

Hydrodynamics of desorbing adsorbate

Lukasz A. Turski

*Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany
and Institute for Theoretical Physics, Polish Academy of Sciences, Aleja Lotników 32/46,*

*PL-02-668 Warszawa, Poland**

(Received 29 November 1982)

A two-dimensional hydrodynamic model of adsorbate behavior is modified by including the isothermal desorption. It is shown that for mobile adsorbates at reasonable temperatures and coverages it is the desorption which provides the dominant momentum nonconserving process and that the short-wavelength sound modes can propagate in the adsorbate provided desorption time is not too short.

In a recent paper¹ Ramaswamy and Mazenko proposed a model of the two-dimensional hydrodynamics, which should describe the behavior of a low-coverage adsorbate gas on a solid surface.

The basic ingredient of their theory is a new friction coefficient σ' which accounts for adsorbate momentum nonconservation due to one-particle adatom-substrate interaction. It turns out that such a "minimal" modification of conventional hydrodynamics already leads to interesting predictions. One of them, very important theoretically, is that the one-particle friction controls the infrared singularities responsible for divergences of the two-dimensional transport coefficients. The other one, of a great applied interest, is that at sufficiently low values of the friction coefficient σ' there should be a short-wavelength sound mode propagating in the adsorbate.

The aim of this Brief Report is to indicate another physical mechanism, namely, isothermal desorption, which can influence and/or leads to the occurrence of these short-wavelength sound modes. We shall also argue that for mobile adsorbates, like Xe on W, it is the desorption which plays the major role in one-particle momentum nonconservation.

According to the model proposed in Ref. 1, one-particle adatom-substrate interaction leads to the appearance of a new momentum nonconserving term in otherwise conventional Navier-Stokes equations. This new term has a form $-\sigma'\bar{v}$, where \bar{v} is the adsorbate fluid velocity. For systems with not too high heat of desorption, isothermal desorption is also a phenomenon leading to not only particle but also momentum nonconservation. The particle number nonconservation can easily be incorporated into the continuity equation by adding a sink term of the form $-\alpha[n(\bar{r},t) - n_0]$, where n_0 is the equilibrium adsorbate density and $n(\bar{r},t)$ is an actual density. Each particle leaving the adsorbate will take with it momentum $-m\bar{v}$, thus the Navier-Stokes equation should also be supplemented with a term $-(\alpha + \sigma')\bar{v}$. Neglecting, similarly as in Ref. 1, the

heat conduction equation, we can write the hydrodynamics equations for our adsorbate in the form

$$\partial_t n(\bar{r},t) + \bar{\nabla} \cdot [n(\bar{r},t)\bar{v}(\bar{r},t)] = -\alpha[n(\bar{r},t) - n_0] , \quad (1)$$

$$\begin{aligned} \partial_t \bar{v}(\bar{r},t) + \bar{v}(\bar{r},t) \cdot \bar{\nabla} \bar{v}(\bar{r},t) \\ = -\bar{\nabla} \mu + \bar{\Omega} \cdot \bar{v}(\bar{r},t) - (\alpha + \sigma')\bar{v}(\bar{r},t) , \quad (2) \end{aligned}$$

where μ is a properly normalized chemical potential for the adsorbate and $\bar{\Omega}$ is a tensor operator containing collective adsorbate transport coefficients—longitudinal and transverse viscosities.

Equation (2) is identical in form to that used in Ref. 1; there is, however, an important difference in the meaning of the coefficient $\sigma = \sigma' + \alpha$ in Eq. (2) and in the previous work.¹ The rate α in Eqs. (1) and (2) should be identified with inverse desorption time t_d^{-1} , and therefore describes a thermally activated process for which not only both activation energies and relevant prefactors in the Arrhenius-Frenkel formula are known experimentally, but the theory of which is relatively well developed.²⁻⁴ On the other hand, σ' was identified in Ref. 1 with, also thermally activated, the surface diffusion process. As we shall see, that identification is not entirely convincing if only for purely numerical reasons.

It is also somewhat disturbing that recent theoretical calculations for one-particle surface diffusion⁵ differ considerably from the Monte Carlo simulations,⁶ while in a different but somewhat related problem of crystal growth with surface diffusion⁷ there is complete agreement between both results. It would be interesting to see the theory of surface diffusion reconsidered possibly along the line of a recent suggestion as to the validity of the Brownian-motion theory of activated processes.⁸

Adding to the right-hand side of Eq. (2) a fluctuating force $\bar{\zeta}$, which as in Ref. 1 is assumed to be a white noise with the correlation function given in the

Fourier space as

$$\langle \zeta_a(\vec{k}, \omega) \zeta_b(\vec{k}', \omega') \rangle = 2k_B T (2\pi)^3 \delta(\omega + \omega') \delta^{(2)}(\vec{k} + \vec{k}') [\sigma \delta_{ab} + \Omega_{ab}(\vec{k})] , \quad (3)$$

where $\Omega_{ab}(\vec{k})$ is the Fourier transform of the viscosities term $\bar{\Omega}$ in Eq. (2), and linearizing resulting equations around ($n = n_0, \vec{v} = 0$) state, one easily calculates all the relevant correlation functions $C(\vec{k}, \omega)$. From all these functions the density-density correlation function $C_{n,n}$ is of main interest as it presumably can be measured in scattering experiments.

