting the cross-velocity contribution and also assuming $D_\alpha \approx D_\beta$ for simplification. Using these approximations in Eq. (4), evaluating the time integral and after some rearrangement, we obtain the simple expression for D_μ given by

$$D_\mu = \frac{k_BT}{\xi_\mu^B}(1 - A_\mu) \approx \frac{k_BT}{\xi_\mu^B}\exp(-A_\mu), \tag{5}$$

where the exponential approximation used here is valid if the quantity A_μ expressed as

$$A_\mu = \frac{1}{24\pi^3}\int d\mathbf{k}\,\{\rho_\alpha h_{\mu\alpha}^2(\mathbf{k}) + \rho_\beta h_{\mu\beta}^2(\mathbf{k}) - \rho x_\alpha x_\beta [h_{\alpha\beta}(\mathbf{k}) - h_{\mu\mu}(\mathbf{k})]^2\} \tag{6}$$

is small, as is the case if the density of the fluid mixture is not very high. Noting that the last term on the right-hand side of Eq. (6) is identically zero for an isotopic mixture for which $\sigma_{\alpha\alpha} = \sigma_{\beta\beta}$ and is small for size ratio close to unity, one can neglect this term in Eq. (6) in comparison to the first two terms and reexpress the $\mathbf{k}$-space integral as a coordinate-space integral involving $g_{\mu\nu}(\mathbf{r})$, to obtain

$$A_\mu = \frac{1}{3}\sum_\nu \rho_\nu \int d\mathbf{r}\,[g_{\mu\nu}(\mathbf{r}) - 1]^2. \tag{7}$$

Now, based on the inequality $[g(\mathbf{r}) - 1]^2 \geq \{g(\mathbf{r}) \times \ln g(\mathbf{r}) - [g(\mathbf{r}) - 1]\}$ which follows from $[g(\mathbf{r}) - 1] \geq \ln g(\mathbf{r})$, we replace $[g_{\mu\nu}(\mathbf{r}) - 1]^2$ by $\{g_{\mu\nu}(\mathbf{r})\ln g_{\mu\nu}(\mathbf{r}) - [g_{\mu\nu}(\mathbf{r}) - 1]\}$ in Eq. (7) and express it as an equality approximation by introducing a single multiplicative constant b which is clearly greater than unity. This leads to the result

$$A_\mu = \frac{b}{3}\left[\sum_\nu \rho_\nu \int d\mathbf{r}\,\{g_{\mu\nu}(\mathbf{r})\ln g_{\mu\nu}(\mathbf{r}) - [g_{\mu\nu}(\mathbf{r}) - 1]\}\right] \tag{8}$$

which clearly equals the entropy term S_μ for the μth component, as defined in Eq. (3), if the value of the constant is chosen as $b = (3/2)$ which is intermediate between the limiting values $b = 2$ and 1 corresponding to the limits $g(\mathbf{r}) = 1$ and 0, respectively. Using Eqs. (5), (8), and (3), the scaled diffusivity $D_\mu^* (= D_\mu/\chi_\mu)$ is thus given by

$$D_\mu^* = \frac{k_BT}{\chi_\mu \xi_\mu^B}\exp(S_\mu). \tag{9}$$

Using now Eq. (2) for the scale factor χ_μ and the Enskog theory expression [10] for ξ_μ^B, the temperature and mass dependence of the prefactor can be shown to almost cancel out. This prompts us to replace the prefactor by a constant, at least for the intermediate density range and size ratio not very different from unity, and write the approximate version of Eq. (9) as

$$D_\mu^* = A\exp(S_\mu), \tag{10}$$

where the prefactor A has been chosen to be the same as that proposed by Dzugutov [6], so that, on specializing to a pure fluid, Eq. (10) becomes identical to the scaling law of Dzugutov. This provides a derivation of a universal scaling law for the self-diffusivities using the MCT of diffusion in a binary mixture. The scaling law of Eq. (10) clearly satisfies $D^* \equiv (D_\alpha^*)^{x_\alpha}(D_\beta^*)^{x_\beta} = A\exp(x_\alpha S_\alpha + x_\beta S_\beta)$, which is the scaling law of Hoyt *et al.* [7] as given by Eq. (1). The newly derived Eq. (10) thus satisfies both Dzugutov [6] and Hoyt *et al.* [7] scaling laws as the appropriate limiting special cases.

