

# Application of nano-Contact Mechanics Methods via AFM to Study the Adhesive Properties of Asphalt Thin-Film Coatings

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## INTRODUCTION

Contact mechanics models are commonly applied to predict the strength of adhesive bonding in polymer coatings. Asphalts are not polymers, but asphalts do exhibit adhesive and viscoelastic behavior similar to that of polymers in certain cases. For this reason, work of adhesion measurements determined for asphalt thin film systems can be interpreted based on contact mechanics models such as the Johnson-Kendall-Roberts (JKR) contact theory and the Derjaguin-Muller-Toporov (DMT) approach. In our research these models have been applied to derive the surface free energies of paving grade asphalts originally prepared as thin-film samples that are solvent spin cast onto glass slide substrates in 1-micrometer to as thin as 150 nm in thickness. In these studies the work of adhesion is measured with an atomic force microscope equipped with cantilevers fabricated with glass micro-bead tips based on “pull-off” force measurements which are acquired as a function of contact rate and loading to derive the surface free energy of these materials under ambient conditions.

Furthermore, when surface free energy values measured for asphalts at ambient temperature in this fashion are combined with temperature dependent surface tension values measured at asphalt’s softening point, Einstein’s approach of interpreting capillarity phenomena may be applied to study the flow properties of these materials. Thus, Einstein proposed that the amount of mechanical work supplied to a liquid,  $\gamma$ , to increase the surface free energy by one unit (not specified) is a cyclic process denoted as

$$\gamma_1 (A_2 - A_1) = \gamma_2 (A_2 - A_1) \quad (1)$$

where,  $(A_2 - A_1)$  is the isothermal increase in the surface area, such that, the total heat supplied to the system is equal to the total heat withdrawn. The enthalpy of this process may then be denoted as

$$dH = c^\sigma AdT + (\gamma + q^\sigma) dA \quad (2)$$

where  $c^\sigma$  is the specific heat defined at the surface  $^\sigma$ , and  $q^\sigma$  is the heat necessary to form a surface of unit area. The free energy of this process is then expressed as

$$dG \equiv \gamma dA = dH - q^\sigma dA - c^\sigma AdT \quad (3)$$

where the entropy is given as

$$dS = (c^\sigma AdT/T) + (q^\sigma /T) dA \quad (4)$$

or

$$-TdS = -c^\sigma AdT - q^\sigma dA \quad (5)$$

The total differentials are then expressed as

$$\partial(c^\sigma A)/\partial A = \partial(\gamma + q^\sigma)/\partial T \quad (6)$$

where it follows that

$$(\gamma + q^\sigma)dA = dH - c^\sigma AdT \quad (7)$$

Thus, the total energy necessary to form a unit (equation 1) of surface is expressed as

$$\gamma + q^\sigma = \gamma - T(\partial\gamma/\partial T) \quad (8)$$

By taking the derivative of this expression in terms of  $T$ ,

$$\partial/\partial T(\gamma + q^\sigma) = \partial/\partial T(\gamma - T(\partial\gamma/\partial T)) \quad (9)$$

gives,

$$c^\sigma = \partial\gamma/\partial T + \partial q^\sigma/\partial T = -T(\partial^2\gamma/\partial T^2) = 0 \quad (10)$$

which suggested to Einstein that no heat should be ascribed to the surface, but rather, that the energy of the surface was potential by nature. Asphalt surface tensions were then measured as a function of temperature employing a duNOÛY ring surface tensiometer where phase transition temperatures could be calculated and/or estimated for eight asphalts based on a non-linear fit of  $\gamma$  vs.  $T$  data points to a third order polynomial equation

$$\gamma(T^\circ C) \approx g_0 + g_1T + g_2T^2 + g_3T^3 \quad (11)$$

where

$$\partial^2\gamma/\partial T^2 = c^\sigma/T = 2a_2 + 6a_3T = 0 \quad (12)$$

Phase-transition temperatures,  $T^*$  °C, were then derived for the eight asphalts by taking the second derivative in the third order polynomial function in order to determine the inflection point, estimated as

$$T^*(^\circ C) \approx -g_2/3g_3 \quad (13)$$

$T^*$  -values were then plotted versus the activation energy of viscous flow of the asphalt,  $E_a(\eta)$  giving a linear correlation, suggesting that this phase transition in asphalts may best be defined as a Newtonian liquid to viscoelastic liquid phase change at the “softening” temperature,  $T^*$  where

$$E_{a,vis} = b_0 + b_1T^* = b_0 - b_1(g_2/3g_3) \quad (14)$$