We found that $C_{n,n}$ has the form

$$C_{n,n}(\vec{k}, \omega; \vec{k}', \omega') = 2k_B T n_0^2 (2\pi)^3 \times \delta^{(2)}(\vec{k} + \vec{k}') \delta(\omega + \omega') S(\vec{k}, \omega) , \quad (4)$$

where the structure factor $S(\vec{k}, \omega)$ is naturally expressed in terms of the dimensionless quantities

$$\xi = \omega/c_k, \quad \gamma = (\sigma + \nu_L k^2)/c_k, \quad \chi = \alpha/c_k , \quad (5)$$

as

$$S(k, \omega) = \gamma / \{c^3 k [(\xi^2 - 1)^2 + \xi^2(\gamma^2 + \chi^2) + 2\gamma\chi]\} . \quad (6)$$

In the above, c is the adsorbate sound velocity and ν_L is the adsorbate longitudinal kinematic viscosity.

$$k_{\pm} = (c/\nu_L) [1 - (\alpha + \sigma')\nu_L/c^2]^{1/2} (1 \pm \{1 - (2\alpha^2 + \sigma'^2 + 2\alpha\sigma')\nu_L^2/[c^2 - (\alpha + \sigma')\nu_L]^2\}^{1/2})^{1/2} . \quad (10)$$

The requirement that this window stay open restricts values of the coefficients σ' and α . We found that

$$\sigma' < c^2/2\nu_L \equiv \sigma_c \quad (11)$$

and

$$\alpha < 2\sigma_c [(2 - \sigma'/\sigma_c)^{1/2} - 1] . \quad (12)$$

Condition (11) is identical to that found in Ref. 1 but condition (12) is entirely new. It says that the desorption rate is bounded from above by $2\sigma_c$ and that in the absence of other one-particle momentum nonconserving processes $\sigma' = 0$, the sound waves will propagate only when the desorption time t_d is larger than $t_{d,c} = 2.414\sigma_c^{-1}$.

For values of $\gamma^2 + \chi^2 > 2$ the structure factor $S(k, \omega)$ develops a broad highly non-Lorentzian shape corresponding to a combined viscous and desorption decay of an excess adsorbate density fluctuation.

Attractive as it is, our result requires careful analysis of the parameters before its physical relevance could be fully appreciated.

Typical systems to which the above analysis presumably applies are those which have been recently studied from the point of view of the desorption

For $\chi = 0$ we recover the Ramaswamy and Mazenko result; for finite χ , however, the structure factor Eq. (6) differs considerably from that in Ref. 1. For values of γ and χ obeying

$$\gamma^2 + \chi^2 < 2 , \quad (7)$$

$S(k, \omega)$ develops a three-peak structure with a central peak and two side peaks corresponding to sound modes. The dispersion relation for these modes can easily be found from Eq. (5), and it reads

$$\xi_{\pm} = \pm [1 - \frac{1}{2}(\gamma^2 + \chi^2)]^{1/2} , \quad (8)$$

or, in usual variables,

$$\omega_{\pm} = \pm ck \{1 - [\alpha^2 + (\alpha + \sigma' + \nu_L k^2)^2]/2c^2 k^2\}^{1/2} . \quad (9)$$

Notice that the sound mode peaks are there even for $\sigma' = 0$ and that their dispersion is essentially different from that in a viscous fluid.

Equation (7) is, in fact, a window condition for the sound waves. Indeed, solving Eq. (7) for wave vectors k , one finds that these waves propagate for k obeying $k_- < k < k_+$, where

kinetics and the surface diffusion. These are Xe, O, and W adsorbates on the (110) surface of tungsten. For these systems kinetic theory of desorption developed in Refs. 3 and 4 should apply at least within the temperature range $\Theta_{DW}/5 < T < 5\Theta_{DW}$, where $\Theta_{DW} = 405$ K is the Debye temperature for tungsten.

On the other hand, there seems to be no satisfactory theory of adsorbate surface diffusion and, as mentioned above, theoretical calculations⁵ for W on W are in disagreement with Monte Carlo simulations.⁶ It therefore appears that it is quite difficult to estimate values of coefficients σ' and ν_L while two others, c and α , can be given with a considerable degree of confidence.

