SIMPLE KELVIN EQUATION APPLICABLE IN THE CRITICAL POINT VICINITY

Valeev A.A.

Kamyshin Technological Institute of Volgograd State Technical University,
Kamyshin, e-mail: waleev@mail.ru

New simple form of the Kelvin equation is offered that applies near the gas-liquid transition critical point.

Well known form of the Kelvin Equation [1, 2]

$$\frac{\tilde{p}_{sat}}{p_{sat}} = \exp\left(-\frac{\mu}{\rho_L RT}\frac{2\sigma}{r}\right) \qquad (1)$$

has been proved to work excellent for the phase equilibrium of rare gas and liquid systems, the ones it was originally designed for. Here p_{sat}, $\tilde{p}_{sat}$ are the saturated vapor pressures against a plain surface and a meniscus with effective curvature radius r, respectively, the latter accounting for such effects as the adsorption at the pore wall. Number "2" stays for spherical geometry of the meniscus. It should be replaced by "1" in the case of the cylindrical geometry. μ is the molar mass of the substance in use, ρ_L is the liquid phase density, R is the universal gas constant. Quite often, this equation is misused when applied to high-presser gases and to liquids at near-critical temperatures.

To account for the gas's nonideality, another equation [3] was developed:

$$\frac{\tilde{f}_{sat}}{f_{sat}} = \exp\left(-\frac{\mu}{\rho_L RT}\frac{2\sigma}{r}\right), \qquad (2)$$

where f is the replacement of the pressure by the fugacity. In the next paragraph, it will be shown that this equation, as well as those obtained in [4], does not work quite well near the critical point and the replacement will be presented.

Kelvin equation from scratch

We consider a liquid-gas equilibrium system divided by a plain surface. Now we can put down the change in the Gibbs energy for each phase:

$$dG_i = d\mu_i n_i = -S_i dT_i + V_i dp_i + \mu_i dn_i, \qquad (3)$$

where i denotes the phase that can be either G or L. μ_i, n_i, S_i, T_i, V_i, p_i are chemical potential, amount of substance, entropy, temperature, volume and pressure of the phase i, respectively. Taking into account that both phases are in the state of thermodynamical equilibrium, we can put:

$$T_G = T_L \equiv T, \quad \mu_G = \mu_L \equiv \mu. \qquad (4)$$

Generally speaking, $p_G \neq p_L$, due to additional pressure by the curved surface tension. The eq. (3) will take the following form:

$$dG_i = d\mu n_i = -S_i dT + V_i dp_i + \mu dn_i. \qquad (5)$$

Now we can put down the change in the chemical potential:

$$d\mu = d(G_i / n_i) = -s_i dT + v_i dp_i, \qquad (6)$$

where s_i, v_i, are the molar entropy and the molar volume, respectively. Now we can see that

$$(d\mu)_{T, n_i} = v_i dp_i. \qquad (7)$$

Taking into account that $p_L = p_G - 2\sigma/r$, we can put

$$(d\mu)_{T, n_i} = v_G dp_G = v_L d(p_G - 2\sigma/r). \qquad (8)$$

Omitting $v_L dp_G$ term is what has been done to obtain the eq's (1), (2) and the analogous equations in [4], because the gas phase there has been considered dilute. This is not our case, because we operate in the critical point vicinity, i.e. v_L is comparable with v_G. Integrating the eq. (8)

$$\int_{p_{sat}}^{\tilde{p}_{sat}} (v_G - v_L)dp_G = -v_L 2\sigma/r \qquad (9)$$

we obtain approximate equation

$$(v_G - v_L)(\tilde{p}_{sat} - p_{sat}) \approx -v_L 2\sigma/r, \qquad (10)$$

which can be used if $v_G - v_L$ does not change significantly within interval $(\tilde{p}_{sat}; p_{sat})$.

Finally, we have

$$\tilde{p}_{sat} - p_{sat} \approx -\frac{v_L}{v_G - v_L} 2\sigma/r = -\frac{\rho_G}{\rho_L - \rho_G} 2\sigma/r, \qquad (11)$$

where ρ_G is the gas phase density.

Now we can rewrite eq. (8) in the following form

$$(d\mu)_{T, n_i} = v_L dp_L = v_G d(p_L + 2\sigma/r). \qquad (8^*)$$

Integrating it we obtain

$$\int\limits_{p_{sat}}^{\tilde{p}_{sat}^{L}} (v_L - v_G)dp_L = v_G 2\sigma / r \ , \qquad (12)$$

where $\tilde{p}_{sat}^{L}$ is the pressure of the liquid phase in equilibrium with the saturated vapor (both divided by the curved meniscus).

$$(v_L - v_G)(\tilde{p}_{sat}^{L} - p_{sat}) \approx v_G 2\sigma / r \ , \qquad (13)$$

Now we can write

$$\tilde{p}_{sat}^{L} - p_{sat} \approx -\frac{v_G}{v_G - v_L} 2\sigma / r = -\frac{\rho_L}{\rho_L - \rho_G} 2\sigma / r. \quad (14)$$

Conclusions

The eq. (11) (along with the eq. (14) and the eq's (9), (12) in the integral form) is the new form of the Kelvin equation that applies near the gas-liquid transition critical point. It can be helpful in researches of nano-structured materials. It should be applied carefully, due to the geometry dependence of the surface tension.

References

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