Another important transport coefficient in a binary fluid mixture is the cross-diffusivity D_d, which has been studied [8], using MCT for the first time, only recently. It is worthwhile to investigate if a universal scaling law exists for the cross-diffusivity since no such scaling law seems to have been considered earlier for this quantity. For this purpose, we again start with the MCT expression proposed for the cross-diffusivity but introduce a simplification based on the experience of numerical calculation [8] which has shown that the cross-correlation contribution to D_d from particles of the same component is smaller than that from dissimilar particles. Thus, retaining cross correlation only from the dissimilar particles, and approximating their distinct dynamic structure factor by the initial value $s_{\alpha\beta}(\mathbf{k})$, one can express D_d as

$$D_d = \frac{(D_\alpha D_\beta)^{1/2}}{24\pi^3\rho}\int d\mathbf{k}\,[\rho_\alpha h_{\alpha\alpha}(\mathbf{k}) + \rho_\beta h_{\beta\alpha}(\mathbf{k})] \times [\rho_\beta h_{\beta\beta}(\mathbf{k}) + \rho_\alpha h_{\alpha\beta}(\mathbf{k})] s_{\alpha\beta}(\mathbf{k}), \qquad (11)$$

where the other approximations used for simplifying the self-diffusivity have also been employed. Owing to the sharpness of the peak of the integrand at $k = k_m$, we replace $s_{\alpha\beta}(k)$ appearing in Eq. (11) by its peak value, i.e., $s_{\alpha\beta}(\mathbf{k}) \approx s_{\alpha\beta}(k_m)$. Applying now Holder's inequality and using the same approximations as those involved in obtaining Eq. (8) from Eq. (6) as well as $D_\alpha \approx D_\beta$, the scaled cross-diffusivity $D_d^* = D_d/D_{\alpha\beta}^0$ is obtained as

$$D_d^* = b_d s_{\alpha\beta}(k_m)\,(S_\alpha S_\beta)^{1/2}, \qquad (12)$$

where $D_{\alpha\beta}^0 = x_\beta D_\alpha + x_\alpha D_\beta$ and the constant b_d is introduced to account for the approximation in replacing the inequality by an equality.

In order to obtain insight into the applicability of the scaling laws derived here, we consider the Lennard-Jones (LJ) fluid mixtures for a wide range of values of the physical parameters. The RDF's $g_{\mu\nu}(r)\;(\mu, \nu = \alpha, \beta)$ for these systems have been calculated through integral equation theory by numerically solving the Orstein-Zernike equation with hypernetted chain approximation along with the bridge function proposed by Duh and Henderson [11]. The entropy S_μ has been evaluated using the calculated RDF in Eq. (3) and using numerical integration. In Fig. 1, we have plotted the scaled self-diffusivities D_μ^* corresponding to simulation [10,12–16] results against the calculated entropies S_μ for both components of LJ fluid mixtures for different values of the physical parameters such as the density, interaction strength, temperature, composition, and size ratio. Excellent agreement of these plots with the line drawn to represent Eq. (10) is clearly evident, demonstrating the accuracy of the new scaling law proposed for the component self-diffusivities. In order to test the scaling law proposed by Dzugutov [6] for a mixture that can be obtained from Eq. (10) by dropping the cross-terms in the expressions for the scale factor as well as the entropy given by Eqs. (2) and (3), respectively, we have plotted, as an inset of Fig. 1, D_μ^* calculated by this prescription along with the simulation results against entropy which is also calculated using the Dzugutov prescription, i.e., by neglecting the cross terms. It is observed that, in this case, the agreement is poorer which establishes the importance of the cross terms in the entropy [as defined in Eq. (3)] and hence also of the present scaling law. Although Hoyt *et al.* [7] were the first to include $g_{\alpha\beta}(\mathbf{r})$ in their scaling law shown in Eq. (1), they studied only the average quantity D^* rather than the individual diffusivities D_μ^*, and also their study was restricted only to liquid metals. We have, therefore, calculated here the quantity D^* for the LJ mixture and plotted the results along with the simulation [10,12–16] as well as MCT results [8] in Fig. 2, and an excellent agreement is observed. It may be noted that this is only an average quantity and does not reflect the behavior of the individual components, while the scaling law proposed in Eq. (10) predicts the component diffusivities and hence is more general. We have also plotted in Fig. 3 the scaled cross-diffusivity $D_d^* = D_d/D_{\alpha\beta}^0$ corresponding to simulation [17] as well as MCT results [8] vs the scaled entropy term $S_d^* = s_{\alpha\beta}(k_m)\,(S_\alpha S_\beta)^{1/2}$, and a linear correlation as suggested in Eq. (12) is observed although the intercept shown by the best fit is different.

