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On the Kirkwood-Modified Tait Equation

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The pairwise additive potential energy and molecular distribution functions are obtained for a one-dimensional fluid satisfying a version of the Kirkwood-modified Tait equation of state.

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An interesting inverse problem in statistical mechanics is: Given an equation of state of a continuous (classical) fluid, find the intermolecular potentials and hierarchy of intermolecular distribution functions that could give rise to this equation of state via an appropriate, Gibbsian grand canonical ensemble.(1) For pairwise additive potentials, to which we restrict ourselves here, one can obtain at least the potential (if not the distribution functions) by Laplace inversion of the second virial coefficient, if the potential belongs to a suitably restricted class of analytic functions,(2,3) or a restricted monotone class of functions and the equation of state can be developed in a virial series.(3) In one dimension a few additive potential models can be completely rigorously investigated.(4–7) As a result of such considerations one knows that the usual empirical equations employed to represent low-pressure *PVT* data(8) (van der Waals, Dietrici, Beattie, Bridgeman, etc.) arise from intermolecular potentials containing a long-ranged contribution similar to the Kac–Uhlenbeck–Hemmer(7) potential as well as short-ranged potential contributions.(9) The empirical equations (Ref. 8, pp. 261 ff) used for dense, three-dimensional fluids, such as the Tait equation and its modification by Kirkwood *et al.*,(10,11) cannot be studied by these techniques (e.g., by Laplace transform inversion) since these equations of state do not possess a virial development in the usual sense. If we restrict ourselves to a model one-dimensional, dense fluid with a Kirkwood-modified Tait equation, then we can carry out such an investi-

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gation. Such a study may provide some insight into the nature of the intermolecular potential and the qualitative structure of the short-range order in the corresponding three-dimensional fluid, even if it cannot provide any information about more delicate mathematical properties of either the three-dimensional potential or the distribution functions.

We choose as dependent variable ρ, the number density of our fluid, which we take to be a function of pressure and temperature T. We write $\rho = \rho(\beta, p)$, where $\beta = 1/kT$ and the real pressure is $\beta^{-1}p$. In terms of these variables the Kirkwood-modified Tait equation can be written (Ref. 8, pp. 261 ff)

$$[p + \alpha(\beta)]\gamma(\beta) = \rho^n \tag{1}$$

where

$$\alpha(\beta) = \beta A(\beta), \qquad \gamma(\beta) = \rho^n(\beta, 0)/\alpha(\beta)$$

with $A(\beta)$ the function which appears in the Tait equation$^{(11)}$ (p is here the real pressure)

$$1 - \frac{\rho(\beta, 0)}{\rho(\beta, p)} = \frac{1}{n}\log\left[1 - \frac{p}{A(\beta)}\right] \tag{2}$$

Modification of (2) is required at high pressures since the right-hand side of the Tait equation (2) approaches infinity while the left-hand side cannot exceed one. The independent variables in (1) are sometimes taken to be entropy and pressure to simplify calculations in which (1) is employed. The parameter n is the specific heat ratio only for the perfect gas equation with $\alpha = 0, n = 1$. A crude but convenient equation for liquid adiabats is obtained by setting $n = 3$.$^{(8)}$ We will carry out our calculations for the case $n = 2$, in one dimension, which leads to a pairwise additive potential $\beta^{-1}V(x, \beta) = \beta^{-1}V(x)$ and distribution functions expressible in terms of elementary transcendental functions, rather than infinite series of such functions.

We suspect that the potential function is temperature dependent. The unique inversion can be obtained readily from Eqs. (3), (5), and (6) of Ref. 12. Writing

$$f(x) = \exp(-px)\exp[-V(x)]$$

one has

$$\begin{aligned}\frac{1}{\rho(p)} &= -\frac{\partial}{\partial p}\ln\int_0^\infty f(x)\,dx \\ &= -\frac{\partial}{\partial p}\ln\int_0^\infty \exp(-px)\exp[-V(x)]\,dx \end{aligned} \tag{3}$$

In terms of the normalized nearest neighbor distribution(13) $f(x)$

$$f(x) = \hat{f}(x) \Big/ \int_0^\infty f(x)\,dx$$

one can express the distribution functions by means of convolutions of $f(x,)$ viz.

$$g(x) = \sum_{n=1}^{\infty} (f * f * \cdots * f)_n(x) \tag{4}$$

and

$$g_n(x_1, \ldots, x_n) = \prod_i g(x_{i+1} - x_i) \tag{5}$$

Setting $[\gamma(\beta)]^{-1/2} = \xi(\beta) < 1$ and solving (1) with $n = 2$ for $\rho(p)$ and substituting into (3), we find

$$\frac{1}{\rho} = \xi(p + \alpha)^{-1/2} = -\frac{\partial}{\partial p} \ln \int_0^\infty f(x)\,dx$$

or

$$\int_0^\infty f(x)\,dx = \int_0^\infty e^{-px} e^{-V(x)}\,dx = \exp[-2\xi(p + \sigma)^{1/2}] \tag{6}$$

The constant of integration can be taken to be zero since it is cancelled in all final expressions involving the normalized $f(x)$, and $V(x)$ is always defined only up to an additive constant. Equation (6) is a Laplace transform of $\exp(-V)$ in the variable p, which yields on inversion

$$\exp[-V(x)] = \frac{\exp(-\alpha x)\exp[-(\xi/x^2)]}{(\pi x^3)^{1/2}}$$

and thus

$$V(x) = \frac{\xi^2}{x} + \alpha x - \ln \frac{\xi}{(\pi x^3)^{1/2}} \tag{7}$$

This temperature-dependent potential diverges to $+\infty$ as $x \to +\infty$. For sufficiently large densities in which (1) is used to fit experimental data almost no molecules are sufficiently far apart to experience this unphysical region.