For low-coverage adsorbates the sound velocity c can be estimated as $(k_B T/m)^{1/2}$, and that gives values of the order of 10^4 cm/sec (1.13×10^4 cm/sec for Xe at 200 K to 2.13×10^4 cm/sec for W at 1000 K). The desorption rate $\alpha \approx t_d^{-1}$ can also be estimated, using results of Refs. 3 and 4, to be of the order of 10^9 sec⁻¹ (5.4×10^9 sec⁻¹ for Xe on W at $T \approx 4\Theta_{DW}$). The surface diffusion for W on W, extrapolated from the high-temperature data,⁶ is given as $D = 3.64 \times 10^{-3} \exp(-11487/T)$ cm²/sec. Thus, for all reasonable temperatures, the bound used in

Ref. 1 overestimates D by several orders of magnitude. The same situation refers to Xe and O on W, when one uses experimental estimates of D . We see, however, no reasons to identify the friction coefficient σ' with c^2/D as suggested in Ref. 1. In order to develop collective or hydrodynamical behavior, the adsorbate has to be rather mobile over the solid surface, and that is what is assumed in the kinetic theory of desorption. In hydrodynamical description surface diffusion has to be linked to the surface kinematic viscosity ν_L by a two-dimensional analog of the Einstein-Stokes relation. Lacking such a theoretical tool we should estimate ν_L as in Ref. 1 using the kinetic theory of gases expression for it. That gives values of ν_L which are density dependent and, for reasonable adsorbate densities $n_0d^2 \approx 0.01 - 0.1$, are of the order of $10^{-2} - 10^{-3}$ cm²/sec. d is the adatom "radius" assumed to be 4 Å. [$\nu_L = 2.54 \times 10^{-2}$ cm²/sec for Xe at $T \approx 2\Theta_{DW}$ and $n_0d^2 = (0.01 - 2.15) \times 10^{-3}$ cm²/sec for W at the same temperature and $n_0d^2 = 0.1$]. Notice that such a value of kinematical viscosity would correspond in three-dimensional hydrodynamics to a reasonable self-diffusion value of the order of 10^{-4} cm²/sec. With these values of the self-diffusion one would think that condition (11) can also be satisfied with the identification $\sigma' = c^2/D$. Let us stress, however, that the one-particle friction cannot be simply linked to the self-diffusion of a particle in the fluid. The physical mechanisms which are likely to determine the value of σ' are these related to adatom-surface defects interactions. Condition (11) gives therefore an upper bound for the possible values of σ' .

Equation (12) gives also an upper bound for the desorption rates α . Using available data for mobile adsorbates (low-coverage physisorbed gases with relatively small activation energies for desorption), one finds that α obeys the inequality (12) for most of the densities and temperatures. Indeed, using the Xe on W values for t_d and for small values of σ' , we found

that Eq. (12) is satisfied for $T > \Theta_{DW}$ at density $n_0d^2 = 0.01$, and for essentially all temperatures at higher density $n_0d^2 = 0.1$.

What remains now is to estimate the width of the wavelength window in which the sound modes (9) can propagate. Using Eq. (10) and again assuming $\sigma' \approx 0$ one finds for Xe on W at $T \approx 2\Theta_{DW}$ and $n_0d^2 = 0.01$, $k_+ = 0.12$ Å⁻¹ and $k_- = 4,5 \times 10^{-4}$ Å⁻¹. That seems to be a convenient wave-vector range for most of the scattering experiments.

We conclude therefore that the sound modes predicted originally by Ramaswamy and Mazenko¹ should propagate in a mobile adsorbate with density $n_0d^2 \leq 0.1$ and for temperatures in between $\Theta_{DW}/2$ and $5\Theta_{DW}$. For these systems the isothermal desorption constitutes the major, if not the only, one-particle momentum nonconserving process.

The open question is whether the theory proposed in Ref. 1 and amended in this Brief Report can be derived from a more microscopic picture. Such a derivation would certainly direct some light not only on the meaning of σ' but also on the role that the one-particle momentum nonconserving processes play in controlling infrared divergences leading to well-known "nonexistence" of two-dimensional transport coefficients. Adding one-particle friction terms of the form $-\sigma\bar{v}$ [cf. Eq. (2)] is physically equivalent to making the system three dimensional. Finally, one should also try to include the two-dimensional energy transport into the full two-dimensional hydrodynamics.

ACKNOWLEDGMENT

The author would like to thank Professor K. Binder for his hospitality at the Institut für Festkörperforschung, Kernforschungsanlage, Jülich during the time that work was performed. Discussions with K. Binder, H. Müller-Krumbhaar, and other colleagues at Jülich are kindly acknowledged.

*Permanent address.

¹S. Ramaswamy and G. F. Mazenko, Phys. Rev. A **26**, 1735 (1982).

²H. J. Kreuzer, in *Proceedings of the Fourteenth International Conference on Thermodynamics and Statistical Mechanics* [Physica (Utrecht) **106A**, 144 (1981)].

³Z. W. Gortel, H. J. Kreuzer, R. Teshima, and L. A. Turski, Phys. Rev. B **24**, 4456 (1981).

⁴H. K. Kreuzer and R. Teshima, Phys. Rev. B **24**, 4470 (1981).

⁵J. R. Banavar, M. H. Cohen, and R. Gomer, Surf. Sci. **107**, 113 (1981).

⁶H. K. McDowell and J. D. Doll, Surf. Sci. **121**, L537 (1982).

⁷Y. Saito and H. Müller-Krumbhaar, J. Chem. Phys. **70**, 1078 (1979).

⁸E. H. Rezayi and H. Suhl, Phys. Rev. B **25**, 2324 (1982).