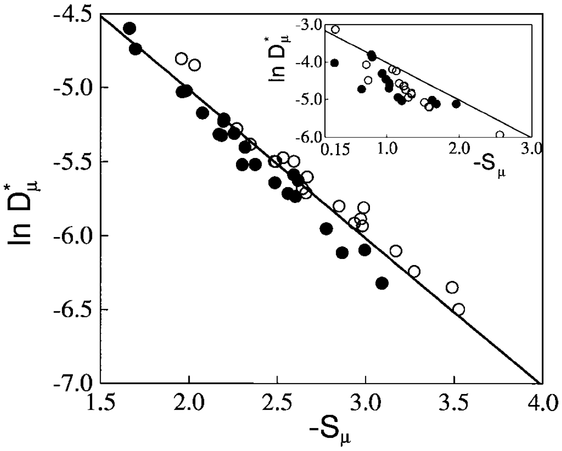

FIG. 1. Plot of the scaled self-diffusivity D_μ^* vs excess partial molar entropy S_μ of the two components ($\mu = \alpha, \beta$) in a binary LJ fluid mixture. The solid line (—) represents the present scaling law of Eq. (10). The simulation results which are taken from Refs. [10,12–16] are shown by filled circles (●) for D_α and open circles (○) for D_β. The inset shows the plot for results corresponding to Dzugutov scaling for which the scale factor and entropy correspond to Eqs. (2) and (3), respectively, without inclusion of the cross-terms. The solid line (—) represents the Dzugutov [6] scaling law results. The key for the simulation results is the same as above.

The major new aspects of this paper may be highlighted as follows. This is the first time the universal scaling laws for diffusivity have been derived from a rigorous theory such as MCT, not only for a pure fluid but also for a binary fluid mixture for which new scaling laws have been obtained for the self-diffusivities of the individual components, which also conform to the earlier empirically proposed scaling laws of both Dzugutov [6] and Hoyt *et al.* [7]

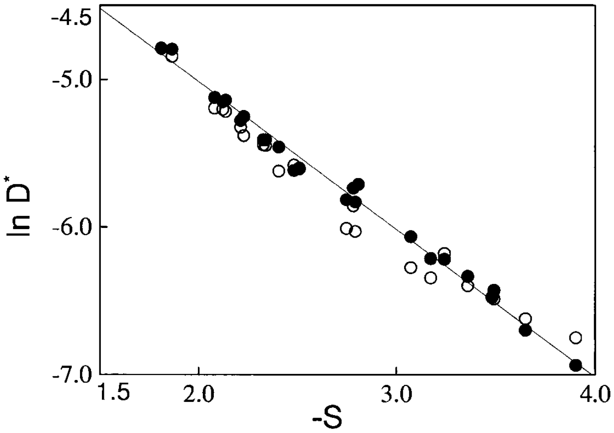

FIG. 2. Plot of the scaled combined diffusivity D^* vs total excess entropy $S(= x_\alpha S_\alpha + x_\beta S_\beta)$ for a binary LJ fluid mixture. The simulation results, which are taken from Refs. [10,12–16], are shown by filled circles (●) and the MCT results [8] are shown by open circles (○). The solid line (—) corresponds to the Hoyt *et al.* [7] scaling law [Eq. (1)] as well as the present scaling law [Eq. (10)].

for the special cases of pure fluids and a single combined diffusivity parameter of mixtures, respectively. The other important quantity is the cross-diffusivity [8,17]. An accurate evaluation of this quantity is more difficult than the self-diffusion constant D^*_μ. We have obtained here for the first time a simple linear relation between the cross-diffusivity and the entropy [Eq. (12)]. Although the slope or intercept of the line is not predicted by the derivation here, the linear dependence on the scaled entropy is predicted and found to provide a quite accurate representation of the results for the cross-diffusivity. To summarize, this investigation has provided insight by establishing a link between the recently proposed MCT of diffusion in a binary fluid mixture and the universal scaling laws, and we believe it will inspire further studies on this important topic.