The normalized $f(x)$ is

$$f(x, p) = \frac{\xi \exp[-(p + \alpha)x - \xi^2/x + 2\xi(p + \alpha)^{1/2}]}{(\pi x^3)^{1/2}} \tag{8}$$

and to find $\rho g(x)$ via (4) we first take the Laplace transform of both sides to obtain, if

$$\rho\bar{g}(s) = \int_0^\infty e^{-sx}\rho g(x)\,dx$$

and

$$\bar{f}(s,p) = \int_0^\infty e^{-sx}f(x)\,dx = \xi\exp\{-2\xi[(s+p+\alpha)^{1/2} - (p+\alpha)^{1/2}]\}$$

the identity

$$\rho\bar{g}(s) = \sum_{n=1}^{\infty}[\bar{f}(s,p)]^n = \frac{\bar{f}(s,p)}{1-\bar{f}(s,p)}$$

$$\frac{\xi\exp[-2\xi(s+p+\alpha)^{1/2}]}{\exp[-2\xi(p+\alpha)^{1/2}] - \xi\exp[-2\xi(s+p+\alpha)^{1/2}]} \tag{9}$$

Using the complex contour integral formulation of the inverse Laplace transform, one finds after some manipulations that

$$\begin{aligned}\rho g(x) = \exp(-bx)\{&Z^{-3/2}[\exp(Zx) - 1]\exp[2\xi(\sqrt{b} - \sqrt{Z})] + \frac{x}{a-1}\\ &+ \frac{\alpha}{\pi}\int_0^\infty dr[\exp(-xr) - 1]r^{-2}\sin(2\xi\sqrt{r})\\ &\times [1 + a^2 - 2a\cos(2\xi\sqrt{r})]^{-1}\}\end{aligned} \tag{10}$$

with

$$b = p + \alpha$$
$$a = \exp(-2\xi\sqrt{b})/\xi$$
$$Z = (\tfrac{1}{2}\xi^{-1}\ln\xi + \sqrt{b})^2 > 0 \qquad (Z < b, \quad \text{providing } \xi < 1)$$

This distribution function vanishes at the origin, decays exponentially for large x, and oscillates at intermediate values of x. Equations (5), (7), and (10) then provide the solution of our inverse problem.

From our result for $n = 2$ we can obtain the potential for all fractional n of the form

$$n = 2m/(2m-1)$$

Writing (1) as

$$\rho^{-1} = \xi_m(p+\alpha)^{-(2m-1)/2m}$$
$$\xi_m = [\gamma(\beta)]^{-(2m-1)/2m}$$

one finds that (6) becomes

$$\int_0^\infty \hat{f}_m(x)\,dx = \int_0^\infty \exp(-px)\exp[-Vm(x)]\,dx$$
$$= \exp[-2\xi_m(p+\alpha)^{1/2m}] \tag{11}$$

Setting

$$V_m(x) = \phi_m(x, \xi_m) + \alpha x \tag{12}$$

one has

$$\int_0^\infty \exp(-px)\exp[-\phi_m(x, \xi_m)]\,dx = \exp(-2\xi_m p^{1/2m}) \tag{13}$$

with

$$\phi_1(x, \xi_1) = (\xi_1{}^2/x) - \ln[\xi_1/(\pi x^3)^{1/2}] \tag{14}$$

by virtue of (7). We now use the following Laplace transform identity: If

$$h(p) = \int_0^\infty [\exp(-px)]\,f(x)\,dx$$

then

$$\int_0^\infty dx\,[\exp(-px)]\left\{\frac{1}{(\pi x)^{1/2}}\int_0^\infty \left[\exp\left(-\frac{s^2}{4x}\right)\right]f(s)\,ds\right\} = \frac{1}{\sqrt{p}}\,h(\sqrt{p}) \tag{15}$$

Noting that for $m = 2$ one has

$$p\exp(-4\xi_2\sqrt{p}) = \int_0^\infty \exp(-px)\,\frac{\partial}{\partial x}\exp[-\phi_1(x, 2\xi_2)]\,dx$$

one finds from (13) and (15) after an integration by parts that

$$\int_0^\infty \exp(-xp)\exp[-\phi_2(x, \xi_2)]\,dx$$
$$= \exp(-4\xi_2 p^{1/4})$$
$$= \int_0^\infty dx\exp(-px)\left\{\frac{1}{2(\pi x^3)^{1/3}}\int_0^\infty \exp\left(-\frac{s^2}{4x}\right)\right.$$
$$\left.\times\exp[-\phi_1(x, 2\xi_2)]s\,ds\right\} \tag{16}$$

and thus

$$\exp[-\phi_2(x, \xi_2) - \alpha x] = \exp[-V_2(x)]$$
$$= \frac{\xi_2\exp(-x)}{(\pi x^3)^{1/2}}\left[\int_0^\infty ds\exp\left(-\frac{s^2}{4x}\right)\frac{\exp(-2\xi_2/s^2)}{(\pi s)^{1/2}}\right] \tag{17}$$

Finally from (16) by induction

$$\exp[-\phi_m(x, \xi_m)] = \frac{1}{2(\pi x^3)^{1/2}} \int_0^\infty ds\, s \exp\left(-\frac{s^2}{4x}\right) \exp\left[-\phi_{m-1}\left(x, \frac{m}{m-1}\, \xi_m\right)\right] \tag{18}$$

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