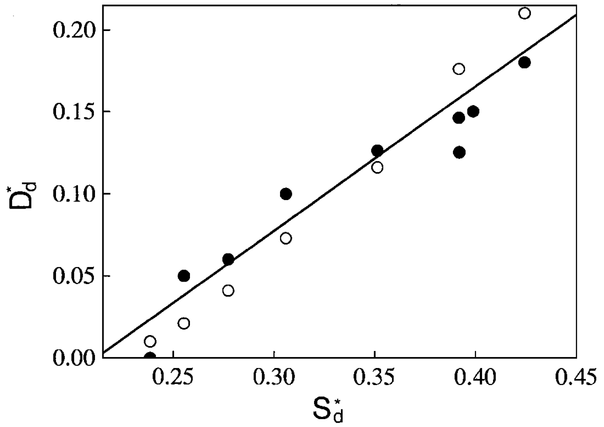

FIG. 3. Plot of the scaled cross-diffusivity D^*_d vs the scaled entropy parameter $S^*_d[= s_{\alpha\beta}(k_m)\,(S_\alpha S_\beta)^{1/2}]$ for a binary LJ fluid mixture. The simulation results, which are taken from Ref. [17], are shown by filled circles (●) and the MCT results [8] are shown by open circles (○). The solid line (—) corresponds to the best linear fit of the simulation results.

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[1] E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems* (Cambridge University Press, Cambridge, UK, 1998), 2nd. ed.
[2] E. G. D. Cohen, Physica (Amsterdam) **194A**, 229 (1993), and references therein. For earlier works on fluid mixtures, see J. M. Kincaid, E. G. D. Cohen, and M. Lopez de Haro, J. Chem. Phys. **86**, 963 (1987).
[3] E. G. D. Cohen, R. Verberg, and I. M. de Schepper, Physica (Amsterdam) **251A**, 251 (1998); I. M. de Schepper, R. Verberg, and E. G. D. Cohen, Mol. Phys. **95**, 595 (1998).
[4] L. Sjogren and A. Sjolander, J. Phys. C **12**, 4369 (1979); U. Baluconi and M. Zoppi, *Dynamics of Liquid State* (Clarendon, Oxford, 1994).
[5] For a review, see B. Bagchi and S. Bhattacharyya, Adv. Chem. Phys. **116**, 67 (2001).
[6] M. Dzugutov, Nature (London) **381**, 137 (1996).
[7] J. J. Hoyt, M. Asta, and B. Sadigh, Phys. Rev. Lett. **85**, 594 (2000).
[8] S. M. Ali, A. Samanta, and S. K. Ghosh, J. Chem. Phys. **114**, 10 419 (2001).
[9] R. Zwanzig, *Lectures in Theoretical Physics* (Interscience, New York, 1961), Vol. III, p. 125; see also T. Keyes, in *Statistical Mechanics-Part B: Time Dependent Processes,* edited by B. J. Berne (Plenum, New York, 1977), p. 259.
[10] G. Jacucci and I. R. McDonald, Physica (Amsterdam) **80A**, 607 (1975).
[11] D. M. Duh and D. Henderson, J. Chem. Phys. **104**, 6742 (1996).
[12] Y. Zhou and G. H. Miller, Phys. Rev. E **53**, 1587 (1996).
[13] K. Nakanishi, H. Narusawa, and K. Toukubo, J. Chem. Phys. **72**, 3089 (1980).
[14] P. J. Gardner, D. M. Heyes, and S. R. Preston, Mol. Phys. **73**, 141 (1991).
[15] R. J. Bearman and D. L. Jolly, Mol. Phys. **44**, 665 (1981).
[16] M. Schoen and C. Hoheisel, Mol. Phys. **52**, 33 (1984).
[17] M. Schoen and C. Hoheisel, Mol. Phys. **52**, 1029 (1984).